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I. INTRODUCTION
The DOE Hydrogen Program (the Program) has conducted comprehensive and focused efforts to enable the widespread commercialization of hydrogen and fuel cell technologies 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 challenges facing the development and deployment of hydrogen and 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 activities in the DOE Offices of Fossil Energy (FE), Nuclear Energy (NE), and Science (SC).

In Fiscal Year (FY) 2010, Congress appropriated approximately $244 million for the DOE Hydrogen Program. The Program is organized into distinct sub-programs focused on specific areas of RD&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, FE, and NE; 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 below. More detail can be found in the sub-program chapters of this report.

PROGRAM PROGRESS AND ACCOMPLISHMENTS

Hydrogen Production

The FY 2010 Hydrogen Production activities continued to focus on developing technologies that enable the long-term viability of hydrogen as an energy carrier for a diverse range of end-use applications including portable power, stationary power, backup power, specialty vehicles, and transportation. The goal of the Program’s production portfolio is to develop low-cost, high-efficiency hydrogen production technologies from diverse, domestic sources, including renewable resources, coal (with carbon sequestration), and nuclear energy. The main objective is to reduce the cost of hydrogen dispensed at the pump to a cost competitive with gasoline. Important FY 2010 accomplishments in the major production technology pathways are summarized below:

**Biomass and Bio-Derived Liquids:** The National Renewable Energy Laboratory (NREL) demonstrated hydrogen production by auto-thermal reforming of bio-oil using a bench-scale reactor system and achieved hydrogen production of 7.3 g/100 g bio-oil (potentially 9.6 g/100 g bio-oil after water-gas shift) with 93% bio-oil to gas conversion. Argonne National Laboratory (ANL) completed an analysis of the economic feasibility of hydrogen production from glycerol derived as a byproduct of the biodiesel industry—estimating the cost of hydrogen for a base case set of conditions at $4.86/kg, where the price of glycerol was assumed to be $1.07/gallon. United Technologies Research Center demonstrated nearly 100% conversion of wood, using an inexpensive base metal catalyst, and completed a study to better understand the impact of base concentration on H₂ yield and selectivity.

**Electrolysis:** Giner Electrochemical Systems reduced hydrogen embrittlement in titanium/carbon cell-separators, demonstrated enhanced dimensionally stable membrane (DSMTM) performance, and projected a decrease in overall capital cost of their electrolyzer stack from >$2,500/kW in 2001 to $463/kW in 2010. In addition, NREL completed an independent review of wind electrolysis, estimating the levelized cost range for state-of-the-art electrolysis to be $4.90–$5.70 per gallon gasoline equivalent (gge) of hydrogen for forecourt refueling stations (including compression, storage and...
dispensing), and $2.70–3.50/gge for central electrolysis operations (at the plant gate, excluding all delivery and dispensing costs).

**Solar Thermochemical Hydrogen Production:** The University of Colorado optimized formulations for hercynite materials, which are more stable and generate hydrogen at lower temperature than the traditional ferrites; they also completed a techno-economic analysis indicating that atomic-layer-deposition of ferrite materials on 100 m²/g supports with an oxidation/reduction cycle every five minutes will meet the DOE 2015 cost targets. In addition, ANL initiated a development and testing project for new membrane materials for the CuCl electrolyzer in the hybrid copper chloride cycle, and demonstrated that a decrease in the reactor pressure reduces the amount of steam required (H₂O/CuCl₂ ratios reduced by more than 30%, from 20–23 to 11–15) for >90% yield of the desired Cu₂OCl₂ product.

**Photoelectrochemical and Biological Production:** Directed Technologies, Inc. (DTI) completed separate technoeconomic boundary analyses of photoelectrochemical (PEC) solar hydrogen production and biological hydrogen production, projecting cost ranges of $2.50–$10/gge H₂ for PEC and $3-$12/gge H₂ for biological production, based on the current state of these technologies. Stanford University achieved the first-ever demonstration of bandgap tailoring in photoactive MoS₂ nanoparticles—increasing the MoS₂ bulk bandgap from 1.2 eV up to 1.8 eV, a more optimal value for PEC water splitting. University of California, Berkeley, developed methods to minimize the size of chlorophyll antennae used in photosynthesis by decreasing the expression of the Truncated-Light-Antenna genes, thereby substantially improving solar light energy utilization efficiencies in plants and microalgal cultures from the 2000 baseline of 3% up to 25%. In addition, NREL, in collaboration with Pennsylvania State University, designed, constructed, and tested a 2.5-L bench-scale prototype microbial electrolysis cell that produced hydrogen gas at a rate up to 1,250 mL/d, demonstrating the usefulness of this design.

**Fossil Energy—Hydrogen from Coal:** Eltron Research Inc., Southwest Research Institute® (SwRI®), and Worcester Polytechnic Institute (WPI) developed membrane separation technologies that achieve a hydrogen recovery rate of 90% with nearly 100% H₂ purity, while simultaneously enabling 90–95% CO₂ capture at high pressure, minimizing CO₂ compression costs.

### Hydrogen Delivery

Hydrogen Delivery sub-program activities continued to focus on developing technologies to reduce the cost and increase the energy efficiency of hydrogen delivery, to enable the widespread use of hydrogen as an 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). FY 2010 accomplishments in the major delivery activities are summarized below:

**Pipelines:** Savannah River National Laboratory (SRNL) completed a life-cycle management plan for fiber reinforced composite (FRC) pipelines, completed a review of existing FRC design specifications and standards and initiated environmental and flaw tolerance testing of FRC. Also, Sandia National Laboratories (SNL) examined the fracture properties of X52 pipeline steel in high-pressure hydrogen gas to evaluate the reliability of current pipeline steel for transmission.

**Tube Trailers and Bulk Storage:** Lincoln Composites completed an assembly that includes an International Organization for Standardization (ISO) frame, four pressure vessels, and relevant plumbing. The American Bureau of Shipping approved the entire ISO assembly for manufacture. In addition, Lawrence Livermore National Laboratory (LLNL) designed a pressure vessel that when incorporated into a trailer could deliver hydrogen at a cost below $1/gge (not including forecourt expenses).

**Compression and Liquefaction:** Concepts ETI Inc. completed a preliminary design of a six-stage H₂ pipeline compressor capable of delivering 240,000 kg H₂/day at 1,250 psig. In addition, five subsystems of a 290 K to 120 K active magnetic regenerative liquefier prototype were designed, fully assembled, and successfully tested by Prometheus Energy.

**Analysis:** ANL upgraded the Hydrogen Delivery Scenario Analysis Model to evaluate three new delivery pathways, two different station configurations for 700-bar dispensing, and an option permitting
user selection of station configuration. Also, NREL upgraded the Hydrogen Rail Components Model with 700-bar and cryo-compressed dispensing and higher tube-trailer delivery pressure, of up to 480 atm.

**Hydrogen Storage**

In FY 2010 the storage sub-program continued to make research and development (R&D) progress on advanced storage technologies for on-board vehicle applications.\(^1\) Investigations have continued to focus on development of materials within the three classes of hydrogen storage materials: hydrogen adsorbents, reversible metal hydrides and chemical hydrogen storage materials. There has also been an increased effort on advancing the state of the art in system engineering for materials-based vehicular storage systems through the Hydrogen Storage Engineering Center of Excellence (HSECoE). Progress has also continued on cryo-compressed physical storage.

**Metal Hydride Center of Excellence (MHCoE):** Over the five-year life of the MHCoE, more than 80 distinct materials have been investigated; work on about 75% of these has been discontinued, based on criteria developed by the MHCoE, such as reversible capacities, absorption thermodynamics, and kinetics. Work at the University of Hawaii and Sandia-Livermore National Laboratory has demonstrated 12 wt% reversibility from Mg(BH\(_4\)\(_2\))\(_2\), using severe re-hydrogenation conditions of 900+ bar H\(_2\) pressure and 400°C. The formation of the stable Mg(B\(_{12}\)H\(_{12}\)) intermediate has been found to be the reason that extreme hydrogenation pressures are needed. Under mild conditions, the group found they could obtain 2.4 wt% with partial cycling of Mg(BH\(_4\)\(_2\))\(_2\) without formation of the Mg(B\(_{12}\)H\(_{12}\)) intermediate. This preliminary work has been shown to extend to other metal borohydrides as well. Work has continued to progress at SRNL in developing a route for electrochemical formation of alanine (AlH\(_3\)) from aluminum metal and hydrogen gas in an electrolyte solution. In FY 2010, an electrocatalytic additive was found that increased the rate of alanine production approximately 1.8 times.

**Hydrogen Sorption Center of Excellence (HSCoE):** Through FY 2010, the HSCoE has identified approximately 210 materials, of which approximately 80% are no longer being investigated due to their failure to meet gravimetric or volumetric capacity targets. The Center has published its Materials Go/No-Go Recommendation Report (NREL), which is available through the DOE Web site at: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/hscoe_recommendation_feb_10.pdf. Additionally, through collaborative center work, boron-substituted carbon materials were synthesized and demonstrated to have increased hydrogen binding energy (isosteric heats of 9–11 kJ/mol) as a function of coverage, agreeing with theory predictions. Several new sorbent materials were synthesized, including: Duke University’s polyether-etherketone (PEEK) material, which was found to have greater than 5 wt% excess hydrogen capacity; Texas A&M University’s PCN-68 framework material with 5,109 m\(^2\)/g surface area and 7.2 wt% excess hydrogen capacity; and Caltech’s Cs and Rb-intercalated graphite with narrow “slit-pore” geometries of 5.3 to 5.8 Å, which were shown to have a near constant isosteric heat of adsorption of 14 and 12 kJ/mol H\(_2\), respectively.

**Chemical Hydrogen Center of Excellence (CHCoE):** The CHCoE has investigated about 150 distinct chemical compositions over its five-year life. Research on approximately 95% of these has ended due to issues related to storage capacities, hydrogen release temperatures, kinetics, and spent fuel regeneration efficiency. FY 2010 advancements in chemical hydrogen storage materials included Los Alamos National Laboratory’s (LANL’s) development of a “one-pot” spent ammonia borane (AB) regeneration process with an overall yield of 90%; demonstration by Pacific Northwest National Laboratory (PNNL) of a new AB first-fill process with higher purity and yield and completion of a reactor scale-up capable of providing 100-gram batches of high purity AB to center partners; and the University of Pennsylvania achieving over 6x rate enhancements with reduced borazine formation and up to 11.4 wt% H\(_2\)-release from 80/20 (w/w)AB/ionic-liquid mixtures at 110°C. Additionally, high release rates for liquid AB at temperatures as low as 70°C with non-platinum group metal catalysts were demonstrated by LANL.

**Hydrogen Storage Engineering Center of Excellence (HSECoE):** FY 2010 was the first full year of effort for the HSECoE. The focus of FY 2010 was to develop preliminary complete system models for the three material classes using data for well-characterized representative materials from each class.

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The Center also developed fuel cell power plant and vehicle models and coupled the models together so that on-board hydrogen storage system performance impacts on vehicle and power plant performance can be readily determined. The model development and coupling was carried out collaboratively primarily by Ford, General Motors, NREL, PNNL, SRNL, and United Technologies Research Center. LANL developed and demonstrated a novel acoustic fuel gauge sensor for use with materials-based storage systems.

In addition to the advancements made within the four Centers, the Storage sub-program continued to advance physical storage systems using compressed and cryo-compressed hydrogen. At Oak Ridge National Laboratory (ORNL), work was initiated to develop new melt-spin precursor preparation processes that could lead to projected cost savings of up to 50% of the carbon fiber precursor costs, potentially leading to a 25% reduction in final carbon fiber costs. ANL and TIAX LLC completed their technical assessments of compressed gas storage tank systems for automotive applications and their final report will be available through the DOE Web site. LLNL has continued progress on cryo-

**FIGURE 1.** Estimates of gravimetric and volumetric capacities projected for on-board storage systems that can supply 5.6 kg of usable hydrogen as compared to DOE targets (based upon engineering analyses). Note that the plotted data points are the average values for all systems analyzed during each year while the bars correspond to the range of maximum and minimum values obtained in each year. Also note that systems with predicted capacities exceeding the gravimetric or volumetric targets do not meet other targets.
compresses systems. An LLNL generation-3 tank design with 5.6 kg of usable H\textsubscript{2} has been projected by ANL to be capable of meeting the 2015 gravimetric and volumetric targets, with greater than 5.5 wt\% and 42 g/L capacities.

**Fuel Cells**

The Fuel Cells sub-program has made continued progress toward meeting 2010 and 2015 targets through advancements achieved in both catalysis and membrane R&D. Technological advances in several component areas have led to significant improvements in performance and durability, with decreased cost. Progress has also been demonstrated in the sub-program’s efforts to develop fuel cell systems for combined heat and power (CHP) applications.

The cost of a hydrogen-fueled 80-kW\textsubscript{e} fuel cell power system projected to high volume production (500,000 units/year) has been estimated to be $51/kW (assuming 2010 technology), as shown in Figure 2.\textsuperscript{2} Cost reduction was a result of simplified architecture and reduction in stack component costs through ongoing R&D efforts. The cost of the fuel cell stack has been estimated to be $25/kW (assuming 2010 technology).

In FY 2010, advancements in platinum group metal (PGM)-based catalysts resulted in significant progress toward improvement of fuel cell performance and reduction in cost through minimization of PGM loading. In FY 2010, 3M increased PtCoMn mass activity 30\%, reaching 0.24 A/mg\textsubscript{PGM} at 0.9 V, and demonstrated Pt\textsubscript{3}Ni\textsubscript{7} alloy with mass activity of 0.40 A/mg\textsubscript{PGM}.

3M operated a membrane over 5,000 hours with load cycling using a membrane electrode assembly (MEA) based on a non-stabilized 20-μm membrane and catalyst loading of 0.15 mg\textsubscript{PGM}/cm\textsuperscript{2}, meeting the DOE 2010/2015 durability target of 5,000 hours.\textsuperscript{3} (The 7,300 hours reported previously was with a higher PGM loading.) With the use of chemical stabilizers in the membrane, 3M exceeded the 200-hour DOE target for stability under open-circuit voltage hold in H\textsubscript{2}/air by more than 300\%.

In FY 2010, Brookhaven National Laboratory (BNL) improved its core-shell catalyst by using an interlayer of Au to separate the Pt shell from the PdCo core. Rotating disk electrode (RDE) testing of the new catalyst has demonstrated mass activity as high as 1.10 A/mg\textsubscript{PGM} and specific activity as high as 1,170 μA/cm\textsuperscript{2} at 0.9 V,\textsuperscript{4} suggesting a high probability of meeting DOE MEA-level and stack-level targets of 0.44 A/mg\textsubscript{PGM} and 720 μA/cm\textsuperscript{2}. RDE testing of an early Pt/Pd/C catalyst yielded 0.35 A/mg\textsubscript{Pt}. A Pt\textsubscript{3}ML/Pd/C core-shell catalyst delivered significantly better oxygen reduction reaction performance than a PtPd/C alloy with the same composition and identical performance as Pt/C, but with one fourth as much Pt at 0.90 V.

\textsuperscript{2} U.S. Department of Energy Hydrogen Program Record #10004, www.hydrogen.energy.gov/program_records.html; costs are based on projections to high-volume manufacturing (500,000 units/year).


Continued work at LANL on PGM-free catalysts yielded significant performance improvements in FY 2010, with current density as high as 60 A/cm² measured at 0.80 V (ir-free) during fuel cell testing with an Fe-cyanamide-C catalyst, representing a 64x improvement over the past two years. Progress also continues on PGM-free polyaniline-based catalysts at LANL, with activity as high as 31 A/cm² measured at 0.80 V, a 36x improvement over the past two years.\(^4\)

3M developed new polymer electrolyte membranes with higher proton conductivity and improved durability under hotter and drier conditions, compared with previously produced membranes, as shown in Figure 3.\(^5\) The new multi acid side-chain polymer membranes have better mechanical properties than conventional single acid side chain perfluorosulfonic acid membranes. In FY 2010, 3M developed innovative polymers in which side chains contain both sulfonic acid and sulfonamide groups.

The Fuel Cells sub-program also includes work on systems other than polymer electrolyte membrane (PEM) fuel cells, and progress is being made in these areas as well. For example, DOE is funding distributed energy and CHP systems based on several technologies. Acumentrics Corporation continues to develop micro-CHP systems based on tubular solid oxide fuel cell (SOFC) technology. In FY 2010, Acumentrics achieved a 24% increase in system power density, enabling a 33% reduction in stack volume and a 15% reduction in stack weight.\(^6\)

**Manufacturing R&D**

FY 2010 saw a number of cost and process advancements in the manufacturing of fuel cells and storage systems. W.L. Gore demonstrated, using their cost model, that a new 3-layer MEA process has the potential to reduce MEA cost by 25%. Quantum and Boeing demonstrated advanced filament winding and fiber placement processes that reduce storage system costs by 10%. BASF developed a predictive model and evaluated the impacts of electrode variation and defects on MEA performance using a new on-line X-ray fluorometer. Ballard developed a process model for controlling gas diffusion layer (GDL) coating conditions resulting in significant improvement in quality yields and GDL cost reduction of 53%. NREL developed and tested an ir-based test stand for defects such as pinholes, shorts, and variations in electrode thickness.

**Basic Research**

The Office of Basic Energy Sciences (BES) within the DOE Office of Science supports fundamental scientific research addressing critical challenges related to hydrogen storage, hydrogen production, and fuel cells. This basic research complements the applied R&D projects supported by other offices in the Program.

Progress in any one area of basic science is likely to spill over to other areas and bring advances on more than one front. The subjects of basic research most relevant to the Program’s key technologies are:

- **Hydrogen Storage:** Nanostructured materials; theory, modeling, and simulation to predict behavior and design new materials; and novel analytical and characterization tools.

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Fuel Cells: Nanostructured catalysts and materials; integrated nanoscale architectures; novel fuel cell membranes; innovative synthetic techniques; theory, modeling, and simulation of catalytic pathways, membranes, and fuel cells; and novel characterization techniques.

Hydrogen Production: Longer-term approaches such as photobiological and direct photochemical production of hydrogen.

By maintaining close coordination between basic science research and applied R&D, the Program ensures that discoveries and related conceptual breakthroughs achieved in basic research programs will provide a foundation for the innovative design of materials and processes that will lead to improvements in the performance, cost, and reliability of fuel cell technologies and technologies for hydrogen production and storage. This is accomplished in various ways—for example, through monthly coordination meetings between the participating offices within DOE, and at the researcher level by having joint meetings with participation from principal investigators who are funded by the participating offices.

Technology Validation

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. These activities include fuel cell vehicle and infrastructure demonstrations, stationary power demonstrations, and projects that integrate renewable power generation and hydrogen production. The Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation Project7 (also known as the “National Hydrogen Learning Demonstration”), launched in April 2004, brought together four teams of industry partners to operate fuel cell vehicles and all essential hydrogen infrastructure elements to evaluate progress and to identify challenges encountered when hydrogen and fuel cell technologies are operated in real-world environments. The teams were led by Chevron and Hyundai-Kia, Mercedes-Benz North America and BP, Ford and BP, and GM and Shell, with additional participation from hydrogen suppliers, fuel cell suppliers, utility or gas companies, fleet operators, system and component suppliers, small businesses, universities, and government entities.

Through the National Hydrogen Learning Demonstration, the Program has deployed 152 fuel cell vehicles and collected data from 24 hydrogen fueling stations. These vehicles have traveled over 2.8 million miles, and the fueling stations have produced or dispensed over 130,000 kg of hydrogen (not all of the hydrogen dispensed has been used in Learning Demonstration vehicles). Vehicles and infrastructure in these demonstrations have validated the status of several key technologies in integrated systems under real-world operating conditions, including vehicular fuel cell efficiency of 53 to 59 percent, projected durability of 2,500 hours (nearly 75,000 miles) for automotive fuel cell systems, and a range of more than 250 miles between refueling. The Technology Validation activity has collected and analyzed data from a total of nine fuel cell buses operated in revenue transit service at five sites in the United States. These buses have shown fuel economies 39 to 141 percent higher than conventional diesel buses and compressed natural gas buses, and they have traveled more than 395,000 miles.

In FY 2011 the final two National Learning Demonstration projects (GM and Mercedes-Benz North America) will conclude and publish final reports. In addition, the Hydrogen Energy Station at Fountain Valley, California, which will co-produce power, heat, and hydrogen, is expected to be fully operational in FY 2011. Data will be collected on power and heat generation, hydrogen production, and vehicle refueling.

Safety, Codes and Standards

The Safety, Codes and Standards sub-program continues to support critical R&D to establish key requirements and close knowledge gaps in safety, codes and standards to enable the commercialization of hydrogen and fuel cell technologies. Building on work from previous years, the sub-program continues to facilitate collaborative activities among relevant stakeholders in an effort to harmonize domestic and international regulations, codes, and standards.

7For more information on the Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation Project, see: www1.eere.energy.gov/hydrogenandfuelcells/tech_validation/fleet_demonstration.html.
The sub-program developed a strong technical basis for a risk-informed approach to update bulk gas storage separation distances in the 2010 edition of National Fire Protection Association (NFPA) 55. Experimental and modeling studies were used to develop new, technically defensible separation distances, which were in some cases reduced by as much as 50%. The sub-program also completed testing to enable the deployment of 100-MPa stationary storage tanks. The sub-program facilitated the development of requirements for forklift tank life-cycle testing used by the Canadian Standards Association Hydrogen Powered Industrial Truck Committee. In cooperation with the Education sub-program, the Safety, Codes and Standards sub-program continued to deploy an advanced-level, prop-based course to support first-responder training; this course has successfully reached over 300 first responders in California.

The sub-program expanded its Web-based safety information tools in FY 2010 including the Technical Reference for Hydrogen Compatibility of Materials and Hydrogen Safety Training for Researchers, which highlights best practices for the safe use of hydrogen in a research setting.

Working with an international team of experts, the sub-program conducted an intensive testing, modeling, and analytical effort to provide data that established a scientific basis for hydrogen fuel quality specifications for PEM fuel cell road vehicles under the ISO and the Society of Automotive Engineers. This effort included a round-robin test of a single-cell PEM fuel cell among laboratories in Japan, the European Commission, and the United States to establish interchangeability of data among the laboratories.

**Education**

The Education sub-program facilitates hydrogen and fuel cell demonstrations and supports commercialization by providing technically accurate and objective information to key target audiences both directly and indirectly involved in the use of hydrogen and fuel cells.

To support early market outreach, the Education sub-program implemented several end-user, state and local government, and safety and code official education activities in FY 2010. Carolina Tractor and Equipment Inc. conducted hydrogen education sessions with hands-on forklift demonstrations at material handling dealerships, customer sites, community colleges, and regional green business expos to educate potential end-users about the benefits of fuel cell forklifts. As evidence of the project’s success, one site has decided to acquire over 100 fuel cell forklifts as a result of their experience with the demonstration units. Seven state and local government outreach projects focused on states with an active hydrogen and fuel cell presence to develop case studies, best practices, and technical assistance resources; these will be used to help decision-makers identify and assess opportunities for future deployment. Many groups have been using these education resources to work directly with state agencies to implement policies, programs, and best practices that can support the growth of hydrogen and fuel cell markets in the local economy. PNNL expanded first responder education by hosting several sessions of an advanced-level, hands-on prop course for firefighters and registering the Web-based “Introduction to Hydrogen Safety for First Responders” on the Training Finder Realtime Affiliate Network (TRAIN) Web site, a central repository for health training courses.

University and secondary education projects introduced future scientists, engineers, technicians, and end-users to hydrogen and fuel cell technologies. Five university projects—at California State University, Los Angeles; Michigan Technological University; the University of North Dakota; Humboldt State University; and the University of Central Florida—targeted a broad student audience through general education courses, specialized science and engineering courses, minor and concentration programs, curriculum modules, internships, labs, lab kits, and textbook chapters. In their second year, these projects are finalizing development of curricula and have moved into teaching, reviewing, and refining the course materials. “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,” deployed a six-unit science curriculum and laboratory kit on hydrogen and fuel cells through professional development workshops and science teacher conferences across the country.
Market Transformation

To ensure that the benefits of its efforts are realized in the marketplace, the Program continues to facilitate the growth of early markets for fuel cells used in portable, stationary, and specialty-vehicle applications. Market transformation activities are helping to reduce the cost of fuel cells by enabling economies of scale through early market deployments and by overcoming a number of barriers, including the lack of operating performance data, the need for applicable codes and standards, and the need for user acceptance.

The development of niche-market applications for hydrogen fuel cells has been identified as the quickest way to achieve early market penetration. A study conducted for the Program by the Battelle Memorial Institute, Identification and Characterization of Near-Term Direct Hydrogen PEM Fuel Cell Markets, identifies fuel cells to power forklifts and to provide backup power for telecommunications and emergency response communications as promising near-term opportunities.

In FY 2010, the Program provided approximately $15 million for market transformation activities, to accelerate the deployment of fuel cells in early market applications. Specific FY 2010 projects included the deployment of nearly 100 lift trucks and a primary power system at Department of Defense sites and 14 hydrogen fuel buses at federal facilities across the country. These projects provide valuable data on the status of the technologies in real-world operation and information that will be used to validate the benefits of the technologies and potential needs for further R&D.

Systems Analysis and Integration

Systems Analysis supports decision-making by providing a greater understanding of technology gaps, options, and risks. 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 stationary fuel cell applications, fuel quality impacts on fuel cell performance, resource needs, and potential infrastructure options.

Accomplishments in FY 2010 included an update of the Macro-System Model (MSM) to include infrastructure and resource analysis for various regions and a variety of hydrogen production pathways. The Fuel Cell Power Model was upgraded to include business and financial analysis useful to multiple entities such as building owners, fuel cell vendors, station owners, utilities, and fleet operators.

Infrastructure analysis identified potential synergies between fuel cells for stationary power generation and transportation applications, particularly in the early phases of market adoption of hydrogen for light-duty fuel cell vehicles. Widespread deployment of combined heat, hydrogen, and power (CHHP) could address the problem of hydrogen availability in the early stages of transition to fuel cell vehicles. Analyses have indicated that the practice of producing hydrogen from CHHP systems could give rise to smaller stations with higher capital utilization and lower hydrogen cost, supplementing the supply of hydrogen from distributed natural gas–based steam methane reforming (SMR). Analysis conducted by NREL with the Fuel Cell Power model predicts that hydrogen produced from a stationary fuel cell would have a lower cost than hydrogen produced from an SMR system at low volumes, as shown in Figure 4.

ANL enhanced well-to-wheels analysis capabilities by modifying the Greenhouse gases, Regulated Emissions and Energy use in Transportation model to include analysis of criteria pollutant emissions from stationary fuel cells for combined heat, power and/or hydrogen generation (CHP/CHHP). The analysis estimates that fuel cell systems for CHP and CHHP emit significantly less carbon monoxide, particulate matter, and nitrogen oxides (NOx) than conventional generation technologies. For example, phosphoric acid fuel cells and molten carbonate fuel cells (MCFCs) emit at least 80% less NOx than other conventional generation technologies without after treatment.

8 For a brief summary of early market opportunities for PEM fuel cells, see the Program’s fact sheets on forklifts and backup power: www1.eere.energy.gov/hydrogenandfuelcells/education/pdfs/early_markets_forklifts.pdf and www1.eere.energy.gov/hydrogenandfuelcells/education/pdfs/early_markets_backup_power.pdf; for the full report by the Battelle Memorial Institute, see: www1.eere.energy.gov/hydrogenandfuelcells/pdfs/pemfc_econ_2006_report_final_0407.pdf.
I. Introduction

American Recovery and Reinvestment Act Projects

The American Recovery and Reinvestment Act (Recovery Act or ARRA) has been a critical component of the Program’s efforts to accelerate the commercialization and deployment of fuel cells in the market. With approximately $41.9 million from the Recovery Act and $54 million in cost-share funding from industry participants—for a total of nearly $96 million—this funding is supporting the deployment of nearly 1,000 fuel cell systems in emergency backup power, material handling, and CHP applications. Twelve projects were competitively selected to develop and deploy a variety of fuel cell technologies including polymer electrolyte, solid oxide, and direct-methanol fuel cells in stationary, portable, and specialty vehicle applications. To date, a total of at least 36 direct jobs have been created or retained as a result of these projects. The Program exceeded its 2010 target by deploying 206 fuel cell-powered lift trucks and installing fuel cells for backup power at 24 cell tower sites. An additional 75 portable fuel cells—handheld power generators for consumer electronics—are being sent to users as test units.

These projects will help build a competitive domestic supply base, decrease costs, and demonstrate the economic and performance benefits of fuel cells as competitive options for stationary, portable, and specialty vehicle applications. These advances will lead to reductions in carbon emissions, the creation of jobs, and a broadening of the nation’s clean energy technology portfolio.

Tracking the Commercialization of Technologies

One indicator of the robustness and innovative vitality of an R&D program is the number of patents applied for and granted, and the number of technologies commercialized. The Program continued to assess the commercial benefits of EERE’s Fuel Cell Technologies (FCT) Program by tracking the commercial products and technologies developed with the support of the Program. The FY 2010 Pathways to Commercial Success Report shows that 198 patents have been issued and 28 products have been commercialized as a result of research funded by the FCT Program in the areas of fuel cells and hydrogen production, delivery, and storage (Figure 5).

FIGURE 4. Delivered Hydrogen Cost from Distributed SMR and Molten-Carbonate Fuel Cell (MCFC) Systems (Source: NREL)

[Image: Delivered Hydrogen Cost from Distributed SMR and Molten-Carbonate Fuel Cell (MCFC) Systems]

OTHER PROGRAM ACTIVITIES

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International Partnership for Hydrogen and Fuel Cells in the Economy

The United States is a founding member of the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE), which includes 17 member countries (Australia, Brazil, Canada, China, France, Germany, Iceland, India, Italy, Japan, New Zealand, Norway, the Republic of Korea, the Russian Federation, South Africa, 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 technologies. IPHE also offers a mechanism for international R&D managers, researchers, and policymakers to share program strategies.

In FY 2010, DOE hosted the IPHE Steering Committee meeting in Washington, D.C., at which the secretariat was transferred from Canada to Germany. Germany and China also hosted two additional joint Steering Committee and Implementation & Liaison Committee meetings. In November 2010, the IPHE released an overview of the global technical and commercialization progress of hydrogen and fuel cell technologies titled, 2010 Hydrogen and Fuel Cell Global Commercialization and Development Update.

IPHE—in collaboration with DOE, the California Fuel Cell Partnership (CaFCP), and NREL—coordinated the IPHE Infrastructure Workshop on February 25–26, 2010, to examine the key drivers and gaps to early market infrastructure development for light-duty vehicles. This interactive workshop engaged more than 80 professionals—representing a wide variety of stakeholders and expertise—in developing creative and practical solutions for establishing hydrogen infrastructure in the near term. Responding to the strategic issues and information gaps discussed during the workshop, the Program plans to conduct a rigorous assessment of challenges and needs—both from an R&D and business case perspective—to develop the appropriate strategy for vehicle and infrastructure rollout. For more information on the IPHE, visit www.iphe.net.

International Energy Agency

The United States is also involved in international collaboration on hydrogen and fuel cell R&D through participation in the International Energy Agency (IEA) implementing agreements, where it is a member of both the Advanced Fuel Cells Implementing Agreement (AFCIA) and the Hydrogen Implementing Agreement (HIA). These agreements provide a mechanism for member countries to share the results of research, development, and analysis activities in their respective areas.
The AFCIA currently comprises six annexes: 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 participating countries are Australia, Austria, Belgium, Canada, Denmark, Finland, France, Germany, Italy, Japan, South Korea, the Netherlands, Mexico, Sweden, Switzerland, Turkey, and the United States. The implementing agreement was recently extended from 2009 to 2013. Information about the IEA AFCIA is available at www.ieafuelcell.com.

The IEA HIA is focused on RD&D and analysis of hydrogen technologies. It includes ten tasks covering safety, hydrogen production, hydrogen storage materials, hydrogen delivery, and systems analysis including: 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, Water photolysis, Near-Market Routes to Hydrogen by Co-Utilization of Biomass with Fossil Fuel, and Large Scale Hydrogen Delivery Infrastructure and Global Hydrogen Systems Analysis. 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, United Nations Industrial Development Organization-International Center for Hydrogen Energy Technologies, and the United States. In the past year, new tasks or annexes in hydrogen delivery infrastructure and global systems analysis have been initiated. A new task, Distributed and Community Hydrogen for Remote Communities, is under definition and is expected to start in FY 2011. Information about the IEA HIA is available at www.ieahia.org.

EXTERNAL COORDINATION, INPUT, AND ASSESSMENT

Hydrogen and Fuel Cell Technical Advisory Committee (HTAC)

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 on the safety, economic, and environmental issues related to hydrogen and fuel cells. 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.

HTAC met three times between August 2009 and August 2010. In March 2010, HTAC released its second annual report, which summarizes hydrogen and fuel cell technology domestic and international progress in RD&D projects; commercialization activities; and policy initiatives. More information about HTAC, including the annual reports, is available at: http://www.hydrogen.energy.gov/advisory_htac.html

Federal Agency Coordination—the Interagency Task Force and the Interagency Working Group

The 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.

In August 2010, the IWG launched an updated Web portal, www.hydrogen.gov. The site serves as an information and government news source on hydrogen and fuel cells and a portal to participating agency activities. The IWG also completed a draft Interagency Action Plan with an expected release in FY 2011 in preparation for the reconvening of the Interagency Task Force.

National Academy of Sciences

The National Research Council (NRC) of the National Academies provides ongoing technical and programmatic reviews and input to the Hydrogen Program. The NRC has conducted independent
reviews of both the Program\textsuperscript{11} and the R&D activities of the FreedomCAR and Fuel Partnership.\textsuperscript{12,13} In 2010, the NRC completed its Phase III review of the Partnership. Key outcomes of the review are documented in the report, \textit{Review of the Research Program of the FreedomCAR and Fuel Partnership: Third Report},\textsuperscript{14} in which the committee expressed an overall opinion that the Partnership “is effective in progressing toward its goals,” and that “there is evidence of solid progress in essentially all areas, even though substantial barriers remain.” In this report, the committee also recognized “three primary alternative pathways” for reducing petroleum consumption and greenhouse gas emissions in the transportation sector: (1) improved internal combustion engine vehicles coupled with greater use of biofuels, (2) expanded use of plug-in electric vehicles and battery electric vehicles, and (3) hydrogen fuel cell vehicles.

In 2010, the NRC’s Committee on Assessment of Resource Needs for Fuel Cell and Hydrogen Technologies released the report, \textit{Transitions to Alternative Transportation Technologies—Plug-In Hybrid Electric Vehicles.}\textsuperscript{15} This report followed the committee’s 2008 report, \textit{Transitions to Alternative Transportation Technologies—A Focus on Hydrogen}. These reports were required by the Energy Policy Act section 1825 to compare hydrogen fuel cell vehicles to alternate advanced vehicle technologies. A key conclusion of the latest report is that a diverse approach to RD&D and market transformation—comprising a portfolio of efforts in hydrogen, batteries, and biofuels—will “enable the greatest reduction in oil use.”

\textbf{FY 2010 Annual Merit Review and Peer Evaluation}

The Annual Merit Review (AMR) took place June 7–11, 2010, providing an opportunity for the Program to obtain an expert peer review of the projects it supports and to report its accomplishments and progress. For the second time, this meeting was held in conjunction with the annual review of DOE’s Vehicle Technologies Program. During the AMR, reviewers evaluate the Program’s projects and make recommendations; DOE uses these evaluations, along with other review processes, to make project funding decisions for the upcoming fiscal year. The review also provides a forum for promoting collaborations, the exchange of ideas, and technology transfer. This year, over 1,700 people attended the review and 349 projects were presented, of which 216 were peer-reviewed. There were 198 contributing reviewers; the report compiling their comments is available at http://www.hydrogen.energy.gov/annual_review.html. In 2011, the AMR will be held May 9–13 in Arlington, Virginia.

\textbf{IN CLOSING…}

The Program will continue to pursue a broad portfolio of RD&D activities for fuel cell applications across multiple sectors. Efforts will span the full spectrum of technology readiness, including: early market applications that are already viable or are expected to become viable in the next few years, such as forklifts, backup power, and portable power applications; mid-term markets that are expected to emerge in the 2012–2015 timeframe, such as residential combined-heat-and-power systems, auxiliary power units, fleet vehicles, and buses; and longer-term markets that are expected to emerge in the 2015–2020 timeframe, including light-duty passenger vehicles and other transportation applications. The Program will also continue to pursue activities to enable commercialization and stimulate the markets for hydrogen and fuel cells as they achieve technology readiness. Supporting these markets will not only help to achieve the economic, environmental, and energy security benefits that fuel


\textsuperscript{14} The full report is available from: http://www.nap.edu/catalog.php?record_id=12939.

\textsuperscript{15} The full report is available from: http://books.nap.edu/catalog.php?record_id=12826.
cells provide in those specific applications, but it will complement the Program’s longer-term R&D efforts by helping to increase current sales and manufacturing volumes, providing essential cost reductions—through economies of scale—for many of the same technologies that will be used in longer-term applications. Supporting earlier markets can also reduce many non-technological barriers to the deployment of hydrogen and fuel cell technologies and lay the groundwork for the larger infrastructure and supply base that will be needed for fuel cell vehicles. The Program released its draft strategic plan in October 2010 (www.eere.energy.gov/hydrogenandfuelcells/pdfs/program_plan2010.pdf); the final version will be released in FY 2011.

We are pleased to present the U.S. Department of Energy’s 2010 Hydrogen Program Annual Progress Report. The report is divided into chapters and is 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 the previous fiscal year. The projects outlined in this document represent the work of the many innovative scientists and engineers supported by DOE. They are the ones responsible for the progress and technical accomplishments reported this year’s Annual Progress Report. We would like to recognize them for their hard work, commitment, and continued progress.

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Fuel Cell Technologies Program
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U.S. Department of Energy
II. HYDROGEN PRODUCTION
II.0 Hydrogen Production Sub-Program Overview

Introduction

Fiscal Year (FY) 2010 Hydrogen Production activities focus on developing technologies that enable the long-term viability of hydrogen as an energy carrier for a diverse range of end-use applications, including portable power, stationary power, backup power, specialty vehicles, and transportation. 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:

- Energy Efficiency and Renewable Energy (EERE) is developing technologies for distributed production of 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 (PEC) water splitting, and biological processes.

- Fossil Energy (FE) is advancing the technologies needed to produce hydrogen from coal-derived synthesis gas, including carbon sequestration and co-production of hydrogen and electricity.

- The Office of Basic Energy Sciences, within the Office of Science, conducts basic research to develop a fundamental understanding of biological and biomimetic hydrogen production, PEC water splitting, catalysis, and membranes for gas separation.

- In Nuclear Energy (NE), the Nuclear Hydrogen Initiative was discontinued as a separate program in FY 2009, after the selection of steam electrolysis as being the hydrogen production pathway most compatible with the Next Generation Nuclear Plant (NGNP). Limited development of high-temperature electrolysis is continuing under the NGNP project, which also includes evaluations of other end-user applications and energy transport systems.

Goal

The goal of the Program’s hydrogen production portfolio is to research and develop low-cost, highly-efficient hydrogen production technologies from diverse, domestic sources, including coal (with sequestration), nuclear, and renewable resources.

Objective

The objective of the Program’s hydrogen production portfolio is to reduce the cost of hydrogen dispensed at the pump to a cost that is competitive with gasoline, on a cents-per-mile basis. This goal applies to all production technology pathways. Specific targets—for when the various technologies will achieve this goal—are based on the technologies’ current states of development.

FY 2010 Technology Status

Recent independent reviews of production pathway costs are summarized in Table 1. The report, Distributed Hydrogen Production from Natural Gas (National Renewable Energy Laboratory [NREL], 2006) provided the basis for DOE to discontinue R&D in steam methane reforming for hydrogen production—it verified that the cost target could be met from distributed reforming of natural gas. Other reports shown in Table 1 reflect the H2A cost projections and cost and performance targets for the Hydrogen Production sub-program’s chapter of the Multi-Year Program Plan, which is currently being updated.

Interim and ultimate pathway-specific targets consistent with the overall targets established for the Program are being revised. These will include verification of the competitive feasibility of hydrogen production from non-ethanol bio-derived liquids by 2015, and of hydrogen production using advanced
renewable technologies (including PEC and biological hydrogen generation, as well as high-temperature thermochemical cycles driven by concentrated solar energy) by 2020.

**TABLE 1. Independent Reviews of Production Pathway Costs**

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Report</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Methane Reforming (SMR)</td>
<td>Distributed Hydrogen Production from Natural Gas, NREL, October 2006²</td>
<td>$2.75–$3.50/gasoline gallon equivalent (gge)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~75% membrane efficiency (Proton Exchange Membrane)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Central: $2.70–$3.50/gge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~75% membrane efficiency (Proton Exchange Membrane)</td>
</tr>
<tr>
<td>PEC</td>
<td>Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production, Directed Technologies Inc., December 2009⁴</td>
<td>$2.50–$10/gge (projected cost based on technology readiness). R&amp;D focus is on materials efficiency, durability and cost.</td>
</tr>
<tr>
<td>Biological</td>
<td>Technoeconomic Boundary Analysis of Biological Pathways to Hydrogen Production, Directed Technologies Inc., December 2009⁵</td>
<td>$3–$12/gge (projected cost based on technology readiness). R&amp;D focus is on organism efficiency, durability, and cost.</td>
</tr>
</tbody>
</table>

¹ Costs for SMR and Electrolysis are projected high-volume costs. Cost projections for PEC and Biological are for technology readiness. Centralized pathway costs do not include delivery and dispensing costs.
⁴ http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/pec_technoeconomic_analysis.pdf
⁵ http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/46674.pdf

The goals and objectives of FE’s efforts in hydrogen production are documented in the *Hydrogen from Coal Program Research, Development and Demonstration Plan* (September 2009). They include proving the feasibility of a near-zero emissions, high-efficiency plant that will produce both hydrogen and electricity from coal and reduce the cost of hydrogen from coal by 25 percent compared with current technology, by 2016.

**FY 2010 Accomplishments**

**Biomass, Bio-Derived Liquids, Coal and Separations Processes**

- NREL demonstrated hydrogen production by auto-thermal reforming of bio-oil using the bench-scale reactor system and achieved hydrogen production of 7.5 g/100 g bio-oil (potentially 9.6 g/100 g bio-oil after water-gas shift) with 93% bio-oil to gas conversion.
- Argonne National Laboratory (ANL) completed an analysis of the economic feasibility of hydrogen production from glycerol derived as a byproduct of the biodiesel industry. The cost of hydrogen for a base case set of conditions was estimated at $4.86 per kg, where the price of glycerol was assumed to be $1.07/gallon. The cost of feedstock (crude glycerol) represented 44% of the cost of hydrogen.
- United Technologies Research Center demonstrated nearly 100% conversion of wood, using an inexpensive base metal catalyst, and completed a study to better understand the impact of base concentration on hydrogen yield and selectivity.
- Eltron Research Inc., Southwest Research Institute®, and Worcester Polytechnic Institute have developed membrane separation technologies that achieve a hydrogen recovery rate of 90% with essentially 100% hydrogen purity, while simultaneously enabling 90–95% CO₂ capture at high pressure, minimizing CO₂ compression costs. (FE project)

**Electrolysis**

- Giner Electrochemical Systems reduced hydrogen embrittlement in titanium/carbon cell-separators, demonstrated enhanced dimensionally stable membrane (DSM™) performance, and projected a decrease in overall capital cost of their electrolyzer stack from >$2,500/kW in 2001 to $463/kW in 2010.
NREL completed an independent review of wind electrolysis, estimating the levelized cost range for state-of-the-art electrolysis to be $4.90–$5.70/gge of hydrogen for forecourt refueling stations (including compression, storage and dispensing), and $2.70–3.50/gge for central electrolysis operations (at the plant-gate, excluding all delivery and dispensing costs).

Solar Thermochemical Hydrogen Production

- The University of Colorado at Boulder optimized formulations for hercynite materials, which are more stable and generate hydrogen at lower temperature than the traditional ferrites; they also completed a techno-economic analysis indicating that atomic-layer-deposition of ferrite materials on 100 m²/g supports with an oxidation/reduction cycle every five minutes will meet the 2015 DOE cost targets.
- ANL initiated a development and testing project for new membrane materials for the CuCl electrolyzer in the hybrid copper chloride cycle, and demonstrated that a decrease in the reactor pressure reduces the amount of steam required (H₂O/CuCl₂ ratios reduced by more than 30%, from 20–23 to 11–15) for >90% yield of the desired Cu₂OCl₂ product.

PEC and Biological Production

- Stanford University achieved the first-ever demonstration of bandgap tailoring in photoactive MoS₂ nanoparticles. The bulk MoS₂ bandgap of 1.2 eV was increased to 1.8 eV, a more optimal value for PEC water splitting, by quantum confinement effects in 5-nm diameter nanoparticles.
- Directed Technologies Inc. completed separate techno-economic boundary analyses of PEC solar hydrogen production and biological hydrogen production, projecting cost ranges of $2.50–$10/gge H₂ for PEC and $3–$12/gge H₂ for biological production, based on the assumption of technology readiness for the PEC materials and biological organisms being developed.
- University of California, Berkeley, developed methods to minimize the size of chlorophyll antennae used in photosynthesis by decreasing the expression of the Truncated-Light-Antenna genes, thereby substantially improving solar light energy utilization efficiencies in plants and microalgal cultures from the 2000 baseline of 3% up to 25%.
- NREL, in collaboration with Pennsylvania State University, designed, constructed, and tested a 2.5-L bench-scale prototype microbial electrolysis cell that produced hydrogen gas at a rate up to 1,250 mL/d, demonstrating the usefulness of this design.

Budget

The FY 2010 appropriation for hydrogen production provided $41 million for continued hydrogen production research. FE received $26.4 million, NE $5 million, and EERE $9.6 million to continue research efforts in FY 2010.

The President’s FY 2011 budget request for EERE includes $40 million for hydrogen fuel R&D, of which $12.8 million is planned for hydrogen production, with an emphasis on materials and processes for hydrogen from renewable resources. The request for FE is $12 million.
II. Hydrogen Production / Overview

FY 2011 Plans

- Continued emphasis on addressing major challenges in hydrogen production. In particular, the sub-program will focus on cost reduction, including the cost of materials and capital equipment. Performance enhancement will remain a priority as cost reductions are expected to result through process optimizations for all production pathways and technologies.
- Completion of an Independent Panel Review of costs for hydrogen production from biomass gasification and an analysis of near-term markets for hydrogen from biomass gasification.
- Update H2A cost projections for hydrogen production pathways.
- Update the Hydrogen Production chapter of EERE’s Multi-Year Program Plan.
- Continue EERE coordination with the Office of Science, which plans up to $50 million in 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 PEC and biological processes, can help address the challenges of hydrogen production.
- Deployment projects funded by the American Recovery and Reinvestment Act will provide lessons-learned related to hydrogen production technologies.
- The National Energy Technology Laboratory will continue to support implementation of the membrane separation test protocols.
- Eltron Research Inc. plans to perform slipstream tests of a 12 lb/day hydrogen separation membrane at Eastman Chemicals’ coal gasification facility.
- Projects will complete 150 hours of laboratory-scale testing of non-precious-metal hydrogen separation membranes to show potential toward cost goals.

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II.A.1 Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming over Co-Based Catalysts

Objectives

To develop precious metal-free catalysts that can operate at lower temperatures with high yields and selectivities for hydrogen steam reforming from bio-ethanol; acquire a fundamental understanding of the reaction networks, active sites and deactivation mechanisms of potential bio-ethanol 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
  - Colloidal templating
  - 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
- To study how the observed catalyst characteristics influence the reaction pathways for:
  - Oxygenate formation
  - Reverse water-gas shift
  - Alkane and olefine 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:
  - Surface acidity control
  - 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

Technical Barriers

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

(A) Reformer Capital Costs
(C) Operation and Maintenance (O&M)
(D) Feedstock Issues

Technical Targets

This is a university project, which involves 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 this study will address many common problems associated with catalyst development, such as choice of materials, pretreatment 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 ($/gasoline gallon equivalent, gge)
- Total Hydrogen Cost from bio-derived liquids: 3.80 ($/gge)

Accomplishments (most recent)

- An advanced X-ray spectroscopy technique, X-ray absorption fine structure spectroscopy (XAFS), that allows monitoring of the transformation of cobalt species during ethanol steam reforming was added to the arsenal of techniques that are being utilized to characterize the developed catalyst formulations under real working conditions.
- In situ XAFS studies provided insight to the changes in the oxidation state and local coordination environment of cobalt species during ethanol steam reforming which would, in turn, result in ease of operation with the elimination catalyst pretreatment step.
- The use of in situ infrared spectroscopy led to the identification of reaction intermediates under actual reaction conditions of ethanol steam reforming which solidified the understanding of the reaction mechanism.

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) such as X-ray photoelectron spectroscopy, laser Raman spectroscopy, diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS), transmission electron microscopy, X-ray diffraction, thermal gravimetric analysis, differential scanning calorimetry, temperature-programmed reduction, temperature-programmed oxidation, temperature-programmed desorption (TPD) and most recently, XAFS. 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 feedback 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

The activities during this reporting period focused on determination of the local coordination environment and oxidation state of cobalt-based catalyst formulations via XAFS spectroscopy. The project had multiple sessions of beam time at the Dow-Northwestern-DuPont Collaborative Access Team bending magnet beam line (5BM-D) at the Advanced Photon Source of Argonne National Laboratory. The primary focus of the XAFS studies was investigation of the effect of pretreatment conditions on the nature of cobalt species in efforts to improve the ease of operation and to shed light to the ongoing debate on the nature of the cobalt active sites in the bio-ethanol steam reforming literature.

XAFS spectra of Co/CeO₂ catalyst following oxidation and reduction pretreatment is shown in Figure 1 together with the XAFS spectra for cobalt (II) oxide and cobalt (II, III) oxide used as standards. Figure 1 clearly shows that the coordination environment of cobalt species in Co/CeO₂ catalyst closely resembles that of cobalt (II, III) oxide following oxidation treatment. Following reduction treatment cobalt species were reduced to a lower oxidation state that closely resembles cobalt (II) oxide. Figure 1 also shows the XANES fit for oxidized and pre-reduced Co/CeO₂ catalysts which have undergone ethanol steam reforming (ESR) for 1-hour at the designated temperature. A comparison of the oxidation states of cobalt species following ESR over the pre-oxidized and pre-reduced samples clearly showed that regardless of the pretreatment procedure the same type of cobalt species were present in almost the same proportions over both of the catalysts.

In addition to the XAFS technique for studying the active cobalt species during reaction conditions, the interactions of ESR reactants, intermediates and products were studied under ESR conditions using in situ DRIFT spectroscopy. Although DRIFTS technique has been used extensively in the project to investigate the thermal evolution of surface species following the room-temperature adsorption of reactants and reaction intermediates (DRIFTS-TPD), these in situ reaction DRIFTS experiments allowed monitoring of the transformation of reactants and especially less stable surface intermediates under reaction conditions. The DRIFTS data collected during reaction were combined with spectra collected during purging for a detailed identification of surface species. Figure 2 shows such a pair of DRIFTS data as a function of temperature for a 10% Co/CeO₂ catalyst during ESR and subsequent purge steps. The 1,731 cm⁻¹ band observed in the spectra collected in situ during ESR above 150°C is of particular
importance since it signifies adsorbed acetaldehyde [1-7]. Although in our steady-state reaction experiments, acetaldehyde was observed as a reaction product, it was not detected in the transient experiments or in the TPD experiment. It is highly likely that these species interact weakly with the surface and get flushed away during the purge, and therefore, the DRIFTS-TPD profiles failed to show the presence of aldehyde species on the surface. Along with the ethoxy groups detected on the surface, this finding provided further evidence for the previously proposed ethanol steam reforming reaction mechanism where an ethanol-to-ethoxy-to-acetaldehyde pathway was proposed to be the initial steps for hydrogen production in bio-ethanol steam reforming (Figure 3).

This year’s work also involved preliminary studies with different feedstocks such as dimethylether (DME). DME is an inert, non-carcinogenic, non-corrosive, non-mutagenic and virtually non-toxic alternative to ethanol. Moreover, it is possible to liquefy DME at 0°C and 6 psig which makes it a versatile feedstock for industrial applications. The DRIFTS spectra presented in Figure 4 shows operando DME steam reforming over a 10% Co/CeO$_2$ catalyst. Strong bands associated with methoxide species, which persisted throughout the investigated temperature range of 25-400°C were observed. Furthermore, the presence absorption bands in the 1,250-1,100 cm$^{-1}$ region pointed to the presence of formates [8]. Co/CeO$_2$ catalyst showed strong single carbon adsorption bands on the surface, which were observed throughout the temperature program in steam reforming conditions.

Conclusions and Future Directions

- New collaboration was initiated with the Argonne National Laboratory.
- Local coordination environment and oxidation state of cobalt over the cobalt-based ESR catalysts were determined via XAFS.
- The role of catalyst pre-treatment was examined by XAFS.
- Operando vibrational spectroscopy techniques were shown to provide new insights into the reaction mechanism.
- Alternative feedstocks such as DME were introduced.
- 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., 2009 American Institute of Chemical Engineers WIC Mentorship Excellence Award.

FY 2010 Publications/Presentations

Books

Journal Articles


Conference Presentations


Invited Lectures


References


II.A.2 Distributed Hydrogen Production from Biomass Reforming

Objectives

- Evaluate and develop bio-derived liquid aqueous phase reforming (APR) technology for hydrogen production that can meet the DOE 2017 cost target of <$3.00/gasoline gallon equivalent (gge).
- 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reformer Capital Cost
(C) Operation & Maintenance
(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). For APR, the cost targets remain the primary drivers. We have been focusing on identifying the specific role of the catalyst components, delineating the mechanistic pathways leading to desired and undesired products, and understanding the causes of catalyst deactivation. This improved understanding is aimed at reducing operating costs, which will lower cost of hydrogen production.

Accomplishments

- Found evidence for dual-functionality of Pt-Re/C under a hydrothermal APR environment:
  - Pt-Re alloy formation provides increased activity toward H₂ production.
  - Acidic ReOₓ facilitates competitive dehydration pathways.
- Advanced the understanding of glycerol APR over Pt-Re/C:
  - Addition of Re increases conversion of glycerol, but also provides additional reaction pathways competing with the H₂-generating C-C cleavage pathway.
  - ReOₓ formed under APR conditions facilitates C-O scission, which consumes H₂ and leads to higher selectivity to alcohols and C₂₊ alkanes.
  - H₂ productivity increases with addition of Re at expense of H₂ selectivity.
  - Addition of KOH to glycerol feed over Pt-Re/C neutralizes acidity of ReOₓ and depresses C-O scission pathways, resulting in increased H₂ productivity via C-C cleavage.
- Preliminary results from APR of sorbitol have been obtained, providing comparative behavior between APR of sorbitol and glycerol, indicating that maintaining selectivity toward C-C bond cleavage vs. C-O bond cleavage is even more challenging.

Introduction

The conversion of biomass-derived liquids to hydrogen is attractive because of their near carbon-neutral footprint and their availability in many regions of the U.S. We target sugars and sugar alcohols, along with other polyols such as glycerol, for distributed production of hydrogen. These sugars and sugar alcohols are thermally unstable if vaporized to reforming temperatures; therefore aqueous phase reforming is the technology of choice. Currently, many researchers are investigating the conversion of sugars and sugar alcohols to liquid products that are infrastructure compatible, with less attention being paid to hydrogen production from these same molecules. Our project focuses on this latter aspect, hydrogen production, which has perhaps a longer time horizon, but over the long-term is an
important approach to meeting the energy needs through the application of fuel cells.

**Approach**

APR is becoming a recognized technology for the production of hydrogen from thermally unstable bio-derived sugars and sugar alcohols. Operation is at relatively low temperatures (225-265°C), placing a significant demand on catalytic activity. The standard catalyst is platinum on carbon (Pt/C), which shows modest 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 APR performance. Our approach has included:

- Detailed study of Pt-Re/C catalyst:
  - Compare catalytic performance with Pt/C for glycerol feedstock.
  - Quantify the effect of Re addition on Pt/C performance.

- Develop advanced catalyst characterization methods to understand interactions between the Pt, Re, and C components: X-ray photoelectron spectroscopy, X-ray absorption near-edge spectroscopy, transmission electron microscopy.

- Examine and quantify effect of base addition on catalyst performance.

- Evaluate options for co-production of hydrogen with CH₄ for compatibility with solid oxide fuel cells (SOFC) for power generation.

**Results**

Our APR work has focused on correlating catalyst structure with performance, and delineating competing reaction pathways with the intention to maximize the H₂ production pathway. Work has progressed this year from glycerol to sorbitol feedstock.

**Affect of Re Addition on Activity and Selectivity**

Figure 1 compares the activity of 3%Pt/C, 3%Pt-1%Re/C and 3%Pt-3%Re/C catalysts. The figure provides this information on a turnover frequency basis, meaning moles (of glycerol converted or product formed) per active Pt metal site (based on CO chemisorption) per minute. It can be seen that the addition of Re dramatically increases turnover frequencies for both glycerol conversion and all products formed, indicating that Re addition more affects activity than selectivity. Figure 2 compares the product selectivity in greater detail for the 3%Pt/C and 3%Pt-3%Re/C catalysts. In this case, the space velocity (flow rate) of the 3%Pt/C catalyst was substantially decreased in order to allow a comparison of performance over the two catalysts to be made at comparable glycerol conversion levels. The figure shows that the catalyst without Re addition is more selective toward H₂, CO₂, and diol formation, whereas addition of Re to the catalyst increases formation of alkanes, mono-alcohols, and carboxylic acids. We believe that the increase in alcohols and alkanes is the result of facilitating a dehydration pathway via the addition of Re, probably present as ReOₓ, in which diols are converted to mono-alcohols, and mono-alcohols converted to alkanes via successive dehydration/hydrogenation pathways. The reason for the increased formation of carboxylic acids is less clear.
Effect of Base Addition to 3%Pt-3%Re/C Catalyst

With the operating assumption being that the increase of mono-alcohols and alkanes was due to acidity present on the catalyst, we have explored the addition of 0.1% KOH base to neutralize the acidity of the catalyst. The net effect is a small increase in hydrogen selectivity, as shown in Figure 3, accompanied by a decrease in alkanes production, the result of significantly removing the dehydration pathway from mono-alcohols to alkanes. On the other hand, the addition of base results in the generation of more liquid phase product. We conclude that although base addition can have some positive effects in controlling reaction pathways, the amount of base added must be carefully controlled to maximize overall hydrogen productivity and minimize accumulation of liquid phase product.

Co-Production of Methane with H₂

This past year, we examined adjusting pH and operating conditions in an effort to maximize the combined production of H₂ and CH₄. The purpose for this was the potential utilization of the APR product with an SOFC, which is capable of processing CH₄. Figures 4 and 5 show that it is possible to maximize both H₂ and CH₄ through a combination of increased residence time and base addition.

Comparison of APR of Glycerol with Sorbitol

We examined the effect of changing feedstock from glycerol to sorbitol on the conversion and product selectivity, keeping the same operating parameters for both. The comparative results are shown in Figure 6a. It can be seen that for the larger (sorbitol) molecule, the hydrogen selectivity is significantly lower. However,
addition of base appears to be quite beneficial in terms of increasing the hydrogen selectivity from sorbitol, as seen in Figure 6b. The relative selectivity of methane vs. other alkanes is also increased on addition of base, pointing toward the possible realistic application of coupling the APR reformer with an SOFC.

Economic Benefits of Coupling APR with an SOFC

Based on a combination of Aspen modeling and H2A analysis, a qualitative assessment of the potential benefits of combining APR of sorbitol with an SOFC was made. These results are summarized in Table 1.

Two conclusions can be drawn from the economic analysis:
- The use of fuel cell waste heat to drive the endothermic APR reaction provides a significant saving on cost of delivered H2.
- The overall production cost for hydrogen is significantly impacted by the cost of the feedstock.

Conclusions

- We have quantified the effect of the addition of Re to Pt/C catalyst in terms of catalyst activity and selectivity. Re addition increases overall catalyst activity, but at a loss of hydrogen selectivity relative to alkanes.
- Addition of KOH base to an aqueous 10% glycerol feed increases hydrogen productivity modestly with 3%Pt-3%Re/C catalyst, primarily through shutting down the production of light alkanes. However, more liquid products are also seen.
- Residence time is important in glycerol APR with the Pt-Re/C catalysts. Longer residence time increases gas phase products, hydrogen, and methane (relative to light alkanes).
- Hydrogen productivity with sorbitol declines relative to glycerol, primarily because more pathways are available, predominantly via dehydration/hydrogenation pathways. This can be ameliorated by employing longer residence times and adding base to the aqueous feed.

Future Directions

We will focus on the following:
- Catalyst synthesis and characterization, focusing on a number of synthesis variables including support characteristics, metal loading, and pretreatment conditions.
- Long-term testing to assess catalyst life.
- Screen catalysts to identify possible replacements for Re as a promoter for Pt, due to the undesired dehydration selectivity associated with Re addition.
- Explore alternate feedstocks, including less pure sorbitol and the effects of impurities on catalyst performance. Also identify purification needs with the raw feed material, as needed.
FY 2010 Publications and Presentations


II.A.3 Hydrogen from Glycerol: A Feasibility Study

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Project Start Date:  October, 2009
Project End Date: Project continuation and direction determined annually by DOE

Objectives

Evaluate the economic feasibility of distributed hydrogen production from glycerol derived as a byproduct of the biodiesel industry.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(D) Feedstock Issues
(E) Greenhouse Gas Emissions

Technical Targets

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

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2012 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Unit Energy Efficiency</td>
<td>%</td>
<td>72.0</td>
</tr>
<tr>
<td>Total Hydrogen Cost</td>
<td>$/gge</td>
<td>3.80</td>
</tr>
</tbody>
</table>

The project is conducting the analysis to determine the feasibility of meeting the efficiency and cost targets for producing hydrogen from glycerol at distributed production centers with a capacity of 1,500 kg of hydrogen per day and operating at 85% of capacity.

Accomplishments

- Completed the study using systems analysis followed by H2A to estimate the cost of hydrogen.
- Defined the process conditions needed to produce hydrogen from glycerol with an efficiency of 72%.
- The cost of hydrogen for a base case set of conditions was estimated at $4.86 per kg, where the price of glycerol was assumed to be $1.07/gal (10 cents/lb). The current price of crude glycerol ranges between 3-10 cents per pound.
- The cost of feedstock (crude glycerol) represents 44% of the cost of hydrogen.

Introduction

Glycerol is a biomass-derived liquid that is being generated by the biodiesel industry as a byproduct (waste stream) in quantities that exceed current demands. As a byproduct of the biodiesel industry the crude glycerol (80–88% pure) contains methanol, water, and salts (soaps). The presence of methanol requires that the crude glycerol be treated as a hazardous waste, which adds to the cost of biodiesel production. A preferred alternative is to convert the waste glycerol to secondary products within the bio-refinery (which has a very limited potential at this time), or to sell the glycerol, either as the crude glycerol as is, or after refining it to commodity grade. Table 2 summarizes some information on the supply, demand, and the price of glycerol.

TABLE 2. Production Rates and Prices

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodiesel Production Capacity in U.S. (2008) [1]</td>
<td>2.6 x 10^9</td>
<td>gal/year</td>
</tr>
<tr>
<td></td>
<td>19.0 x 10^8</td>
<td>lb/year</td>
</tr>
<tr>
<td>Biodiesel Production in U.S. (2008) [1]</td>
<td>0.7 x 10^9</td>
<td>gal/year</td>
</tr>
<tr>
<td></td>
<td>5.2 x 10^8</td>
<td>lb/year</td>
</tr>
<tr>
<td>Crude Glycerol from Biodiesel Production in U.S. (2008)*</td>
<td>5.2 x 10^8</td>
<td>lb/year</td>
</tr>
<tr>
<td>World Demand for Glycerol (2005) [2]</td>
<td>19.8 x 10^8</td>
<td>lb/year</td>
</tr>
<tr>
<td></td>
<td>9.0 x 10^8</td>
<td>kg/year</td>
</tr>
<tr>
<td>World Production of Glycerol (2008) [3]</td>
<td>3.8 x 10^8</td>
<td>lb/year</td>
</tr>
<tr>
<td></td>
<td>1.7 x 10^8</td>
<td>kg/year</td>
</tr>
<tr>
<td>Price of Crude Glycerol [4-8]</td>
<td>3.5 – 10</td>
<td>cents/lb</td>
</tr>
</tbody>
</table>

*Each pound of biodiesel produced generates approximately 0.1 pound of crude glycerol byproduct
The burgeoning demand for hydrogen, preferably produced from renewable sources, and the growing availability of glycerol has attracted attention as a potential pathway for the distributed production of hydrogen from glycerol. A distributed hydrogen refueling infrastructure can potentially use this surplus renewable resource to produce hydrogen. This approach would simultaneously help manage a waste/surplus stream (to reduce the cost of biodiesel production costs) and produce hydrogen from a renewable resource. The economic viability of this pathway will be determined, in part, by the availability and cost of glycerol, and the cost of producing hydrogen from it.

Approach

The project reviewed the availability of glycerol which was then used to estimate the amount of hydrogen that can be produced annually in the U.S.

The process was based on the steam reforming of glycerol followed by purification using pressure swing adsorption. The model was set up, along with a set of assumptions, to determine the process conditions that would be needed to meet DOE’s efficiency target. The inputs and results from the base case were used to estimate the cost of hydrogen and the cost contributors.

Results

Glycerol can be steam reformed to produce up to 7 mol of hydrogen per mol of glycerol, according to the reaction,

\[
C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2, \quad \Delta H_1 = +347 \text{ kJ} \quad (1)
\]

The reaction is strongly endothermic and requires a combination of catalysts, excess steam, and temperatures greater than 500°C to achieve high conversions of glycerol to hydrogen and carbon oxides. The actual reaction mechanism is complex, beginning with the decomposition of glycerol to intermediates including CO and H₂, followed by steam reforming of the intermediate carbonaceous species (Eqn.(2)) and water-gas shift (WGS) reaction (Eqn.(3)).

\[
C_{n}H_{m}O_{p} + H_2O \rightarrow CO + H_2, \quad \Delta H_2 > 0 \quad (2)
\]

\[
CO + H_2O = CO_2 + H_2, \quad \Delta H_3 = -41 \text{ kJ} \quad (3)
\]

Figure 1 shows the process schematic where hydrogen is produced at 72\%\(^1\) efficiency in the base case scenario for the production of 1,500 kg of H₂/day. The reforming process is based on 20 atm (~300 psi) steam-reforming/WGS reaction followed by a pressure-swing adsorption (PSA) unit for hydrogen purification. The steam reformer is operated with a molar steam-to-carbon ratio (S/C) of 3. The product stream leaving the reformer (reformate at chemical equilibrium at 800°C) is cooled and then processed in a high-temperature WGS reactor at 400°C. The reformate, composition is shown

\(^1\)Energy efficiency is defined as the energy of the hydrogen (lower heating value, LHV) out of the production unit divided by the sum of energy inputs into the process, i.e., \(\Sigma\) (Feedstock (LHV) + Natural Gas (LHV) + electricity). Electrical energy utilized does not include efficiency losses from the production and the transmission of electricity.
in Table 3, then enters the PSA unit where high purity hydrogen is extracted with 80% recovery, exiting the production unit at 20 atm.

The PSA off-gas containing the carbon oxides and methane, along with the un-recovered hydrogen is combusted in the burner to generate heat for the reforming process. Additional fuel (natural gas) is used in the burner, if needed.

**TABLE 3. Reformate Composition to PSA**

<table>
<thead>
<tr>
<th>Reformate</th>
<th>Composition (mol-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>65.52</td>
</tr>
<tr>
<td>CO₂</td>
<td>28.76</td>
</tr>
<tr>
<td>CO</td>
<td>2.17</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.08</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.47</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>trace</td>
</tr>
</tbody>
</table>

For the base case, the cost of hydrogen (untaxed) from the steam-reforming of glycerol was calculated to be $4.86/kg-H₂. For this set of (base case) conditions, the estimated cost is 27% higher than the 2012 DOE target of 3.8/kg-H₂ from bio-derived liquids. The contributions of various elements to the cost of hydrogen are shown in Figure 2. The production unit accounts for ~60% ($2.97/kg) of the hydrogen cost, with feedstock being the main cost contributor. The refueling station part accounts for almost 40% ($1.88/kg) of the delivered hydrogen cost, where the majority of that cost is due to the required capital investment. Overall, the highest cost contributors for the delivered hydrogen are the feedstock costs (44%) and the combined capital investment costs for the production unit and refueling station (37%).

The production unit efficiency, affecting feedstock utilization, influences the cost of the delivered hydrogen. Figure 3 shows the cost of hydrogen as a function of production efficiency for four different feedstock prices. When the price of glycerol is high (>10 cents/lb), efficiency has a significant impact on hydrogen cost. At such a high feedstock price, however, the cost of delivered hydrogen exceeds the target by over 50%, even at 72% efficiency. The targeted cost of hydrogen for 2012 ($3.80) can be met with the glycerol price at 5 cents/lb. At this price, the efficiency has only a marginal impact on the hydrogen cost. At the low feedstock prices (2.4 cents/lb), efficiencies above 68% actually increase the cost of the delivered hydrogen, since the cost of the natural gas which is assumed to provide supplemental heat to the reformer is more expensive (LHV basis) than the glycerol feedstock.

**Conclusions**

- Glycerol supply is outpacing its demand as a result of the biodiesel industry.
Glycerol is renewable and can be efficiently converted to hydrogen.

With glycerol at $1.07/gal (10¢/lb) the estimated cost of H₂ is $4.86/kg.

The cost of hydrogen is highly sensitive to the price of the feedstock.

The U.S. biodiesel plants (capacity in 2008) can produce sufficient crude glycerol to enable 200,000 kg/day of hydrogen.

References

II.A.4 Distributed Bio-Oil Reforming

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Subcontractor:  
University of Minnesota, Minneapolis, MN

Project Start Date:  October 1, 2004  
Projected 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: bio-oil injection, catalytic auto-thermal reforming, water-gas shift, and hydrogen isolation.
- 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 (FY) 2010, demonstrate the process of auto-thermal reforming of bio-oil including a long-term catalyst performance, yields of hydrogen, and mass balances.
- 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Fuel Processor Capital  
(C) Operation & Maintenance  
(D) Feedstock Issues

Technical Targets

<table>
<thead>
<tr>
<th>TABLE 1. Progress toward Meeting DOE Distributed Hydrogen Production Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Characteristics</td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>Total Energy Efficiency</td>
</tr>
<tr>
<td>Production Energy Efficiency</td>
</tr>
<tr>
<td>Storage, Compression, Dispensing Efficiency</td>
</tr>
<tr>
<td>Total Hydrogen Costs Hydrogen Production Costs</td>
</tr>
<tr>
<td>Hydrogen Production Costs</td>
</tr>
</tbody>
</table>

Accomplishments

- Demonstrated hydrogen production by auto-thermal reforming of bio-oil using the bench-scale reactor system.
- Achieved hydrogen production of 7.3 g/100 g bio-oil (potentially 9.6 g/100 g bio-oil after water-gas shift) with 93% bio-oil to gas conversion.
- Demonstrated 60 hours of steady performance of a research catalyst in several reforming/regeneration cycles.
- Achieved similar performance data for a commercial catalyst.

Introduction

Renewable biomass is an attractive near-term alternative to fossil resources because it has near-zero life-cycle 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.
- 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.

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 bench-scale auto-thermal reforming tests were carried out in the systems shown in Figure 1. Poplar pyrolysis bio-oil diluted with 10 wt% methanol was fed at 60 g/h using a membrane pump to the top of the 34 mm internal diameter, 45 cm long tubular quartz reactor. The bottom section of the reactor contained a fixed bed comprising 38 g of catalyst (1 wt% Rh, 1 wt% Ce on alumina) prepared at University of Minnesota mixed with 62 g of α-alumina. In the freeboard, the liquid in the form of a very fine mist produced by a 60 KHz ultrasonic nozzle (Sono-Tek) contacted air and steam; steam was produced by a home-made micro-generator. The non-catalytic oxidation was followed...
by the reactions in the catalytic bed. The optimum conditions that assured a smooth operation, high hydrogen yields and high bio-oil to gas conversion were process temperature of 800-850°C, oxygen-to-carbon ratio O/C=1.5, molar steam-to-carbon ratio S/C=1.6, and methane-equivalent volumetric hourly space velocity equal to 5,200 h⁻¹. The steam excess and some organics were collected in two condensers. The outlet gas flow rate was measured by a dry test meter. The concentrations of CO₂, CO, and CH₄ in the product gas were monitored by a non-dispersive infra-red analyzer (NDIR Model 300 from California Analytical Instruments); the hydrogen concentration was tracked by a thermal conductivity monitor TCM4. In addition, the gas was analyzed every 4 minutes by an on-line Varian (Model 4900) micro gas chromatograph, which provided concentrations of H₂, CO, CO₂, CH₄, C₂H₄, O₂, and N₂. The temperatures in the system, as well as the flows, were recorded and controlled by an OPTO 22 data acquisition and control system. Based on the flows and compositions of the process streams, mass balances as well as the yields of hydrogen generated from the feed were calculated.

A series of auto-thermal reforming tests included several production and regeneration cycles. After each hydrogen production test, the catalyst was regenerated by air oxidation and reused in the subsequent tests carried out at the same process conditions. The catalyst performance gradually decreased during the reforming cycle but was restored after every regeneration cycle. Gas composition as a function of time is shown in Figure 2. The average hydrogen production during this time span was 7.3 g/100 g bio-oil. This yield could increase to 9.6 g/100 g bio-oil if CO in the gas were further converted by water-gas shift. The carbon-to-gas conversion was 91-93% with the remaining carbon recovered mostly in the form of solid cenospheres (very light weight hollow spheres). These carbon deposits caused pressure drop increase during the tests and had to be removed by burn-off.

The next step in our research on the process development was the application of a commercial catalyst similar to that prepared by University of Minnesota. Previously, noble metal catalysts provided by Engelhard showed significantly lower performance than the University catalyst in micro-scale tests. This year, we obtained new rhodium and platinum catalysts that are being developed by BASF for commercial applications. These were alumina-based catalysts with a noble metal content of only 0.5 wt% compared to 1 wt% for the University of Minnesota catalysts. The gas composition from reforming bio-oil using BASF rhodium catalyst is shown in Figure 3. This figure shows combined results of two reforming experiments separated by the catalyst regeneration after five hours on stream. Remarkably, the system operation was even more stable than during previous tests using the University of Minnesota catalyst. The catalyst did not show any deactivation during tests but similarly to the experiments described above, the pressure drop due to the carbon deposits was observed. The hydrogen production was 7.4 g/100 g bio-oil with the potential to increase to 10.3 g/100 g bio-oil after completing water-gas shift. The carbon-to-gas conversion was 93% with the remaining carbon forming cenospheres. Though the BASF catalyst was tested for only 11 hours compared to 60 hours for the University catalyst, the results allow us to expect that its performance will remain at the same level.

Conclusions and Future Directions

- Bench-scale reactor tests of catalytic auto-thermal reforming of bio-oil performed using 90 wt% bio-oil/10 wt% methanol mixtures produced hydrogen...
yields of 7.3-7.4 g/100 g bio-oil with 91-95% of carbon-to-gas conversion.

- Rh/Ce catalyst prepared at University of Minnesota performed satisfactorily during 60 hours of operation that included reforming and regeneration cycles. Noble metal catalysts produced by BASF also showed very promising performance and will be used extensively in further tests.
- Tests will continue with bio-oil containing more inorganic impurities to assess their impact on the catalyst performance.
- A prototype system including catalytic reformer, water-gas shift reactor, and electrochemical hydrogen separator will be constructed and operated to demonstrate the integrated process performance.

FY 2010 Publications/Presentations


References


II.A.5 Distributed Reforming of Renewable Liquids Using Oxygen Transport Membranes

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Subcontractor: Directed Technologies, Inc. (DTI), Arlington, VA
Project Start Date:  May, 2005
Project End Date:  Project continuation and direction determined annually by DOE

Objectives

Develop a compact ceramic membrane reactor that meets the DOE 2017 cost target for producing hydrogen by reforming renewable liquids. Specific objectives for Fiscal Year (FY) 2010 were:

• Use oxygen transport membrane (OTM) to reform ethanol (EtOH) at ≤700°C.
• Generate data for detailed analysis to assess benefits of approach.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Fuel Cell 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
(P) Flux
(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 EtOH 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/gasoline gallon equivalent (gge) (delivered) at the pump by 2012
  – <$3.00/gge (delivered) at the pump by 2017

A preliminary techno-economic analysis estimated a cost of ≈$3.40/gge for producing hydrogen by reforming EtOH with an OTM. DOE's hydrogen cost target is being revised at the present.

Accomplishments

• Significantly increased EtOH conversion with a new OTM, but analysis of the products of reforming indicated that a suitable catalyst is needed in order to increase hydrogen production during reforming.
• Enhanced H₂ production rate by increasing EtOH concentration and H₂O/EtOH in feed during EtOH reforming with OTM.
• Developed BFZ1 (BaFe₀.₉Zr₀.₁Oₓ) a new OTM whose significantly higher oxygen flux might enhance EtOH conversion at low temperature (∼500°C).
• Provided data to Directed Technologies, Inc. (DTI), whose preliminary analysis indicated a hydrogen production cost of ≈$3.40/gge for a station capacity of 1,500 kg H₂/day.

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Introduction

Previous study has shown that supplying oxygen with an OTM reduced the costs of methane reforming by ≈30–40% and energy consumption by ≈50%. Similarly, it has been shown that supplying oxygen during EtOH reforming increases EtOH conversion and enhances catalyst performance by preventing coke formation [1]. An OTM can supply high-purity oxygen for EtOH reforming by separating it from air without using a separate gas separation unit. Because the OTM is a mixed conductor, the oxygen transport requires neither electrodes nor external power circuitry, i.e., the process is non-galvanic. The oxygen flux through the membrane depends on the membrane's electron and oxygen-ion conductivities, its surface oxygen exchange kinetics, and the oxygen partial pressure (pO₂) gradient across the membrane.

The goal of this subtask is to develop a dense OTM that provides oxygen for efficiently and economically producing hydrogen through the reforming of renewable liquid fuels such as EtOH and bio-oil. Using an OTM to supply high-purity oxygen from air can reduce the cost and energy consumption associated with EtOH reforming, but a detailed system analysis must be done to determine the cost and energy benefits. In this project, we are generating data for the system analysis. While generating the necessary data, we are also developing OTMs that transport oxygen at an industrially significant rate at low temperature (≈500°C) and possess sufficient mechanical and chemical stability to withstand the large stresses that develop from having air on one side of the OTM and carbonaceous fuels on the other side.

Approach

In order for our approach to be cost-effective in reforming renewable liquids, an OTM must efficiently transport oxygen. In order to efficiently transport oxygen, an OTM must have an appropriate combination of electronic and ionic conductivity; therefore, we use conductivity measurements to identify promising membrane materials. If a material has sufficient conductivity (>10⁻¹ ohm⁻¹·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 adjust the OTM’s composition, decrease its 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 ≈1,000 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. In order to evaluate the expected cost and energy benefits of reforming renewable liquids with an OTM, we are generating the necessary data for an independent party, Directed Technologies, Inc., to conduct a detailed system analysis.

Results

OTMs made of La₀.₇Sr₀.₃Cu₀.₂Fe₀.₈Oₓ (LSCF), Sr₀.₆Fe₀.₉Ti₀.₁Oₓ (SFT1), BaFe₀.₉7₅Zr₀.₀₂₅O₃ (BFZ0), and BFZ1 were tested. Powders for the OTMs were prepared by conventional solid state reaction between the constituent oxides. Dense OTMs were prepared in the shape of disks, tubes, or OTM thin films on porous disks or tubes. Before measuring an OTM’s oxygen flux or its hydrogen production during EtOH reforming, the OTM was tested for interconnected porosity and/or microcracks by checking if isopropyl alcohol (IPA) penetrated it. Penetration of the OTM by even a small amount of IPA was easily seen as darkening of its surface and indicated that the OTM contains cracks or interconnected porosity.

If IPA did not penetrate an OTM, it was tested on a fixture that allowed separate gases to be flowed over opposite faces of the OTM. The oxygen flux was measured while air flowed on the “feed” side of the OTM and ultra-high purity He on the “sweep” side, both gases flowing at a rate of 150 ml/min. The oxygen concentration in the sweep gas was measured with a Hewlett-Packard 6890 gas chromatograph (GC); the nitrogen concentration in the sweep gas was measured to correct for minor oxygen leakage through the gas seal. EtOH reforming was studied while feed with a steam/EtOH ratio ranging from 0/1 to 5/1 flowed on one side of the OTM, while air flowed on the opposite side. As a reference, EtOH reforming was also done with a dense, oxygen-impermeable Al₂O₃ cap instead of an OTM. The concentrations of EtOH reforming products were measured during the tests with the GC.

Figure 1 compares the compositions of the product streams during EtOH reforming at 550°C with a thin-film OTM tube (LSCF, thickness ≈30 μm) and with a dense, oxygen-impermeable Al₂O₃ “blank.” Steam was not added to the feed during these tests. The hydrogen formation rate with the OTM, although not large in this experiment without a catalyst, was more than twice that with the Al₂O₃ blank. Whereas the formation rates of CO, H₂O, and CO₂ were negligible with the blank, they all increased significantly when an OTM was used. The amount of un-reacted EtOH decreased by >50% with an OTM, giving an EtOH conversion of ≈63% as compared to the EtOH conversion of ≈47% that was reported in FY 2009.

The higher formation rates for products and the smaller concentration of un-reacted EtOH clearly show
that oxygen supplied by the OTM enhanced EtOH reforming. The high formation rate of H\textsubscript{2}O indicates that much of the hydrogen formed by reforming reacts with the oxygen supplied by the OTM. The high H\textsubscript{2}O formation rate demonstrates that a catalyst is needed to promote preferential oxidation of carbon-containing products. Although the formation rate of ethylene formed by dehydration of EtOH was not high, its presence is highly undesirable because ethylene is a precursor of coke formation, and may lead to catalyst deactivation [2].

EtOH reforming with an LSCF tube (thickness ≈1.5 mm) was studied using steam/EtOH ratios up to 5/1. As before, reforming experiments were also done with oxygen-impermeable Al\textsubscript{2}O\textsubscript{3} as a reference. Steam/EtOH mixtures were prepared by mixing two gas streams (N\textsubscript{2} or He), one saturated with EtOH at room temperature (23°C), giving P\textsubscript{EtOH}=0.067 atm, and the other saturated with water at a controlled temperature (38.5-72.1°C).

Figure 2 shows the effect of steam/EtOH ratio on the hydrogen formation rate. The hydrogen formation rate increased as the steam/EtOH ratio increased in both experiments. In the blank experiment, the hydrogen formation rate increased the most as the steam/EtOH ratio increased to 3/1 and only slightly more as the steam/EtOH ratio increased to 5/1. With P\textsubscript{EtOH}=0.067 atm, the hydrogen formation rate with the OTM tube was measured only for steam/EtOH ratios of 0/1 and 3/1. Under both conditions, the hydrogen formation rate with the OTM tube was about twice as high as that measured in blank experiments. When P\textsubscript{EtOH} was increased to 0.135 atm (with a steam/EtOH ratio of 0/1), the hydrogen formation rate increased to ≈1.7 cm\textsuperscript{3}/min. A blank experiment was not done with the higher P\textsubscript{EtOH}.

Figure 3 shows the oxygen flux (normalized for thickness of 1.0 mm) of BF20, BFZ1, SFT1, and LSCF disks.
appears promising for use during EtOH reforming at low temperature, provided that it exhibits good chemical stability during reforming.

DTI is performing a detailed techno-economic analysis of EtOH reforming with an OTM to evaluate its cost- and energy-benefits. For the analysis, Argonne is providing oxygen flux and EtOH conversion data for promising OTMs. A preliminary analysis shows that the cost of the EtOH feedstock comprises a major fraction (~70%) of the cost of producing hydrogen by EtOH reforming with an OTM. Figure 4 shows the cost of producing hydrogen by EtOH reforming with an OTM is $3.10-$3.60/kg H₂, depending on the EtOH fuel efficiency. A more detailed analysis is underway.

Conclusions and Future Directions

Significant progress has been made in demonstrating that a dense OTM can enhance the reforming of renewable liquids. In order to further evaluate the benefits of this approach, we will:

- Reform EtOH with OTM in presence of catalyst(s).
- Generate key data for performing a detailed economic analysis of our approach.
- Continue testing the performance of OTMs during EtOH reforming at ~500°C.
- Study effect of EtOH concentration, gas flow rates, and OTM thickness.
- Evaluate chemical stability of OTM during reforming of EtOH.
- Work with DTI to perform a detailed cost and energy analysis to judge the merits of using OTM to enhance H₂ production by EtOH reforming.
- Compare the cost of hydrogen production by OTM-assisted EtOH reforming with conventional steam reforming.

FY 2010 Publications/Presentations


References

II.B.1  A Novel Slurry-Based Biomass Reforming Process

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 H₂ cost targets of 43% (based on feedstock LHV) and $1.60/kg H₂, respectively. 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.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2012 Target</th>
<th>Current Status</th>
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</thead>
<tbody>
<tr>
<td>Hydrogen Cost (Plant Gate)</td>
<td>$/gge</td>
<td>1.60</td>
<td>1.27 (0.95–2.13)</td>
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<tr>
<td>Total Capital Investment</td>
<td>$M</td>
<td>150</td>
<td>177 (71–365)</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>%</td>
<td>43</td>
<td>55 (55–58)</td>
</tr>
</tbody>
</table>

Accomplishments

- Demonstrated 100% conversion of wood using an inexpensive base metal catalyst.
- Examined the effect of base concentration on liquid phase reforming H₂ selectivity.
- Developed a promoted nickel (Ni) catalyst that maintains a high selectivity to H₂ with minimal base.
- Elucidated the liquid phase reforming reaction pathways for ethylene glycol via atomistic modeling.
- Demonstrated palladium (Pd) membrane integration with a liquid phase reforming flow reactor.

Introduction

This project is focused on developing a catalytic means of producing H₂ 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 H₂ in that the carbon dioxide produced from the process can be used in the environment to produce additional biomass. For economically viable production of H₂, 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 corrosive environment 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 solid catalyst. A Pd alloy membrane allows the continuous removal of pure H\textsubscript{2}, while the retentate, including methane, is used as fuel in the proposed plant.

**Results**

Following the successful demonstration of the near 100% conversion of wood to hydrogen-containing gas using liquid-phase reforming (LPR), the project efforts were focused on further understanding the durability and kinetics of the process in a plug flow reactor system. Model compounds, such as ethanol, 1,4-butanediol, and ethylene glycol, were used to study a fixed bed reactor system using UTRC’s Pt-Re based catalyst. Tests showed that the catalyst could reform the model compounds for periods greater than 250 hours without signs of degradation.

During the model compound study, the coupling of the flow reactor with a Pd alloy H\textsubscript{2} separation membrane was also demonstrated. A 10% ethanol in 0.1M K\textsubscript{2}CO\textsubscript{3} solution was flowed through the reactor bed at 310°C at 3 mL/min. The effluent gas stream from the reforming reactor was approximated 213 mL/min and composed of approximately 64% H\textsubscript{2}. The effluent gas stream was fed to a palladium-copper alloy membrane held at 450°C at a pressure of 193 psig. The system was allowed to run for 45 minutes to stabilize and collect data. The data from the experiment is given in Figure 2. The system behaved as expected, with a 93% H\textsubscript{2} recovery, indicating maximum recovery of the H\textsubscript{2} from the reformate gas stream.

As part of the goal of reducing catalyst costs, and thus capital costs, the project focused on transitioning from a precious metal-based catalyst to one with base metal as the active component. At the same time, a study was performed to better understand the impact of base concentration on H\textsubscript{2} yield and selectivity. It was determined that for a commercially available Raney Ni catalyst, the selectivity toward H\textsubscript{2} could be adjusted by changing base concentration. By increasing base concentration, methane generation could be significantly suppressed, but at the expense of a reduced H\textsubscript{2} yield due to the formation of high levels of intractable organic acids. Figure 3 shows the impact of H\textsubscript{2} selectivity as a function of residence time and base concentration for a 5% ethylene glycol feed.

First principles atomistic modeling was used to gain an insight into the factors that control the activity and selectivity toward H\textsubscript{2} production by ethylene glycol reforming on Ni catalysts. The schematic diagram of reforming pathways is depicted in Figure 4. For ethylene glycol on a Ni surface, the first step after adsorption is hydroxyl bond breaking to form an ethylenedioxy intermediate. At the surface coverage considered, the activation of the C-O bond in ethylenedioxy and rearrangement to form the acetaldehyde intermediate and adsorbed oxygen are thermodynamically favorable. Subsequent dehydrogenation and C-C bond scission...
of acetaldehyde yields the CO and CH₃ as final decomposition intermediates. CO is shifted in water to CO₂ and H₂ while the methyl is hydrogenated into methane. In a basic environment, CO can also be converted to a formate ion in solution through hydrophilic attack, consistent with the experimental observation of formic acid in the spent liquor.

As the reaction pathway for LPR on Ni consists of three major paths toward either H₂, methane, or organic acid, modifications were performed to standard Raney Ni catalysts to adjust their selectivity. As a result, a modified Raney Ni catalyst was developed that enabled the use of dilute carbonate bases while still maintaining high selectivity as well as high H₂ yield. Figure 5 shows the impact of H₂ selectivity as a function of residence time and base concentration for a 2.5% ethylene glycol feed. This performance was also reproduced using yellow poplar in a batch reactor.

Conclusions and Future Directions

Based on the successful work with base metal catalysts, the next step of the project is to construct a demonstration unit for H₂ production. The demonstrator shall integrate a liquid phase reformer with a Pd membrane separator and show the integration...
of the major process components into a small system. Construction of a 12 L/min H₂ generation demonstrator fed by wood slurry has begun and shall be in operation later in 2010.

**FY 2010 Publications/Presentations**


**References**

II.B.2 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

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.

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.

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

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

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>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2005 Status</th>
<th>2012 Target</th>
<th>2017 Target</th>
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<tr>
<td>H₂ Cost (Plant Gate)</td>
<td>$/gge</td>
<td>&lt;$2.00</td>
<td>$1.60</td>
<td>$1.10</td>
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<tr>
<td>Total Capital Investment</td>
<td>$M</td>
<td>&lt;$194</td>
<td>$150</td>
<td>$1</td>
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<tr>
<td>Energy Efficiency</td>
<td>%</td>
<td>&gt;35%</td>
<td>&gt;43%</td>
<td>&gt;60%</td>
</tr>
</tbody>
</table>

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:
  - 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 cellulosics into hydrogen 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 CO₂-neutral, renewable hydrogen is an attractive pathway to meet the DOE goal of producing hydrogen at a cost of $2-3/gge. 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 50% 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 cellulosics to generate a sugar feedstock stream for downstream APR, and 2) solubilization of lignocellulosics followed by aqueous phase reaction (APRxn) of oligomeric, soluble cellulose.

LANL will conduct screening experiments for evidence of direct APRxg 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.

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 mass spectrometry 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 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:
  - 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.B.3 One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

Objectives

GTI together with its partners, NETL, Schott North America and ATI Wah Chang are working to determine the technical and economic feasibility of using the membrane gasifier to produce hydrogen from biomass. Specifically, the team plans to:

- Reduce the cost of hydrogen from biomass to $1.60/kg \( \text{H}_2 \) (excluding delivery).\(^1\)
- Develop an efficient membrane reactor that combines biomass gasification, reforming, shift reaction and \( \text{H}_2 \) separation in one step.
- Develop hydrogen-selective membrane materials compatible with the biomass gasification conditions.
- Demonstrate the feasibility of the concept in a bench-scale biomass gasifier.

Technical Barriers

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

- Impurities
- Hydrogen Selectivity
- Operating Temperature
- Flux

Technical Targets

This project is directed at developing a membrane reactor that can be closely-coupled with a gasification reactor while having a sufficiently high hydrogen flux to achieve a hydrogen production cost of $1.60/kg (without delivery) per the DOE 2012 technical target.

Accomplishments

- Project was restarted (February 2010) after 1 year hiatus. Selected team members completed contractual activities with GTI.
- Development of metallic, glass-ceramic membranes is in progress.
- Process development and economic analysis with initial candidate membrane is in progress.
- Membrane module design with initial candidate membrane is in progress.

Introduction

GTI has developed a novel concept of membrane reactor for clean, efficient, and low cost production of hydrogen from biomass-derived syngas. Our approach is presented in Figure 1 and shows a hydrogen-selective membrane closely coupled with a reforming or gasification reactor for direct extraction of hydrogen from the syngas. The specific objective of the project is to develop high temperature metallic or glass membranes that can be used closely-coupled with a biomass gasifier. The technical feasibility of using the membrane reactor to produce hydrogen from a biomass gasifier will be evaluated. GTI with its project team (SCHOTT North America, NETL, and ATI Wah Chang) has been evaluating potential membranes (metal, ceramic and glass) suitable for high temperature, high pressure, and the harsh environment of a biomass gasifier. The project team has been screening and testing each type of material, investigating its thermal and chemical stability, and conducting durability tests.

\(^1\) From 2007 H2 Production technical plan. During the 2010 Annual Merit Review, the need to rebaseline costs was stated.
Approach

To conduct commercially successful research, GTI has developed a plan where efforts are concentrated in four major areas: membrane material development, membrane module development, membrane process development and membrane gasifier scale up. The initial focus of the project has been concentrated on membrane material development. Metallic and glass-based membranes have been identified as hydrogen selective membranes under the conditions of the biomass gasification, temperatures above 700°C and pressures up to 30 atmospheres. Membranes are synthesized by arc-rolling for metallic type membranes and incorporating Pd into a glass matrix for glass membranes. Testing for hydrogen permeability properties have been completed and the effects of hydrogen sulfide and carbon monoxide were investigated for perspective membranes. The initial candidate membrane chosen in 2008 was selected for preliminary reactor design and cost estimates. The overall economics of hydrogen production from this new process will be assessed and compared with traditional hydrogen production technologies from biomass. The final deliverable of the project will be a gasification membrane reactor system that is expected to meet or exceed the DOE’s cost target for hydrogen production from biomass. This will be demonstrated by a bench scale gasification membrane reactor that can process approximately 2~10 kg/hr of woody biomass for hydrogen production.

Results

The project was restarted after a one year hiatus. The Arizona State University work on ceramic membranes was discontinued due to an inability to show sufficient promise for flux improvement to compete with the metallic or glass/ceramic membrane work during the project’s timeframe.

NETL is pursuing a new approach for stabilizing Pd alloys for high temperature use. This approach is modeled on a strategy that has been used to strengthen and stabilize certain high performance alloys such as Ni-based super alloys for high temperature applications. This approach utilizes a two-phase microstructure for stabilization. Unlike previous approaches where the additive is concentrated at grain boundaries, the two phases in the system under consideration can form a uniform dispersion of grains rather than be concentrated at grain boundaries. In this scenario, the primary phase transports hydrogen while the secondary phase improves the high temperature strength. NETL has fabricated new alloy combinations and hydrogen permeability tests were subsequently conducted. A 55 wt% Ni-Pt alloy was successfully rolled. Figure 2 shows permeability of the alloy at 600, 700 and 800°C. Permeability of a Pd,Pt,Al alloy is also shown. A Pd,Pt,Al alloy was synthesized and oxidized in an attempt to convert the Al to oxide for grain boundaries stabilization. Pt was added to this alloy to possibly improve the strength and sulfur resistance of the membrane. Due to failure of the membrane at 700°C, there is no data of hydrogen permeability at higher temperatures to determine a potential Pt effect on alloy characteristics. Scanning electron microscopy shows that the Al is located along the grain boundaries. So, Al incorporation into an alloy with subsequent oxidation of Al to Al,2O3 allows us to have Al located along the grain boundaries. The hydrogen permeability of synthesized alloys is lower than the permeability of the initial candidate membrane (Pd-Cu).

Glass membranes were obtained from SCHOTT and tested for hydrogen permeation. Table 1 summarizes results obtained for membranes synthesized by SCHOTT. Membranes with Pd have palladium content of about 0.05 wt%. At T=850°C, hydrogen flux was 0.02 SCFH/ft² at pressure difference 7.3 psi for membrane containing palladium. Pure glass synthesized at the same conditions with no palladium has no hydrogen permeation. From these results, one deduces that hydrogen transports only through the metal network in the glass.

SCHOTT has focused to synthesize metal-glass-ceramic membranes using a reducing agent. Addition of a reducing agent
agent (sugar) may assist hydrogen permeation by further reduction of Pd incorporated in the matrix. A few formulations with sugar additions were completed and total conductivity was measured. Also, a new melting protocol has nearly been completed this quarter that should enable SCHOTT to produce larger quantities of higher homogeneity material for permeability testing.

GTI continued to test membranes fabricated by GTI and other team members as they become available. Testing of the initial candidate membrane for 50 hours with a gas containing H₂S to try and duplicate NETL results for grain boundary failure is in progress.

GTI has resumed work on HYSYS modeling of downstream processes and variations; some modifications were implemented into three schemes for downstream processes after the biomass reactor. Different variations of process systems for producing hydrogen from biomass are being evaluated and are shown in Figure 3. Construction of HYSYS process schemes for downstream processes after biomass gasification is completed. Input data for UGAS software based on gasifier sizing, biomass types and operational conditions were selected: feedstock feed rate, temperature and pressure of gasifier, oxygen/carbon molar ratio, types of feedstock, etc. Based on gasifier design, diameters of lower and upper sections of gasifier were specified. Preliminary results were obtained to be used in HYSYS modeling. A detailed gasifier reactor drawing is in the final stage of development. A planar design for the hydrogen membrane module based on initial candidate membrane has been selected.

Conclusions and Future Directions

GTI selected Pd_{80}Cu_{20} as an initial candidate membrane for integrated testing with a biomass gasifier:
- GTI and partners will continue to pursue development of membranes with greater flux and higher resistance to contaminants for the best candidate membrane.
- GTI will continue development of the membrane gasifier process and an economic analysis will be performed.
- GTI will utilize a biomass gasifier currently under construction for future membrane integration.

FY 2010 Publications/Presentations


<table>
<thead>
<tr>
<th>Date</th>
<th>Membrane</th>
<th>Ceramization Conditions: Temperature, Atmosphere</th>
<th>Electronic Conductivity, S/cm at 600°C</th>
<th>Hydrogen Permeation SCFH/ft²</th>
<th>Temp, °C</th>
<th>Pressure Difference, psi</th>
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<tr>
<td>05/30/08</td>
<td>CMAS-1/2D w/Pd</td>
<td>1.100°C, H₂/N₂</td>
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<td>07/21/08</td>
<td>CMAS-1/3 Glass-no Pd</td>
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<tr>
<td>07/28/08</td>
<td>CMAS-1/2 w/Pd Glass</td>
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<td>CMAS-1/3E</td>
<td>875°C, H₂/N₂</td>
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II.C.1 High-Performance Palladium-Based Membrane for Hydrogen Separation and Purification

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 such as ethanol at a cost of $2-3/gge by 2011.
- The objectives for the past year were to improve the membrane fabrication process to retain high flux and purity in water-gas shift (WGS) reaction environment and gas streams.
- An objective for last year was to extend the testing of Pd-Au alloy membranes to include H₂S-containing WGS streams.
- Another objective was to incorporate a potential end user on the program that will provide the system economic and energy analysis/assessment of the membrane technology and compare it to current state-of-the art hydrogen production processes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan and the technical targets indicated in Table 1:
- (K) Durability
- (L) Tolerance to Impurities
- (M) Membrane defects
- (N) Hydrogen selectivity
- (O) Operating temperature
- (P) Flux
- (Q) Testing and analysis
- (R) Cost

<table>
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<tr>
<th>Performance Criteria</th>
<th>2010 Target</th>
<th>2015 Target</th>
<th>Pall Status 2009</th>
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</thead>
<tbody>
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<td>Flux SCFH ft⁻² @ 20 psi ∆P H₂ partial pressure and 15 psig permeate side pressure</td>
<td>250</td>
<td>300</td>
<td>270*</td>
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<tr>
<td>Membrane Cost, $/ft² (including all module costs)</td>
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<td>&lt;500</td>
<td>&lt;$1,000</td>
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<td>∆P Operating Capability, system pressure, psi</td>
<td>400</td>
<td>400-600</td>
<td>400 psi</td>
</tr>
<tr>
<td>Hydrogen Recovery (% of total gas)</td>
<td>&gt;80</td>
<td>&gt;90</td>
<td>&gt;60**</td>
</tr>
<tr>
<td>Hydrogen Permeate Quality</td>
<td>99.99%</td>
<td>&gt;99.99%</td>
<td>99.999%***</td>
</tr>
<tr>
<td>Stability/Durability</td>
<td>2 years</td>
<td>&gt;5 years</td>
<td>to be determined</td>
</tr>
</tbody>
</table>

*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.

Accomplishments To-Date with Specific Barriers Addressed

- Increased operating capabilities to 400 psi at 550°C through use of 310SC stainless steel tubular substrate.
- Optimized and scaled up the diffusion barrier coating process to 12-inch lengths with the 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 (N, R).
- Developed additional sequential steps in the membrane synthesis process (air oxidation...
II.C Hydrogen Production / Separations

Introduction

This project is focused on optimizing the overall composition of the Pd alloy, intermediate layers and tubular support, as well as on 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 reformate. 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 bio-derived liquid fuels 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. An end-user will be conducting system economic and energy analyses and comparing the results to pressure swing adsorption (PSA) and amine-based systems.

Results

1. Membrane Development and Testing

Optimization and characterization continued on the membrane formation process with emphasis being placed on developing a technique with a sequence of multiple thin layers and treatments to maximize performance over extended time periods in WGS streams. Some mechanical issues have been observed.
with regard to bonding between the membrane layers. Positive results were obtained with membrane #286 fabricated using the multi-layer process as shown in Figure 1. The hydrogen flux remained constant at 70 scfh/ft² and the hydrogen permeate purity varied between 99.98 and 99.99% with methane as the only detected impurity until ~175 hours of test time. Membrane #286 is 8.4 micron thick and has the following alloy composition Pd₈₃Au₁₇. Additionally, there was no observed downward trend in the permeate hydrogen purity over the duration of the test that included shutdown cycles.

Scale up of the membrane process to deposit 10-inch long Pd-Au alloy membrane on a 12-inch long diffusion barrier coated AccuSep substrate tube has been initiated.

2. Membrane Durability in Pure Gas Streams

In order to test the ΔP capability of the membrane, ORNL determined the maximum operating pressure of the Pd-alloy membrane at room temperature. The membrane tube didn’t collapse even with external pressure of up to 4,000 psia.

The membrane housing is rated for 1,596 psi at 537°C exceeding the 400 psi and 400°C DOE target goal.

3. Membrane Durability in WGS Streams

Effect of WGS Environment on the Hydrogen Flux of Pd and Pd-Alloy Membranes

A primary goal of this project is to determine the performance trends as a function of Au level and membrane thickness in WGS streams. One test series was completed. As shown in Figure 2, Pd-Au alloy membranes exhibited a 10% flux reduction, whereas a pure Pd membrane exhibited a 30% flux reduction in a WGS atmosphere. The pure Pd membrane showed a sharp decrease in H₂ purity indicating leaks. Additional tests are in progress.

Effect of WGS Environment on Stability of Membrane Hydrogen Flux with Time

A Pd-Au alloy membrane was tested in WGS environment to determine the stability of H₂ flux with time up to 500 hours. As shown in Figure 3, flux remained constant at 65 scfh/ft² for 460 hours after an initial decline (consistent with the acclimatization of the membrane to the syngas composition) from 73 scfh/ft² in the first 40 hours. H₂ flux remained constant at 65 scfh/ft² through 500 hrs H₂. The H₂ recovery was 56% and the purity was 99.8%.

At a high feed pressure of 170 psig and 6 l/min WGS feed flow rate in a 2” single membrane tube module, the
H₂ flux was 285 scfh/ft² for >100 hours tested and the H₂ purity was 99.997% with a H₂ recovery of 78%.

**Effect of WGS Environment on Membrane Performance as a Function of Feed Flow Rate**

H₂ flux increased by 20% as the feed flow rate was increased from 2 to 6 l/min. This was attributed to a reduction in the concentration polarization effect. Hydrogen purity remained high.

**Effect of WGS on the Performance of Pd-Au Alloy Membranes as a Function of Steam/CO Ratio**

The membrane performed well at steam/CO ratios above 1.5.

**Effect of Various Concentrations of H₂S in WGS on Membrane Hydrogen Flux**

As shown in the Figure 4, the H₂ flux decreased with increasing H₂S content, however, the flux was almost fully recovered when the H₂S was removed from the feed stream. The membrane was a Pd₉₀Au₁₀ alloy, 2.8 microns thick with a 2-inch active length. The WGS composition was 51% H₂, 26% CO₂, 2% CO, 21% H₂O plus up to 25 ppm H₂S. The feed flow rate was 2 l/min, feed pressure was 50 psig and the temperature was 450ºC.

4. System Economic and Energy Analysis

Agreement was reached with an end-user to work with Pall on this project. The end-user will carry out system economic and energy analyses at no cost to the project but with certain restrictions on confidentiality. The end-user will provide the results of a confidential report that they will prepare on a cost comparison between Pall’s membrane system, an amine-based solvent system and a PSA system. They will compare the cost of producing H₂ and the cost of carbon capture for all three processes. The cost for the membrane system capital equipment will be based on performance and cost figures provided by Pall Corporation to the end-user, based on our test performance results in WGS atmospheres.

**Conclusions**

- Improvements were made in membrane synthesis process and membranes were evaluated for their performance in a synthesis gas environment in the 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. The membrane synthesis process is capable of producing membranes in the appropriate thickness range.
- An end-user has agreed to work with Pall Corporation to provide information on the system economic and energy analysis task.

**Future plans**

- Improvements in the membrane synthesis process will be verified and scaled up for manufacturability.
- The optimum alloy composition and membrane thickness with respect to performance and durability in WGS streams will be determined.
- 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 H₂S) and hydrogen recovery. The membrane performance data collected from these tests will be used for system economic and energy modeling analysis.
- System analysis and energy analyses will be conducted by an end user. It will include the cost of producing H₂ and the cost of carbon capture for Pall’s membrane system, an amine-based solvent system and a PSA system.

**FY 2010 Publications/Presentations**


II.C.2 Development of Hydrogen Selective Membranes/Modules as Reactors/Separators for Distributed Hydrogen Production

Project Objective

The water-gas shift (WGS) reaction becomes less efficient when the high 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 Production section (3.1) of the Fuel Cell 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

Technical targets for dense metallic membranes for 2010 are listed below:

- Flux Rate - 250 scfh/sq foot at 20 psig pressure
- Membrane Material and all Module Costs - $1,000/sq. foot of membrane
- Durability – 2,680 hours of testing has been completed
- Operating Capability - 400 psi
- Hydrogen Recovery - >80% (of total gas)
- Hydrogen Quality - 99.99%

Accomplishments

- **Balanced Performance vs. Cost for our H₂ Selective Membrane.** Through evaluation of a range of ceramic membrane substrates with various permeances, we have been successful in developing our H₂-selective membrane product to meet the low cost feature requested by our commercialization partner.

- **Corrected Leakage Issue of the 1st Generation Module and Ready for the Field Test.** Our first field test failed due to module leakage. The leakage of the 1st generation module has been corrected and the module is now ready for the field test scheduled in the second quarter.

- **Designed and Fabricated the 2nd Generation Module using Ceramic Membrane Bundles.** We have successfully developed the membrane bundle for our tubular H₂-selective membrane. This bundle approach can minimize module leak and reduce the module cost, and will be used for our field test in Phase II.

- **Conducted Membrane Reactor Test using our Full-Scale Membrane Tubes.** The WGS-membrane reactor process we developed from a bench-scale unit previously has been verified experimentally using a full-scale tubular membrane. Approximately 99% CO conversion, >85% H₂ recovery and >99.9% purity H₂ were achieved with this full-scale membrane reactor module.

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Contract Number: DE-FG36-05GO15092
Subcontractor:
University of Southern California, Los Angeles, CA

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

Membrane separation has been traditionally considered to be a simple, low cost and compact process. Thus, the 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. During 2009-2010, we have completed the first field test using our full-scale Pd membrane bundle/module. In addition, we have generated the WGS membrane reactor database using our full-scale Pd membrane and a commercial catalyst for the design and construction of the full-scale membrane reactor module for Phase II study.

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. Successfully Prepared an 11-tube 24” Length Full Pd Membrane Bundle as Our 2nd Generation Pd Membrane Module
   a. Excellent pure gas permeation characteristics consistent with our single-tube membrane performance. The H₂ permeance of our Pd Bundle #2 is ca. 7.3 m³/m²/hr/bar. Single-tube permeances typically range from ca. 8 to 11 m³/m²/hr/bar.

2. Excellent pure gas selectivity. Pure component N₂ permeance is ca. 0.006 m³/m²/hr/bar, yielding selectivities on the order of 1,200 which is typical of our single-tube results.

3. Excellent mixed gas performance in a H₂/CO₂ blend. A blend of H₂/CO₂ (80/20 vol%) was also tested. Mixed gas H₂ permeance was ca. 7.5 m³/m²/hr/bar and H₂/CO₂ selectivity was ~1,200, consistent with the single tube results.

4. Additional bundle in production. Pd Bundles #3 and #4 have been produced and are ready for testing.

2. Pilot and Field tests of the 1st Generation Pd Membrane Module

The 1st generation full-scale module was field tested last year; however, severe module leaks were encountered. During this year, we have redesigned the module seal to overcome this problem. Since leaking from the individual tubes after thermal cycling does not follow the sequence of thermal cycles for most tubes, we concluded that the tube seal was stable through multiple thermal cycles. Further, N₂ measurement of ~0.08 m³/m²/hr/bar in average is equivalent to ~0.006 m³/m²/hr/bar at 350°C based upon Knudsen diffusion, which is consistent with the measurement on the module basis. The selectivity of about 1,000 for H₂ over N₂ was obtained. The field test at our end user site using the actual reformate delivered performance consistent the laboratory using synthetic reformate.

3. Effect of Substrate on Permeance and Selectivity of Pd Membranes

A wide range of commercial and experimental ceramic membranes, with permeances ranging from 50 to 800 m³/m²/hr/bar in N₂ at room temperature, were selected to study the Pd membrane performance and permeate quality. Hydrogen permeances of up to 25 m³/m²/hr/bar at 350°C and H₂/N₂ selectivities ranging from 350 to >10,000 were obtained. Although the higher permeance substrates delivered higher H₂ permeances as a result of the reduced resistance, the selectivities, as expected, decreased because of the surface topography. As a result, an intermediate substrate has been selected for commercial product development, with hydrogen permeance of 15 to 25 m³/m²/hr/bar and the selectivity of 1,000 to 3,000 at 350°C as presented in Figure 1.

4. Cost vs. Performance Evaluation with Regard to Our End-User Application

As shown in Figure 1, our cost vs. performance relationship is 2-10 times lower than the relationship target set by DOE for 2010. However, our end-user cost target is much more stringent than the DOE target.
II.C Hydrogen Production / Separations

COST ALLOCATIONS FOR A 5 kW FUEL CELL-BASED GENSET
Based upon a conventional diesel fuel forming (provided by our end user participant)

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical Equipment</th>
<th>Cost ($)</th>
<th>$/kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purifier</td>
<td>Pd membrane*</td>
<td>400</td>
<td>80</td>
</tr>
</tbody>
</table>

* in scfh/ft² at 20 psig

**FIGURE 1.** Cost analysis of our Pd membranes for stationary power generators and the cost target set by our end-user participant.

**FIGURE 2.** Experimental results from the membrane reactor operation at 50 psig with no sweep using a full-scale H₂ selective membrane.
Based upon the input from our end user, for a 5 kW genset, about $400 at 121 scfh H₂ at 20 psig pressure drop is required, which is about 2.5 times lower cost than the DOE target on a comparable throughput basis. The cost vs. performance analysis of our products meets this stringent target set by our customer.

5. CO Conversion and H₂ Separation via Our Full-Scale Palladium Membrane Reactor

Although numerous bench top membrane reactor studies have been performed, no experimental work has been performed using a full-scale Pd membrane. During this year, we successfully demonstrated the membrane reactor using a 30"L Pd membrane as summarized in Figure 2 as a transition step for us to move this technology to the field. Using the synthetic reformate as feed, the low-temperature WGS reaction was performed at 300°C using a commercial catalyst at 30 and 50 psi under the conditions of with and without permeate purge. High CO conversion and high purity hydrogen product at a high hydrogen recovery ratio was obtained. Specifically, ~83% H₂ recovery ratio and 99% CO conversion at >99.9% H₂ purity were obtained from this experimental study.

Conclusions and Future Direction

• The low-cost Pd membranes supported on our ceramic substrate were developed, which can meet the very stringent cost target set by our commercialization partner.
• We have improved the 1st generation module and successfully verified its stability (i.e., acceptable leak through thermal cycling, Figure 3) and performance, which was successfully field tested at our end user side for hydrogen separation from reformate.
• The 2nd generation module, i.e., Pd membrane bundle, which is more economical and less prone to leaks, has been developed and successfully tested (Figure 4). This module will be used for field test in Phase II.
• Greater than 99% CO conversion and >99.9% purity hydrogen at >83% hydrogen recovery ratio was demonstrated experimentally using a reactor packed in our full-scale Pd membrane with a commercial catalyst. We are now ready to move to the field test of the membrane reactor to be undertaken in Phase II.

Our Phase II activities will focus on:

• Prepare 2nd generation membrane/modules for use as a full-scale WGS-membrane reactor.
• Design and construct the full-scale membrane reactor for field test at the selected end-user site.
• Conduct field test at the participated end-user site.

FY 2010 Publications and Presentations

II.C Hydrogen Production / Separations


II.C.3 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  
• Ohio State University, Columbus, OH  

Start Date: July 1, 2005  
End Date: October 30, 2011

Objectives

• To synthesize chemically and thermally stable silicalite membranes with hydrogen permeance \( >5 \times 10^{-7} \text{ mol/m}^2\text{s.Pa} \) and \( \text{H}_2/\text{CO}_2 \) 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 \( \text{CO}_2 \) stream with 97% purity.

Technical Targets

This project is focused on fundamental studies of zeolite membrane reactor for the WGS 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/ft\(^2\)
• Hydrogen recovery: >80%
• Hydrogen quality: 99.5%
• Operating capability: 400 psi
• Durability: 26,280 hr

Accomplishments

• Optimized the template-free secondary growth for MFI (a zeolite structure code) zeolite membrane synthesis.
• Improved MFI zeolite membrane stability by applying a yttrium-stabilized zirconia (YSZ) barrier layer between the \( \alpha \)-alumina porous support and MFI zeolite membrane.
• Conducted the WGS reaction in chemical vapor deposition (CVD)-modified tubular MFI membrane reactors at different conditions and the optimal operating conditions were obtained.
• Modeled WGS reactions in CVD-modified MFI tubular membrane reactors with different catalyst packing configurations.
• Optimized the process for centrifugal casting of tubular supports with reduced resistance for gas flow.
• Developed and characterized the most effective catalysts for high-temperature water-gas shift (HTWGS).

Introduction

Gasification of biomass or heavy feedstock 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 \( \text{H}_2\text{S} \)) from the \( \text{CO}_2 \) 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 (~400°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 permeable and thermally/chemically stable zeolite membrane and its use in the membrane reactor for the WGS reaction to produce hydrogen- and CO2-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 (1-3 μm), aluminum-free silicalite film without intercrystalline micro pores 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/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 H2 permeability, (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 SO2 and H2S 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 MFI zeolite membranes during the reporting period was focused on the experiments and simulations of HTWGS reactions in CVD-modified zeolite membrane reactors. Several different kinds of ferrite-based WGS catalysts were developed and tested in this research. The best catalyst was packed in central composite design-modified tubular membrane reactors for WGS reactions. The feasibility of applying a YSZ barrier layer between the α-alumina porous support and zeolite membrane to improve the stability of MFI membranes was demonstrated successfully on the disk membranes. This technique will be transferred onto the tubular membrane to improve the stability of modified tubular membrane reactor during WGS reactions.

In this research, tubular zeolite membranes for WGS reaction were synthesized and CVD-modified according to the procedure reported in the previous annual reports. The CVD-modified tubular zeolite membrane reactor was packed with the best catalyst that was synthesized in the project. Extensive tests of HTWGS reactions have been conducted in the modified tubular MFI zeolite membrane reactor and a traditional reactor as a function of H2/CO ratio (H2/CO ratio=1-3.5) at a fixed weight-hourly-space-velocity (WHSV) (60,000 h-1) and temperature. The results showed that the highest CO conversion and hydrogen recovery were obtained at H2/CO=3.5 in both the modified MFI tubular membrane reactor and traditional reactor (Figure 1). The results also showed that the CO-conversion in the modified membrane reactor is higher than that in the traditional reactor due to the on-stream separation of H2 from the membrane reactor.

Based on these experimental results, the WGS reaction was further tested at different temperatures and different WHSVs while keeping H2/CO at 3.5 to obtain the optimum operating conditions. Figure 2 shows the experimental χCOe (CO-conversion) and RH22 (H2-recovery) for WGS reactions in a zeolite membrane reactor and packed-bed traditional reactor, as a function of WHSV. As can be seen from this figure, The χCO in both membrane and traditional reactors increased with decreasing WHSV because of the prolonged residence time for WGS reaction and H2 transport. The enhancement of χCO by reducing WHSV was more pronounced at low temperatures where kinetic and mass transport limits are severe. The gas permeation and separation performance of the modified membrane before and after WGS reactions was also studied. The HTWGS reactions lasted about 300 h in the modified MFI zeolite membrane reactor. It was found that the
silicalite seed layer on the YSZ coated porous support (Figure 3(b)), and the MFI zeolite membrane grown on a YSZ coated porous support (Figure 3(c)). Similarly, a YSZ will be applied between the tubular porous support and zeolite membrane to improve the stability MFI tubular zeolite membrane reactor during WGS reactions. To accomplish it, a YSZ will be coated onto the inner surface of the α-alumina tubular supports through centrifugal casting of YSZ slurry.

WGS reactions in the modified membrane reactor have also been modeled at different conditions with more attention focused on studying the effect of different membrane reactor configurations on the CO-conversion and H₂ recovery of a membrane reactor. The schematic diagrams of the MFI tubular membrane reactors with different catalyst packing configurations for WGS reactions are shown in Figure 4(a): (1) the catalyst particles are packed in part of the membrane permeation zone, (2) the catalyst particles are packed in the whole membrane permeation zone, and (3) the catalyst particles are packed in both the membrane permeation zone and non-permeation zone. The non-permeation zone was glazed with dense glass. Note that the mass of the active catalyst and the particles packing density for these cases are assumed to be the same. Figure 4(b) and (c) show that the reactor configuration has some effect on the performance of the MFI membrane reactor. The final CO conversions of these cases are in the order of: case 3 > case 2 > case 1 > conventional fixed-bed reactor, and the order of H₂ recovery in these membrane reactor configurations is: case 1 > case 3 > case 2 at different temperatures. At a fixed contact time and feeding conditions, the performance of the membrane reactor is mainly determined by the permeation of a gas species through the membrane, while the permeation is determined by both the driving force and the effective permeation area. As expected, the CO conversions of these three cases are all higher than those of the conventional fixed-bed reactor due to the on-stream removal of the product H₂. In particular, the equilibrium of the WGS reaction can be overcome by the MFI membranes reactors, as shown in Figure 4(b).

During the reporting period, the work on catalysts was focused on screening the best catalysts for HTWGS reactions. Several different kinds of ferrite-based WGS catalysts were synthesized according to the procedure reported in the previous annual report. The activity of the synthesized catalysts was tested at different conditions (temperature, steam/CO ratio, and WHSV) in a fixed-bed traditional reactor. The results showed that Fe/Cr and Fe/Ce catalysts with various Fe/Cr and Fe/Ce ratios are the best catalysts for HTWGS reactions. Figure 5 shows the WGS activity results of Fe/Cr- and Fe/Ce-based catalysts with various Fe/Cr and Fe/Ce atomic ratios. In this study, WGS reactions were performed at a constant steam to CO ratio of 3.5 and at temperatures 400°C and 500°C. A relatively
high space velocity of 60,000 h\(^{-1}\) was maintained in all experiments. Figure 5 (a) shows the activity results of Fe/Ce catalysts with different atomic ratios. The order of WGS activity for the Fe/Ce catalysts is Fe\(_2\)O\(_3\) < Fe/Ce (10:0.5) < Fe/Ce (10:1) < Fe/Ce (10:2) > Fe/Ce (10:2.5).

The rapid increase in WGS activity with increase in reaction temperature from 400\(^\circ\)C to 500\(^\circ\)C is due to the improvement in the oxygen storage capacity of ceria at higher reaction temperatures.

FIGURE 2. Effect of WHSV on CO-conversion for a fixed \(R_{\text{H}_2\text{O}/\text{CO}}\) of 3.5: \((-\cdots-\) \(\chi_{\text{CO}_e}\); \((-\cdot--\cdot-\cdot-\) \(\chi_{\text{CO}}\) in a membrane reactor; \((-\Delta-)\) \(\chi_{\text{CO}}\) in traditional reactor; \((\times)\) \(\text{H}_2\)-recovery.

FIGURE 3. SEM micrographs: (a) YSZ barrier layer on an \(\alpha\)-alumina porous support, (b) silicalite seed layer on the YSZ barrier layer, and (c) MFI zeolite membrane.
Among the various Fe/Cr catalysts, Fe/Cr (10:0.5) shows better WGS activity compared to the other catalysts as shown in Figure 5(b). X-ray diffraction and crystallite size measurements suggest that the addition of Cr decreases the crystallite size of hematite up to the Fe/Cr (10:0.5) atomic ratio and further increase in the amount of chromium increases the crystallite size slightly. Mossbauer spectroscopic results inferred that in the pure magnetite, structural rearrangements of Fe$^{2+}$ and Fe$^{3+}$ ions take place during the WGS reaction which leads to the lower WGS activity. These rearrangements continue to happen in Fe/Cr (10:0.2) catalyst as well. On the other hand, in the other Fe/Cr catalysts with the atomic ratios 10:0.5, 10:1, 10:2, chromium stabilizes the magnetite phase during the WGS reaction and thus leads to a higher WGS activity. A slight decrease in the WGS activity for Fe/Cr (10:1) and Fe/Cr (10:2) catalysts compared to Fe/Cr (10:0.5) might be due to the smaller Brunauer-Emmett-Teller surface area as well as larger crystallite size.

Previously, centrifugal casting of membrane supports has been performed with AKP30 $\alpha$-$\text{Al}_2\text{O}_3$ powder (300 nm particle size, Sumitomo Chemical Corp.) which resulted in an optically smooth inner tube surface. To reduce gas flow resistance, centrifugal casting is currently being performed with AA3 $\alpha$-$\text{Al}_2\text{O}_3$ powder (Sumitomo Chemical Corp.) with a particle size of ~3 μm. Due to the increased particle size of the AA3 particles, colloidal stabilization with pH 2 HNO$_3$ is not sufficient to prevent particle sedimentation. To produce AA3 $\alpha$-$\text{Al}_2\text{O}_3$ (Sumitomo Chemical Corp.) tubular supports with sufficient green strength for removal after centrifugal casting, cross-linking of polyvinyl alcohol (PVA) is being investigated. The cross-linker that was selected is 2,5-dimethoxy-2,5-dihydrofuran (DMDF) which is reported to increase the green strength of gel-cast parts. It was found that gelation of ~3 mL dispersion/solution of 79.82 wt% AA3, 0.76 wt% PVA, 0.55 wt% HNO$_3$, and 0.26 wt% DMDF, resulted in a rigid body in about 10 min. at 65°C. First, the mold was filled with the above AA3 dispersion and placed in a preheated oven at 80°C for approximately 15 min. Then, the mold was removed from the oven and allowed to cool at room temperature. After drying.

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**FIGURE 4.** Modeling of WGS Reactions in a Membrane Reactor  (a) schematic diagrams of the tubular MFI membrane reactor with different catalyst packing configurations (1-3); (b) effect of temperature on the CO conversion in different catalyst packing configurations; and (c) effect of the temperature on the hydrogen recovery in different catalyst packing configurations.
particles did not form a cast and remained in dispersion. This is believed to be caused by excessive stability or viscosity of the dispersion. The dispersion chemistry will be adjusted in the future by reducing the binder and cross-linking agent content. Preheating of the Delrin mold to accelerate the rigidification of the cast tube will also be investigated.

Conclusions and Future Directions

Conclusions

- The stability of the MFI zeolite membranes was improved by applying a YSZ barrier layer between the \( \alpha \)-alumina porous support and MFI zeolite membrane layer to avoid the diffusion of \( \text{Al}^{3+} \) from the porous support into the zeolite membrane.
- WGS reactions were conducted in CVD-modified MFI tubular membrane reactors at different WHSV, \( \text{H}_2\text{O/CO} \) ratio, and temperatures. Optimum WGS conditions were obtained.
- WGS reactions were modeled at different operating conditions and catalyst packing geometries to guide the WGS reaction experiments.
- \( \alpha\text{-Al}_2\text{O}_3 \) tubular porous supports with reduced resistance for gas flow are prepared by centrifugal casting of \( \alpha\text{-Al}_2\text{O}_3 \) powder with particle size of \( \sim 3 \mu\text{m} \). The dispersion chemistry of the slurry was optimized to obtain integral and robust porous supports.
- Several different kinds of ferrite-based catalysts were synthesized and tested in a fixed-bed traditional reactor, the best catalyst was selected for sulfur-tolerant HTWGS reactions.

Future Work

- Further optimization of MFI zeolite membrane synthesis and CVD modification for enhancement of the \( \text{H}_2/\text{CO}_2 \) separation factor of the modified membranes.
- Improve the stability of MFI tubular zeolite membrane reactor for WGS reactions by applying a YSZ barrier layer between the tubular porous support and zeolite membrane. The YSZ layer will be coated onto the inner surface of tubular supports by a centrifugal casting technique.
- Optimize the dispersion chemistry and improve the centrifugal casting process for fabrication of tubular porous supports with reduced resistance for gas flow.
- Perform high-pressure kinetics of two most effective WGS catalysts.
- Develop highly active and time stable (extensive up to time on stream: up to 2 months on stream)
catalysts for WGS reaction in the modified MFI zeolite tubular membrane reactor.

- Economic evaluation of the project results to validate the scale up and operation in an industrial scale.

**FY 2010 Publications/Presentations**

**Journal Papers**


**Conference Presentations**


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

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Contract Number: DE-FC26-07NT43058

Subcontractor:
Adsorption Research, Inc., Dublin, OH

Project Start Date: May 7, 2007
Project End Date: May 6, 2011

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

(N) Hydrogen Selectivity
(P) Flux
(N) Hydrogen Selectivity
(K) Durability

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.

Accomplishments

- Successfully synthesized Pd, Pd/Cu and Pd/Au membranes on 316L porous stainless steel and porous Inconel supports and demonstrated high permeances and selectivities which exceeded the DOE 2010 targets.
- Completed characterizations and stability testing of the Pd, Pd/Au and Pd/Cu membranes in the temperature range of 350-525°C.
- Successfully implemented a one-dimensional simulation to predict the optimal operating conditions for isothermal and adiabatic WGS-composite membrane reactors (CMRs) for process intensification. The model was accurate in predicting the experimental CO conversion values.
- Demonstrated the cost effectiveness of the isothermal CMRs over the non-isothermal CMRs with an unsteady-state WGS-CMR process control model.
- Achieved experimentally a 98% CO conversion and 87 and 85% H₂ recovery at 400 and 450°C, respectively in a Pd-based WGS–CMR operated at: \( \Delta P = 212 \text{ psi (} P_{\text{Low}}=14.7 \text{ psia)} \), \( H₂O/CO = 2.6 \) and gas hourly space velocity (GHSV) = 1,000 h⁻¹. The
long-term stability of the CO conversion and H$_2$ recovery were demonstrated for 80 h.

- Demonstrated the tolerance of Pd/Au and Pd/Cu membranes to H$_2$S over the temperature range of 350-500°C and atmospheres of 0.2–50 ppm H$_2$S/H$_2$ mixtures.

- Demonstrated for pressure swing absorption (PSA) that for five component gas mixtures with 1,000 ppm H$_2$S, the H$_2$S absorbent 5A achieved He recoveries of 99% and the product stream contained less than 0.05 ppm H$_2$S if a recycle of the blowdown gas was used.


\[
\text{Combining} \quad \text{the} \quad \text{WGS} \quad \text{reaction} \quad \text{and} \quad \text{hydrogen} \quad \text{separation} \\
\text{reduces} \quad \text{capital} \quad \text{costs} \quad \text{and} \quad \text{improves} \quad \text{efficiency.}
\]

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 application.

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. (ARI), Worcester Polytechnic Institute (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 CO$_2$ 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.

**Approaches**

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 ~2 μm 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 valuation 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.

**Results**

Several high permeance Pd, Pd/Au and Pd/Cu membranes were tested in pure H\textsubscript{2} and He atmospheres for permeation and selectivity characterization. Figure 2 shows the Sieverts’ Law regressions performed at 450°C for the Pd membranes #038 and #039. Figure 2 shows that both #038 and #039 followed Sieverts’ Law and exceeded the DOE 2010 target with fluxes of 250 and 225 scf/h ft\textsuperscript{2} respectively, at a ΔP of 100 psi (P\textsubscript{low} = 14.7 psia). The selectivities were 250 and 240 respectively, yielding a H\textsubscript{2} purity of 99.6 and 99.58%, also meeting the 2010 DOE target. Furthermore, the Pd and Pd/alloy membranes also exceeded DOE 2010 flux and hydrogen purity targets.
• WGS-CMR experiments using syngas feed (41.6% CO, 40.3% H₂ and 18.1% CO₂ [dry basis]) achieved CO conversions of 97.9% (15% above equilibrium) at 400°C with a ΔP of 212 psi (P_{rev} = 14.7 psia) and GHSV values of 1,100 h⁻¹. Conversions of 98.2% (5.2% above equilibrium) were achieved at 450°C with a GHSV of 2,900 h⁻¹. A simple mathematical model predicted the experimental conversion data reasonably well.

• H₂ recoveries of 87% were achieved at 400°C and a GHSV of 1,000 h⁻¹. However, the simulation exceeded the experimental H₂ recovery data by as much as 20% at high GHSV values due to not accounting for radial mass transfer resistance in the simple model. The model further predicted that the flux ratio of H₂ to the other components (CO, CO₂, H₂O) had little effect on the CO conversion for both isothermal and adiabatic CMRs. However, to prevent the conversion from decreasing by 3% or more, the separation factors of the isothermal and adiabatic CMRs would need to be at or above 15,000 and 7,500, respectively. Reducing the catalyst weight from 15 to 0.3 g resulted in no decrease in the conversion for both adiabatic and isothermal CMRs, allowing for a more efficient use of catalyst.

• The model predicted that isothermal operation at 450°C resulted in a maximum CO conversion and H₂ recovery of 97 and 91% respectively, while operating at and above 60% permeability of the Pd foil. Adiabatic operation yielded slightly higher conversions than the isothermal operation at 98–99% for GHSV values below 4,000 h⁻¹ at a permeability of 60% of the Pd foil. However, adiabatic operation caused hot spots to form exceeding 565°C, which would be detrimental to the stability of both the membrane permeance and selectivity.

• The model further predicted that the flux ratio of H₂ to the other components (CO, CO₂, H₂O) had little effect on the CO conversion for both isothermal and adiabatic CMRs. However, to prevent the conversion from decreasing by 3% or more, the separation factors of the isothermal and adiabatic CMRs would need to be at or above 15,000 and 7,500, respectively. Reducing the catalyst weight from 15 to 0.3 g resulted in no decrease in the conversion for both adiabatic and isothermal CMRs, allowing for a more efficient use of catalyst.

• Exposing Pd and Pd alloy membranes to H₂S resulted in an increasing permeance decline with increasing H₂S feed concentration. However, at 15 ppm the Pd membrane formed a bulk Pd₃S which destroyed the membrane. The Pd/Cu and Pd/Au membranes both reached a steady-state values of permeance, retained their selective properties and did not form bulk sulfides within the H₂ selective layer even up to 50 ppm H₂S/H₂ mixtures. At concentrations <5 ppm H₂S, the Pd/Cu membrane performed better than the Pd/Au membrane which performed better than the Pd membrane.

• Higher temperatures were required to recover the permeance loss during poisoning due to the exothermic nature of H₂S adsorption on metals. Roughly 80% of the permeance of the Pd/Cu membrane could be recovered at 500°C after poisoning. At 500°C, the recovery in H₂ was nearly 100% for Pd/Au membranes.

• Based on the isotherms and diffusivity tests for the gas phase components, the two best adsorbent candidates for H₂S were 5A and Hisiv 3000. 5A was deemed the better choice due to the higher adsorption capacity and H₂ recovery and lower cost.

• For five component mixtures with 200 ppm H₂S, He recoveries up to 98.76% could be achieved with no H₂S detected in the product stream if a recycle of the blowdown gas was used. Increasing the H₂S concentration to 1,000 ppm resulted in several hundred ppb H₂S detected in the product stream with He recoveries up to 99.10%. Further increasing the H₂S concentration to 4,800 and 9,500 ppm reduced the He recoveries to roughly 91 and 88% respectively, and increased the H₂S in the product stream to a few ppm.

Conclusions and Future Directions

The membranes developed and tested during this period exceeded both the DOE 2010 flux and selectivity targets. The membrane stability during long-term WGS reactions and atmospheres containing small quantities of H₂S has been demonstrated. High CO conversions (98%) and H₂ recoveries (87%) have been achieved in the Pd-based WGS-CMRs and simulations incorporating process control, capable of predicting the experimental CO conversion values, have predicted the optimal conditions for isothermal and non-isothermal WGS-CMR operation for process intensification. The adsorbent 5A was deemed to be the best choice for PSA and yielded He recoveries as high as 99% for five component gas mixtures which included 1,000 ppm H₂S.

Future work will:

• Continue long-term WGS reaction studies with and without H₂S for Pd, Pd/Au and Pd/Cu membranes.
• Complete 2010 technical target screening and qualification tests.
• Improve flux and selectivity of Pd, Pd/Au and Pd/Cu membranes.
• Initiate economical analysis for the proposed process intensification framework.
• Add carbon oxysulfide to the feed mixture for PSA testing.

**FY 2010 Publications/Presentations**


II.D.2 Development of Robust Hydrogen Separation Membranes

Objectives

The main objective of this research is the development of robust hydrogen separation membrane(s) for integration into coal conversion processes, including integrated water-gas shift (WGS) membrane reactor. Studies suggest that incorporating separation membranes into coal conversion processes can reduce costs by 8%.

Included in the primary project objectives are the definition of a \( \text{H}_2 \)-membrane test protocol that:

- Will advance the technology towards application to coal conversion processes.
- Is consistent with overall Fossil Energy Program metrics.
- Yields a basis for an “apples-to-apples” comparison.

Research will be divided into two tasks: Task 1: Performance testing of external membranes and the “NETL \( \text{H}_2 \) Membrane Test Protocol” and Task 2: Robust Metal Membrane Development.

Technical Barriers

This project addresses the following technical barriers from the 2008 Hydrogen from Coal Program: Research, Development and Demonstration Plan:

(G) \( \text{H}_2 \) Embrittlement
(H) Thermal Cycling
(I) Poisoning of Catalytic Surface
(J) Loss of Structural Integrity and Performance

Technical Targets

The technical targets are DOE’s 2015 targets as shown in Table 1.

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* For 100 psi \( \Delta \text{P} \) (hydrogen partial pressure basis)

\( \Delta \text{P} = \text{total pressure differential across the membrane reactor} \)

Accomplishments

- Completed a survey to determine the effluent composition of a WGS unit (Figure 1).
- Developed COMSOL model to predict the influence of WGS reaction and/or \( \text{H}_2 \) removal on overall gas composition:
  - Identified the test conditions and gas compositions that are relevant to syngas conversion flowsheet options:
    - Test 1: Shifted syngas, with no sulfur
    - Test 2a: Shifted syngas with 20 ppm \( \text{H}_2\text{S} \)
    - Test 2b: Shifted syngas with ~50% \( \text{H}_2 \) removal
    - Test 2c: Shifted syngas with ~90% \( \text{H}_2 \) removal
- Moved the membrane test units to a new location:
  - Modified membrane units to accommodate the “test protocol”.
- Flow ranges and membranes to test:
  - Conducted detailed analysis of the flow requirements to test a variety of membranes being developed:
    - Disks, tubes
    - Performing at 2015 targets
Determined that for surface stability:
- Pd-terminated surfaces are least stable.
- S-Pd-terminated surfaces are most stable.

Determined that for catalytic activity:
- Incorporation of S into the Pd system decreases catalytic activity.
- Pd-participation in the surface reaction allows rates high enough to meet DOE targets (either Pd-terminated or Sub-surface Pd).

Hydrogen-Deuterium exchange study:
- Modified quartz reactor system.
- Developed kinetic model.
- Initiated experimentation on Pd, Cu and 80Pd-Cu. The 80Pd-Cu system is “more catalytic” than pure Pd in H2.

Synthesis of multi-layered membranes:
- 25 μm PdCu substrate (corrosion resistance).
- Synthesized continuous and dispersed overlayers.
- Mono-layer Mo film:
  - Expected performance in H2.
  - H2S catalyzed the corrosion of PdCu substrate.

Directly measured the H2 permeability of Pd4S:
- In the presence of H2, appears to follow Sievert’s law.
- Permeability of Pd4S is ~10x less than Pd and consistent with face-centered cubic-phase 60Pd-Cu.

Collaborations:
- The research team conducting the work on the task consisted of participants from Carnegie Mellon University.
- NETL Reaction Chemistry & Engineering Group.
- NETL Computational Research Group (Dominic Alfonso).
- Provide unbiased performance verification testing:
  - REB Research
  - Oak Ridge National Laboratory
  - Eltron Research
  - Western Research Institute

Introduction
Hydrogen is viewed as the fuel source for the 21st century. The objective of this project is to support the development of test protocols to include more “commercially relevant” conditions.

Approaches
- This project will apply an understanding of engineering principles, membrane technology and coal conversion processes to define a sequential protocol to test various membranes for an “apples-to-apples” comparison.
- The development of a multi-layered membrane system (Figure 2) that utilizes the catalytic activity shown with Pd4S and the corrosion resistance of select PdCu alloys:
  - Use computational and experimental techniques to understand the catalytic activity at the gas-scale interface (Pd, Cu, Mo, Fe, Ni, Co, etc.).
  - Hydrogen transport properties of the layers and interfaces stability and growth scale.
Conclusions and Future Directions

Conclusions

- A test protocol has been developed and NETL’s test systems have been modified to allow testing of various membrane geometries and performance levels.
- Evaluation of the catalytic activity of potential membrane catalyst layers has been initiated utilizing density functional theory, kinetic Monte Carlo and H2-D2 exchange in the presence of H2. 80Pd-Cu appears more catalytic than Pd.
- Pd,S shows catalytic properties for H2 dissociation.
- Several multi-layered membrane systems have been fabricated using both continuous and dispersed catalysts. Thin catalyst layers appear to catalyze the corrosion of a corrosion resistance PdCuAlloy.
- The characterization of sulfide permeability has been initiated. Pd4S is approximately 10x lower than pure Pd.

Future work

- Continue to support the development of test protocols to include more “commercially relevant” conditions.
- Higher transmembrane pressure differentials.
- Contaminants other than H2S.
- For example, Cl-and N-compounds for biomass co-feed.
- Integration of WGS reactor and membrane separator.

FY 2010 Publications/Presentations

5. “Inhibition of Hydrogen Transport through Palladium and Pd47Cu53Membranes by Hydrogen Sulfide at 350 °C”;
II.D.3 Scale Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

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Arun C. Bose  
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Contract Number:  
DE-FC26-05NT42469

Subcontractor:  
Eastman Chemical Company, Kingsport, TN

Project Start Date:  
October 1, 2005

Project End Date:  
September 30, 2010

Phase II will continue till 2012.

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 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
  
  (K) Durability

(L) Impurities
(N) Hydrogen Selectivity
(P) Flux
(R) Cost

Technical Targets

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>2010 Target</th>
<th>2015 Target</th>
<th>Current Eltron Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux, SCFH/ft²</td>
<td>200</td>
<td>300</td>
<td>450</td>
</tr>
<tr>
<td>Operating Temperature (°C)</td>
<td>300-600</td>
<td>250-500</td>
<td>250-440</td>
</tr>
<tr>
<td>Sulfur Tolerance (ppmv)</td>
<td>2</td>
<td>20</td>
<td>20 (prelim.)</td>
</tr>
<tr>
<td>System Cost ($/ft²)</td>
<td>500</td>
<td>&lt;250</td>
<td>&lt;200</td>
</tr>
<tr>
<td>ΔP Operating Capability (psi)</td>
<td>400</td>
<td>800-1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Carbon Monoxide Tolerance</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Hydrogen Purity (%)</td>
<td>99.5</td>
<td>99.99</td>
<td>&gt;99.99</td>
</tr>
<tr>
<td>Stability/Durability (years)</td>
<td>3</td>
<td>&gt;5</td>
<td>0.9</td>
</tr>
<tr>
<td>Permeate Pressure (psi)</td>
<td>N/A</td>
<td>N/A</td>
<td>400</td>
</tr>
</tbody>
</table>

N/A - not applicable

Accomplishments

- Partnered with Eastman Chemical Company to perform scale up testing of Eltron’s membranes.
- Continued development of Eltron’s 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.
- Down-selected tubular membranes for scale up and procured 250’ of ½” outside diameter, 500 micron wall tubing.
- Developed electrodeposition techniques for depositing catalyst on the inside and outside surface of tubular membrane up to 5’ long.
- Tested tubular membranes between 6” and 2’ long under a variety of conditions including pressures up to 600 psig. Hydrogen recoveries as high as 90% were observed.
- Continued development of modeling tools to characterize and design membranes systems.
Introduction

The objective of this multi-year project is to develop and scale up a membrane-based system enabling >95% carbon capture from an integrated gasification combined cycle (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 sub-scale engineering prototype that will be tested on “live” coal-derived syngas in an operating facility.

Results

During the past year Eltron Research & Development, Inc. has partnered with Eastman Chemical Co. to scale up Eltron’s hydrogen membrane technology for pilot plant testing in a gasified coal feed stream. This partnership will result in a pilot plant demonstration of a hydrogen membrane reactor integrated with warm gas cleaning run on a gasified coal slip-stream. During the proposed work plan Eltron and Eastman will design, construct, and operate two different scale-up reactors. First, a 12 lbs/day hydrogen membrane reactor will be designed, constructed, and operated to demonstrate membrane performance on real syngas. Second, a 250 lbs/day reactor will be integrated with appropriate sorbent beds or with Eastman’s warm gas cleaning pilot unit and operated.

Eltron down-selected tubular membranes and procured 250’ of membrane substrate tubing from 2 different suppliers. This tubing was down-selected by Eltron based on performance and engineering considerations. The tubing is ½” outside diameter with a 500 micron wall thickness. Tubing received from one supplier is shown in Figure 1.

Eltron scaled up the equipment and techniques for depositing catalyst on tubular membranes. Catalyst was successfully deposited onto both the inside and outside feed stream. This partnership will result in a pilot plant demonstration of a hydrogen membrane reactor integrated with warm gas cleaning run on a gasified coal slip-stream. During the proposed work plan Eltron and Eastman will design, construct, and operate two different scale-up reactors. First, a 12 lbs/day hydrogen membrane reactor will be designed, constructed, and operated to demonstrate membrane performance on real syngas. Second, a 250 lbs/day reactor will be integrated with appropriate sorbent beds or with Eastman’s warm gas cleaning pilot unit and operated.

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Tubular membranes up to two feet long have been tested under a variety of conditions. Tubes were tested under simulated WGS gas compositions at temperatures between 300 and 400°C and at feed stream pressures up to 700 psig. Figure 3 shows data collected for a membrane tested up 600 psig feed pressure in a 100% H₂ feed stream. Flux rates up to 175 SCFH/ft² were observed at these high hydrogen partial pressures.

Once it was demonstrated that tubes could survive high hydrogen partial pressures, Eltron tested longer tubular membranes. The longest tube that Eltron can test in our facilities in Boulder, CO is a two foot tubular membrane. Eltron successfully tested a two foot long membrane in two separate tests. Each test was performed at pressures up to 600 psig. The first test utilized a feed stream mixture containing H₂ and N₂ and the second test was conducted under a simulated WGS feed stream. Results showed that in both cases the two foot long tubular membranes were limited by the low flow rates of gases relative to the high surface area of the membranes. High hydrogen recoveries were observed up to 85% H₂ recovery; however, low flux rates were observed. This was attributed to bulk diffusion limitations on the feed side of the membrane.

To determine the effect of impurities on membrane performance, planar and tubular membranes were exposed to a live gasified coal feed streams. Eltron membranes were sent to Eastman and exposed to gasified coal syngas that had passed through a ZnO sorbent bed. This exposure was performed at 340°C and 700 psig. Following exposure the membranes were sent back to Eltron for characterization and permeation testing. The exposed membranes were tested in a 50% H₂/50% He stream at 300 psig and 340°C. Permeation results for exposed membranes were compared to membranes that had not been exposed, as shown in Figure 4.

Figure 4 shows that the membrane that had been exposed to gasified coal syngas had a hydrogen flux rate ~50% lower than a membrane that had not been exposed. Scanning electron microscopy and X-ray diffraction analysis showed that this drop in flux was due to the presence of sulfur, arsenic, and mercury on the surface of the membrane.

Eltron and Eastman have completed design and construction of a 12 lbs/day membrane reactor. Design specifications for the reactor included:

- 300 SCFH coal-derived syngas
- 450–900 psig feed pressure
- 500°C maximum operating temperature
- 85% H₂ recovery
The reactor will contain ten feet of Eltron’s tubular membrane. Engineering design activities included preparation of piping and instrumentation diagrams, associated interlock narratives, and a process hazards analysis. Equipment was specified and procured and the reactor skid was constructed by Continental Technologies.

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:

- Construct and operate 12 lbs/day H₂ membrane reactor on gasified coal slip-stream.
- Design, construct, and operate 250 lbs/day H₂ membrane reactor integrated with warm-gas cleaning on a gasified coal slip-stream.
- Continue life and impurity testing on new materials as required.
- Maintain and improve techno-economic models.

Special Recognitions & Awards/Patents Issued


FY 2010 Publications/Presentations


II.D.4 Amorphous Alloy Membranes for High Temperature Hydrogen Separation

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DOE Technology Development Manager: Dan Driscoll
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DOE Project Officer: Steven R. Markovich
Phone: (412) 386-7537
E-mail: steven.markovich@netl.doe.gov

Contract Number: DE-FE0001057

Subcontractors:
• David Sholl, Georgia Institute of Technology (Georgia Tech), Atlanta, GA
• Thomas Barton, Western Research Institute (WRI), Laramie, WY

Project Start Date: September 30, 2009
Project End Date: September 29, 2012

Objectives

The objective of this project is to model, fabricate, and test thin film amorphous alloy membranes which separate hydrogen from a coal-based system with performance meeting the DOE 2015 targets of flux, selectivity, cost and chemical and mechanical robustness, without the use of platinum group metals.

Technical Targets

Year 1: The first year consisted of demonstrating an amorphous alloy with the following targets identified for this initial phase:
- Fabricated at least six membrane samples with compositions consistent with those used by Georgia Tech for H₂ flux modeling.
- Tested and established thermal stability of amorphous alloys.

Year 2: The focus of the effort will be to evaluate the performance and fabrication options to produce membranes that are an improvement over those published in the literature. The following targets have been identified for this second phase:
- SwRI® will fabricate a minimum of 20 doped amorphous alloy membrane specimens based on Georgia Tech hydrogen transport predictions for the most promising ternary element additions.
- Testing at WRI of a second set (≤12) of alloys from the optimization trials by pure gas (H₂ and N₂) permeation experiments.

Year 3: The final year will focus on optimization of identified compositions and fabrication techniques through an iterative progress approach of modeling, making and testing the amorphous alloys. The following targets have been identified in this final phase:
- SwRI® will produce a minimum of four optimized membranes for testing at WRI.
- Complete two gasifier tests (or a smaller number of longer duration tests) at WRI on optimized membrane materials with multiple additions of H₂S, carbon oxysulfide, HCl, and metallic impurities.

Table 1 lists current test information for a number of membranes and compares it with DOE target values.

Accomplishments

- Have demonstrated our modeling approach is sufficient to generate realistic samples of these amorphous materials.
- Have concluded that the quantitative discrepancy between theoretical predictions and the amorphous film experiments is relatively small and that our methods are capable of making useful predictions about these properties.
II.D  Hydrogen Production / Hydrogen From Coal

**TABLE 1. Progress towards Meeting DOE Targets**

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>2010 Target</th>
<th>2015 Target</th>
<th>SwRI® Membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux (scfh/ft²)</td>
<td>200</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Operating Temperature (°C)</td>
<td>300-600</td>
<td>250-500</td>
<td>200-300</td>
</tr>
<tr>
<td>Sulfur Tolerance (ppmv)</td>
<td>2</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>System Cost ($/ft²)</td>
<td>500</td>
<td>&lt;250</td>
<td></td>
</tr>
<tr>
<td>ΔP Operating Capability (psi)</td>
<td>400</td>
<td>800-1,000</td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide Tolerance</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Purity (%)</td>
<td>99.5</td>
<td>99.99</td>
<td></td>
</tr>
<tr>
<td>Stability/Durability (years)</td>
<td>3</td>
<td>&gt;5</td>
<td></td>
</tr>
</tbody>
</table>

- Have demonstrated the permeabilities by 32 atom cells are in good agreement with those by 108 atom cells as published in J.Mem.Sci. 350, 402 (2010).
- Have identified several new novel binary and ternary amorphous alloys with predicted permeabilities similar to Pd.
- The precise deposition of metal coatings by two magnetron sources and by co-deposition using two magnetron sources have been demonstrated for deposition of NiZr coatings.
- WRI has conducted all X-ray powder crystallography and elemental composition tests of the as deposited samples and has begun thermal annealing tests.
- Completed multiple project conference calls and joint calls with the other DOE-funded team at the University of Nevada, Reno working on amorphous alloy membranes.

**Approach**

The approach of the project is to incorporate modeling, fabricating, and testing all operating concurrently to develop thin film amorphous alloy membranes which separate hydrogen from a coal-based system with performance meeting the DOE 2015 targets of flux, selectivity, cost and chemical and mechanical robustness, without the use of precious group metals. This collaborative effort will involve work at SwRI®, Georgia Tech and WRI. The proposed project can be summarized in the three primary tasks that will run concurrently:

1. **Materials modeling and composition selection:** Building upon recent work at Georgia Tech using density functional theory (DFT) to identify promising ZrNi alloy compositions with improved hydrogen permeability, an expanding range of additive concentrations will be investigated. New calculations based on refined assumptions and boundary conditions will be used to direct the materials development effort in an iterative manner.

2. **Fabrication of high-performance amorphous alloy membranes:** SwRI® will lead the development of thin amorphous alloy membranes using advanced physical vapor deposition methods including magnetron sputtering. The unique feature of these techniques is the ability to rapidly produce membranes of almost any alloy composition with good uniformity and large areas (up to 100 in²) onto stainless steel supports.

3. **Membrane testing and evaluation:** WRI will perform initial screening testing of experimental membranes under controlled atmospheres and confirm that the targeted structures and compositions have been produced. Initial performance data will be used to further refine DFT-based modeling and guide the vacuum deposition effort. Once one or more promising classes of alloys have been identified, WRI will evaluate these membranes under DOE specified test conditions for extended periods up to several hours. Compositional and structural analysis of exposed membranes by scanning electron microscopy (SEM), energy dispersive X-ray, and X-ray diffraction (XRD) will be employed in an effort to identify likely degradation pathways.

**Introduction**

Thin film amorphous alloy membranes are a nascent but promising new technology for industrial-scale hydrogen gas separations from coal-derived syngas. This project uses a combination of theoretical modeling, advanced physical vapor deposition fabricating, and laboratory and gasifier testing to develop amorphous alloy membranes that have the potential to meet all DOE targets in the testing strategies outlined in the National Energy Technology Laboratory Membrane Test Protocol.

**Results**

**Modeling**

Georgia Tech has developed a general method based on first-principles calculations and statistical modeling to predict the permeability of pure H₂ through amorphous metal films [1,2]. This approach requires no
experimental input or parameterization, so it is suitable for use in materials screening efforts. However, this method was based on DFT calculations with 108 atom supercells, which requires large amount of calculations and thus is time-consuming to perform screening from multiple candidates.

To accelerate the calculation, we use different size supercells to check the convergence of the calculated permeability convergence for Zr55Co25Al20. We use 32, 64, 108-atom supercells to calculate solubilities, diffusivities and permeabilities. Figure 1 shows the calculated permeability. Although there is some variation between the calculations with the smaller supercells and the results when using a 108-atom supercell, these differences are small enough that we can use the smaller calculations as a screening tool.

We have therefore performed extensive calculations for amorphous alloys that have not been studied in previous experiments with the aim of novel materials discovery using 32-atom supercells. To this end, we examine amorphous Ta40Ni60, Ta25Ni50Ti25, Ti32Co67, Hf44Cu56, Hf25Cu60Ti15, Zr45Cu45Al10, Zr30Cu60Ti10, Zr54Cu46, and Nd60Fe30Al10. Selection of these materials are based on the relative high crystallization temperatures reported experimentally for these materials (at least >720 K). To make permeability predictions, first principles methods were used to predict the solubility and net diffusivity of interstitial H in each amorphous material.

Membrane Deposition, Composition and Microstructure Optimization

The coating system setup used in this work is shown in Figure 2. Two direct current magnetrons using 4” diameter targets were installed at the bottom of the vacuum processing chamber for a co-sputtering deposition process of the amorphous alloy with argon as the processing gas.

XRD analysis of the crystallinity of NiZr coatings and ribbons has demonstrated a strong correlation between their structure and thermal stability vs. their composition. Coatings with higher concentrations of Zr survived annealing for 1 hour at 250°C without re-crystallization. The re-crystallization started during 1 hr of annealing at 300°C in coatings with lower Zr content (Figure 3 plot #1), while coatings with Zr content >12 at% (#4 & 5) do not re-crystallize, showing XRD patterns after annealing similar to the melt-spin ribbon (#13) with optimal Zr content associated with amorphous NiZr alloy as shown in Figure 3 (Ni0.64Zr0.36 ribbon sample #12). On the other hand, the ribbon sample #13 having Ni0.3Zr0.7 composition was fully transformed into the polycrystalline state after 1 hr of annealing at 300°C. The optimal composition of

![FIGURE 2. Magnetron Co-Sputtering Scheme](image)

![FIGURE 3. XRD Patterns of NixZr1-x Coatings and Bulk Metallic Glass Ribbons Subjected to 1 Hour Annealing at 300°C.](image)
the NiZr amorphous alloys with Zr concentration near 30 at% is in agreement with published work presented in Refs. [3,4].

Conclusions and Future Directions

The project is on schedule and on budget with SwRI®, Georgia Tech, and WRI all operating independently and concurrently. Georgia Tech has demonstrated the modeling approach is sufficient to generate realistic samples of these amorphous materials. The precise deposition of metal coatings by one magnetron source and by co-deposition using two magnetron sources have been demonstrated for deposition of NiZr coatings. NiXZr1-x coatings with x ranging from 0.71 to 0.93 were deposited by magnetron co-sputtering process. It was found that as-deposited films are more amorphous with an increase of Zr content starting from x = 0.9 and reaching a XRD-amorphous state at x >0.88. Mechanical properties of these coatings are strongly correlated with their composition. Amorphous films with higher Zr content have retained their XRD measured amorphous state after 1 hr annealing in an argon/2% hydrogen atmosphere at 300°C. Further amorphization of some of the coatings, with lower Zr content, occur during thermal annealing below their re-crystallization temperature which may indicate the influence of a solid reaction amorphization mechanism on the coating structure evolution. The partial re-crystallization in films with the highest Zr content occurs after 24 hours of annealing. The Ni0.71Zr0.29 coating has demonstrated the best thermal chemical stability developing a mixture of a polycrystalline phase embedded within an amorphous matrix during annealing. The XRD spectrum of this film is nearly identical to the XRD spectrum of a melt-spun bulk metallic glass ribbon subjected to the same annealing treatment, indicating that thin film coatings deposited by co-sputtering and bulk metallic glass ribbons prepared by the melt-spinning technique have about the same thermal stability which is determined by their elemental composition and not by the method of fabrication.

Future work will consist of:

- Georgia Tech performing both solubility and diffusion calculations on ZrCu, ZrCuTi, HfCu, and HfCuTi systems.
- Future work will be conducted to better understand the mechanisms of formation of amorphous metal coatings and their thermal stability, which is critical for their applications in hydrogen separation membranes.
- SwRI® will fabricate a minimum of 20 doped amorphous alloy membrane specimens based on Georgia Tech hydrogen transport predictions for the most promising ternary element additions.
- Testing at WRI of (≤12) of alloys from the optimization trials by pure gas (H2 and N2) permeation experiments.
- Complete two gasifier tests (or a smaller number of longer duration tests) at WRI on optimized membrane materials with multiple additions of H2S, carbon oxysulfide, HCl, and metallic impurities.

References

II.D.5 Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production

Objectives

- Develop and construct hydrogen (H₂) 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 (NH₃).
- Develop a sulfur-, halide-, and NH₃-resistant alloy membrane with a projected H₂ permeance of 25 m³m⁻² atm⁻¹ h⁻¹ at 400°C and capable of operating at pressures of 12.1 MPa (∼120 atm, 1,750 psia).
- Construct and experimentally validate the performance of 0.1 kg/day H₂ PdCuTM trimetallic alloy membrane separators at feed pressures of 2 MPa (290 psia) in the presence of hydrogen sulfide (H₂S), NH₃, and hydrogen chloride (HCl).

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell 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, H₂ 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” H₂ selective separators will be completed. The progress toward achieving the DOE technical targets based on the atomistic modeling predictions and experimental data is shown in Table 1.

Accomplishments

- Developed an atomistic modeling screening approach to evaluate materials for susceptibility to sulfur attack.
- Evaluated the performance of face-centered cubic (FCC) PdCu separators under the DOE testing protocol.
- Confirmed the sulfur resistance and stability of the PdCu alloy.
- Produced single tube separators with the UTRC ternary PdCuTM composition with doubled performance versus early 2009 results.
- Identified a polishing process to remove the surface barrier produced during manufacture of PdCuTM tubes.

Introduction

This project is focused on increasing the technology readiness level of Pd-based metallic membranes for H₂ separation from coal-biomass gasifier exhaust or similar H₂-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. The
BCC phase of PdCu has a much higher H₂ permeability than the FCC materials and the FCC materials have been shown to have good sulfur resistance. Thus, a stabilized BCC alloy should be able to obtain the high permeability of alloys like PdAg with the sulfur tolerance of FCC PdCu. One of the major objectives of this work is to experimentally validate the UTRC PdCu ternary alloy performance. An additional objective is to experimentally evaluate the best commercially available FCC PdCu alloy from Power+Energy for meeting the DOE technical targets.

**Approach**

The approach for this project is to experimentally validate two different PdCu-based alloys for H₂ separation. Additional atomistic modeling has been performed to examine performance characteristics, such as resistance to carbon formation and sulfur poisoning. In parallel with the modeling, separator units of both the Power+Energy and UTRC alloys were manufactured by Power+Energy and tested for their H₂ separation capabilities at UTRC.

The experimental efforts were 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 objectives of the low pressure (<10 atm) laboratory testing were to characterize the membrane separator H₂ 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 involved testing with gases containing different concentrations of poisons such as H₂S and NH₃, including DOE membrane testing protocol conditions. The high pressure mixed gas was used in the >500-hour durability tests to quantify the effect of gas mixtures and poisons on the H₂ permeability of the PdCu separators.

**Results**

Although irreversible corrosion product formation (i.e. Pd₄S) has been reported on a number of Pd-based alloys exposed to sulfur (S)-bearing atmospheres [1,2], S adsorption has been observed at UTRC to be reversible on PdCu alloys with recoverable H₂ permeability at higher temperatures. This finding motivated a systematic, first principles, atomic modeling study to pinpoint alloy characteristics that control the reversibility/irreversibility of S interactions on a range of Pd-based alloys. This understanding could then be used to develop a predictive tool to guide the development of S-tolerant alloys for dense metallic H₂-selective membranes.

Figure 1 provides a graphical representation of a useful approach to evaluate Pd-alloys for their susceptibility to irreversible sulfur attack. On the abscissa is plotted the reaction enthalpy for S absorption. The reaction enthalpy for Pd segregation and Pd₄S formation upon S absorption is plotted on the ordinate. A positive value on the abscissa implies that sulfur absorption on the surface is not favorable, while a negative value suggests the material can incorporate sulfur into the subsurface lattice structure. If sulfur is incorporated into the structure, a negative value on the ordinate predicts the material should undergo sulfur corrosion. For example, pure FCC Pd (111) and FCC Pd₃Ag (111) surfaces, both known to be sulfur intolerant
UTRC has previously demonstrated the reversible sulfur tolerance of PdCu alloys. After the project inception, the DOE developed a testing protocol for evaluating membrane performance [3]. Figure 2 shows the results of DOE test protocol testing on an FCC PdCu membrane produced for this project which lasted 527 hours. The testing was performed under pure H\textsubscript{2} as well as test conditions 1, 2a, and 2b. The data in Figure 2 show that under the specific test conditions, the pure H\textsubscript{2} flux of this separator was 45±2 ft\textsuperscript{3}ft\textsuperscript{-2}h\textsuperscript{-1}.

![Figure 1](image1.png)

**FIGURE 1.** The analysis of reaction enthalpy for Pd segregation and Pd\textsubscript{S} formation upon S absorption versus the change in enthalpy for S incorporation by absorption relative to S adsorption. This serves as a predictive tool to delineate irreversible from reversible S interactions.

![Figure 2](image2.png)

**FIGURE 2.** DOE protocol test data for an FCC PdCu separator which had been tested for 527 hours at DOE protocol test conditions 1, 2a, & 2b at 450°C.
with a $H_2$ recovery of $>80\%$ at 450°C and 200 psia. Upon exposure to the DOE test 1 conditions, this flux decreased to $14\pm 2 \text{ ft}^3\text{ft}^{-2}\text{h}^{-1}$ with a similar recovery. When 20 ppmv $H_2S$ was introduced during test 2a conditions, the flux was further reduced to $11\pm 1 \text{ ft}^3\text{ft}^{-2}\text{h}^{-1}$ with a corresponding decrease in recovery to $(61\pm 7)\%$, however, membrane performance remained stable during the 100+ hours at each condition. Finally, when the $H_2$ concentration was decreased and the sulfur level increased to 40 ppmv, the flux was reduced to $6\pm 1 \text{ ft}^3\text{ft}^{-2}\text{h}^{-1}$ with a $H_2$ recovery of $(50\pm 6)\%$. The decrease in $H_2$ flux due to composition effects was completely reversible based on measurements taken with pure $H_2$ between each of the gas compositions and also the fact that the membrane did not leak. This further supports the conclusion that FCC PdCu is sulfur resistant and not susceptible to sulfur corrosion.

Development of the UTRC ternary PdCuTM alloy resulted in a permeability performance in July 2009 that was similar to that of the FCC PdCu alloy (see Figure 3). Further characterization was performed to determine the root cause of the lower than expected performance. An unwanted TM-oxide surface scale forms during manufacturing of the separator tubes and requires removal. The separator performance in July 2009 was measured after chemical etching which resulted in selective dissolution of the Cu, leaving the surface Pd-rich. It is known from the literature [4,5] that a PdCu alloy with greater than $\approx 50 \text{ at}\% \text{ Pd}$ has a rather poor permeability compared to pure Pd. As a result, a mechanical polishing technique was developed to remove the surface oxide scale without affecting the surface PdCu composition. The data for the polished separator tubes, measured in April 2010, is also given in Figure 3 and shows that the performance was improved by a factor of two.

A technical and economic modeling analysis was performed for the FCC PdCu dense metallic membranes. Similar assumptions to those used in the DOE test protocol [3] were used in the calculations. A mean flow rate of $6.425\times10^5 \text{ kg.h}^{-1}$ was used for membrane sizing calculations based on different gasifier systems operating in the range of 520 MW to 640 MW [6]. For the purposes of the analysis, the gas was assumed to be at the DOE protocol test 1 composition (50% $H_2$, 1% CO, 30.0% $CO_2$, and 19.0% $H_2O$). Figure 4 shows the $H_2$ recovery as a function of membrane surface area at 450°C. The recovery curves are presented as a function of the membrane feed pressure. Higher feed pressures result in higher fluxes and thus a reduced area for the same $H_2$ recovery.
For a high $H_2$ recovery, a dense metallic PdCu membrane for this size system would require an area approaching 60,000 m$^2$ and the metal would cost on the order of $200,000,000. However, one advantage of the dense metallic membranes is that the raw materials can be recycled and the Pd cost can be significantly reduced by a lease and recycling strategy. In addition, the very high $H_2$ purity achievable by dense metallic membranes, along with their higher technology readiness level, makes the dense metallic approach a viable path forward for $H_2$ separation while other, longer-term, low-cost technology paths are further developed.

Conclusions and Future Directions

- An atomistic modeling screening approach for evaluating susceptibility to irreversible sulfur attack was developed that could assist other development projects on $H_2$ separation membranes.
- Dense metallic FCC PdCu separators can operate under the DOE testing protocol conditions and maintain their stability. In addition, the impact of poisons, such as sulfur, has been found to be reversible.
- Single tube separators with the UTRC ternary PdCuTM composition showed doubled performance versus early 2009 results after an improved polishing process was identified to remove the surface barrier produced during manufacturing of the PdCuTM tubes.
- No additional work is planned on the current project.
- Future work in this area should move in the direction of larger scale demonstrations with real gasifier exhaust.

FY 2010 Publications/Presentations


References

II.D.6 Supported Molten Metal Membrane (SMMM) for Hydrogen Separation

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Contract Number: DE-FE0001050
Project Start Date: September 30, 2009
Project End Date: September 29, 2012

Objectives

The overall goal of this project is to develop and test novel supported molten metal membranes (SMMMs) suitable for hydrogen separation in conjunction with a coal gasification plant, based on low-melting, non-precious group metals (non-PGM) or alloys, supported as thin films on an inert porous ceramic, or on a porous metal support with or without an intermetallic diffusion barrier. The specific objectives of the project are:

- Identify non-PGM molten metals and alloy candidates for membranes that provide good hydrogen dissociation ability, solubility, and diffusivity, and are tolerant to other syngas species such as carbon monoxide, and to poisons such as sulfur.
- Identify porous ceramic and porous metal supports with an intermetallic diffusion barrier that are readily wetted by the molten metals, and allow stable molten metal membranes to be fabricated.
- Develop fabrication procedures for supported molten metal membranes on porous supports that allow inexpensive, rapid, and reproducible membrane synthesis.
- Establish the basic feasibility of the SMMM technique.
- Narrow down the list of promising SMMM candidates based on preliminary permeability experiments.
- Investigate in detail the permeability, selectivity, and durability of the most promising SMMM candidates vis-à-vis DOE technical targets.
- Relate membrane development/optimization to a fundamental experimental and theoretical characterization of the SMMM structure, composition, and mechanism.
- Fully investigate the best SMMM candidate(s) under increasingly realistic conditions based on the DOE Test Protocol and to compare their performance against exceeding the DOE 2010 Technical Targets.

Technical Barriers

This project addresses the following technical barriers within the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan for the Pd-based dense metallic membranes:

- Hydrogen embrittlement at temperatures below 500°C
- Thermal mismatch between metal membrane and support
- Pinhole formation
- Membrane sintering at higher temperatures
- Poisoning by S, CO, and other trace contaminants in coal derived H₂
- High cost of PGM-based membranes

Technical Targets

The project is currently in its initial stages of identifying molten metal and alloy candidates, porous supports, and in developing the fabrication procedures for these novel membranes. Once these steps are completed, and following initial feasibility investigations, the membranes will be developed further in an effort to meet or exceed the 2010 DOE technical targets listed in Table 1.

Accomplishments

During the first three quarters of Year 1 (Phase I) of this project, the following technical accomplishments have been made:

- The initial candidates for low-melting metals (M₁) have been identified (Sn, In, Ga, and Bi).
The initial non-PGM candidates for catalytic metals (M2) have been identified (Ni, Co, Cu, Fe, Ag, W, Mo, Nb, Ti, and Ta).

- The metallic (Inconel, porous stainless steel) and ceramic (Al2O3, ZrO2, TiO2, SiC, and Porous Vycor® glass) porous supports have been identified.
- SMMM fabrication procedures have been developed based on electroless- and electro-plating, soldering, and melt imbibition.
- SMMM membrane candidates of Sn and In have been fabricated on porous Inconel and on α-Al2O3 supports.
- Initial feasibility studies of these fabricated membranes have been completed.
- The reasons for failure of these first two candidates have been identified. For the case of metal supports, thus, the molten metal diffuses, reacts, and forms a dense non-permeable solid film with the substrate metal. For the ceramic membrane tested so far (α-Al2O3), the molten metal is found not to wet it, so that a microporous, rather than a dense, membrane results.
- From these early results, promising support candidates to be tested next have been identified, and include ZrO2, TiO2, SiC, Porous Vycor® glass as ceramic support candidates, and porous stainless steel (PSS) with a ZrO2 layer as a metal support candidate.
- A new permeability apparatus suitable for both tubular and disk (coupon) membranes capable of going up to 650°C and of recording permeation data automatically over an extended period based on LabVIEW® has been designed and built.

### TABLE 1. The DOE Technical Targets for Dense Metallic Membranes for Hydrogen Separation

<table>
<thead>
<tr>
<th>Property</th>
<th>2010 Target</th>
<th>2015 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2 Flux (std m³/m².h)</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>H2 Feed Pressure, $p_{H2,feed}$ (psia)</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>H2 Permeate Pressure, $p_{H2,perm}$ (psia)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Operating Δ$p_{H2}$ =$p_{H2,feed} - p_{H2,perm}$ (psi)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Operating Temperature, $T$ (°C)</td>
<td>300–600</td>
<td>250–500</td>
</tr>
<tr>
<td>Pressure Tolerance, Δ$p$ (psi)</td>
<td>400</td>
<td>800–1,000</td>
</tr>
<tr>
<td>Sulfur Tolerance (ppm)</td>
<td>Yes</td>
<td>&gt;100</td>
</tr>
<tr>
<td>CO Tolerance</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Water-Gas Shift Activity</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>H2 Purity (%)</td>
<td>99.5</td>
<td>99.99</td>
</tr>
<tr>
<td>Cost ($/ft²)</td>
<td>500</td>
<td>&lt;250</td>
</tr>
<tr>
<td>Durability (years)</td>
<td>3</td>
<td>&gt;5</td>
</tr>
</tbody>
</table>

- The DOE Hydrogen Program FY 2010 Annual Progress Report

## Introduction

Coal gasification is promising for the centralized co-production of electric power and hydrogen via integrated gasification combined-cycle (IGCC) technology, when combined with carbon dioxide sequestration. For this, the main commercial technologies available for separating H2 from other syngas components, i.e., pressure-swing adsorption (PSA) and cryogenic distillation, however, are expensive and energy intensive. Thus, membrane separation of H2 is being investigated. The current dense metallic membranes based on Pd, however, are expensive, and still fall short of the desired permeability, selectivity, low cost, chemical and mechanical robustness, and durability. Hence, novel dense membranes based on non-PGM metals are sought that might overcome these barriers.

Thus, we have proposed a novel dense membrane technology for the separation of H2 from syngas based on non-PGM SMMMs, comprising of a thin film (<25 μm) of a liquid metal or alloy, with a melting point in the range of 200-500°C, and supported on a porous ceramic or porous metal support. The proposed membranes would be less expensive, more robust to species such as CO, and resistant to poisons such as sulfur. In addition, they would obviate issues related to solid dense membranes, i.e., sintering, H2 embrittlement, thermal mismatch between the membrane and the support, and formation of pin-holes.

## Approach

Figure 1 shows a schematic of the proposed SMMM. It comprises of a porous ceramic/metal support on which a thin but dense layer of a molten metal or molten metal alloy is deposited. Further, an oxide/ceramic layer is interposed in the case of a porous metallic support to...
avoid any diffusion and alloying reaction between the molten metal and the porous metal support.

The dense molten metal membrane comprises of two components: 1) a low-melting metal (M₁) to provide an open and fluid lattice desirable for ready dissolution and diffusion of hydrogen atoms, H₂; and 2) a non-precious group transition, or other catalytic, metal (M₂), to facilitate dissociation of hydrogen molecules at the membrane surface, in keeping with the accepted mechanism of hydrogen diffusion through a dense metallic membrane, wherein the H₂ molecule first dissociates and adsorbs on the surface, followed by ingress into the lattice, and subsequent diffusion through it, both of which steps are presumably facilitated by lattice defects and vacancies present in a liquid metal film.

Results

Due to the novelty of the proposed membranes, the work had to start from scratch, namely, identification of initial metal and support candidates, and development of the fabrication procedures for the membranes. Thus, as a start, it was decided to pick Sn as our initial choice for the molten metal M₁, since it has a large liquidus range (melting point [M.P.] = 232°C, boiling point [B.P.] = 2,602°C), and is relatively resistant to sulfur and carbonaceous deposits. This choice was subsequently supplemented with In (M.P. = 157°C, B.P. = 2,072°C), also abundant and nontoxic like Sn. As our initial choices for the porous supports, we picked: 1) a porous Inconel support as a porous ceramic support; 2) a porous alumina support as the porous ceramic support; and 3) a PSS with a ZrO₂ layer obtained from Pall Corporation. With the initial choice of the molten metal and the porous supports in hand, the next focus of the work was on developing a protocol for the fabrication of the SMMM. The various techniques investigated were: 1) electroless plating, 2) electroplating, 3) molten metal imbibition, and 4) soldering.

During the deposition of Sn on porous Inconel support, it was found that Sn is not conducive to thick deposits via electroless plating, because of the self-passivating nature of the metal, i.e., unlike, Pd, or Cu, for instance, it has low catalytic activity for the reductant oxidation reaction at room temperature. Thus, the plating stops once an impenetrable self-passivating layer of the metal has been deposited on the substrate. As a result, only a thin layer of Sn on porous Inconel could be obtained via electroless plating. Consequently, in order to deposit thicker tin layers, electro-plating was utilized. The electrodiposition experiment was carried out using four electrodes configuration in a cylindrical cell. The porous Inconel tube support was the cathode. The three cleaned tin rods were used as the anodes and symmetrically placed around the cathode to obtain uniform deposition. In this manner, any deposit thickness could be readily obtained. However, it was found that Sn electrodiposition is prone to whisker formation. However, these could be readily scraped off. The resulting Sn/Inconel membrane is shown in Figure 2.

However, when this membrane was tested for hydrogen/helium permeability above the M.P. of Sn, it was found that it was rendered virtually impermeable. The membrane post permeability testing is shown in Figure 3.

It appears thus that an alloying reaction has taken place between the Sn and Inconel, possibly forming a solid, dense, impermeable layer. Post-mortem microscopic characterization via scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) is planned to confirm the alloying and formation of a dense solid film. It, thus, appears that porous metal supports without an intermetallic diffusion barrier are unsuitable for SMMM due to the ingress and reaction of the molten metal with the porous metal substrate.

Since porous metal supports are not, thus, suitable for SMMM, the fabrication of a Sn/α-Al₂O₃ ceramic support membrane was undertaken. A thin 2-µm layer of Sn/Cu was first predeposited on the α-Al₂O₃ support via electroless plating, over which, subsequently, a thick layer of Sn was deposited via electroplating at a low current density. The predeposition of the Sn/Cu layer is, of course, essential to allow the support to be used as an electrode. The resulting membrane is shown in Figure 4.

When this membrane was subjected to permeability testing at elevated temperatures, a very high flux and low selectivity between H₂ and He were found, characteristic of a microporous membrane (Figure 5) rather than a dense membrane. In other words, upon melting, only a thin microporous layer of Sn remained on the Cu/α-Al₂O₃ porous substrate. It was, thus, determined that α-Al₂O₃ is not wetted by the molten Sn.

![FIGURE 2. A 20 µm Dense Layer of Sn on the Porous Inconel Support before Permeability Test](image)

![FIGURE 3. The used Sn/Inconel Membrane after Permeation Experiments up to 600°C](image)
Conclusions and Future Directions

In summary, we are still working on fabricating a dense supported molten metal membrane, and hope to accomplish this shortly. The following work is planned for the upcoming year (Year 2):

- We will test the suitability of other ceramic supports (ZrO₂, SiC, TiO₂, Vycor glass), along with metal supports with intermetallic diffusion barrier ceramic layers, for forming stable molten metal membranes.
- Once molten metal membranes with our initial choice for M₁ are thus fabricated and tested for basic permeability, the next step would be to alloy them with the catalytic metal M₂, and narrow down the selection to a handful of final SMMM candidates.
- The most promising SMMM candidates hence fabricated will be subjected to H₂ permeability, selectivity, and durability testing under increasingly realistic conditions of temperature, pressure, gas composition, poisons.
- The best SMMM membranes will be subjected to detailed physical, microstructural, and chemical characterization before and after the permeation test.
- We will develop a detailed kinetic/diffusion theoretical model for SMMM, including dynamics of all the sequential steps including dissociative adsorption/desorption and diffusion, so that no arbitrary assumptions are necessary regarding the rate-limiting step.

In the third and final year of the project, we will fully investigate the best SMMM candidate(s) under increasingly realistic conditions based on the DOE test protocol and compare their performance against exceeding the DOE 2010 targets (Table 1).

FY 2010 Publications/Presentations

II.E.1 High-Capacity, High-Pressure Electrolysis with Renewable Power Sources

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Contract Number:  DE-FG36-08GO18066
Subcontractor:
HyPerComp Engineering, Inc., Brigham City, UT
Project Start Date:  May, 2008
Project End Date:  September, 2011

Objectives

- Achieve a 15x increase in the gas production rate of a single high-pressure hydrogen production cell over the current standard Avalance cell.
- Demonstrate the high-pressure cell composite wrap which results in significant weight reduction.
- Build and test a 1/10th scale pilot plant.
- Create fabrication-ready drawings for a full-scale plant (300 kg/day, 750 kW).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Generation by Water Electrolysis section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(G) Capital Costs
(H) System Efficiency
(J) Renewable Electricity Generation Integration

Technical Targets

**TABLE 1. DOE Technical Targets: Distributed Water Electrolysis Hydrogen Production**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2012 Target</th>
<th>2017 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Cost</td>
<td>$/gge</td>
<td>3.70</td>
<td>&lt;3.00</td>
</tr>
<tr>
<td>Electrolyzer Capital Cost</td>
<td>$/gge</td>
<td>0.70</td>
<td>0.30</td>
</tr>
<tr>
<td>Electrolyzer Energy Efficiency</td>
<td>% (LHV)</td>
<td>69</td>
<td>74</td>
</tr>
</tbody>
</table>

* gge = gasoline gallon equivalent; LHV = lower heating value

Distributed Water Electrolysis Hydrogen Production

In this project Avalance is developing an enlarged version of its present electrolyzer design that will have 15x the capacity of the current single tubular cell. To achieve this, the diameter of the current Avalance design individual tubular cell is being enlarged to enable an innovative cell core design: multiple coaxially arranged cylindrical electrodes, nested in a uni-polar configuration. This design is the core of a distributed water electrolysis hydrogen production system that will meet the following DOE 2017 targets:

- Hydrogen Cost: $3.00/gge
- Electrolyzer energy efficiency: 74 kWh/kg

Accomplishments

- Identified and tested formable sheet membrane material. (Figure 1)
- Successfully demonstrated membrane tube forming and seam joining. (Figure 2)
- Identified vendor and ordered 6,500 psi capable electrical isolation hoses.
- Completed design of single-cell test article and test apparatus.
- Demonstrated 6,500 psi production on small capacity cells.
- Began construction of the test cells to test the recirculation approach to enable 6,500 psi operation. (See Figure 3).
- Initial testing of 6,500 psi operation on the existing small-scale units has been completed demonstrating long-term operating potential of the core technology at very high pressure. Avalance completed the initial round of testing to evaluate the present cell design operation at 6,250 psi with the entire array of
IIE. Hydrogen Production / Electrolysis

Avâlence, LLC

II.E Hydrogen Production / Electrolysis

Introduction

Avâlence has existing technology that is globally unique in its ability to deliver hydrogen directly at storage-ready pressures of 2,500 and 6,500 psi without a separate compressor. Using an alkaline electrolyte process, the Avâlence 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 project completed in April 2005) that the electrolyzer operates through the full range of voltages output from the connected photovoltaic 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 and compressor system sets. The smaller scale Hydrofillers are based on a single cathode/anode tubular cell design with production capability of about 0.1 kg/day per cell. 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, an enlarged version of the current Avâlence design is being developed that will have at least 15x the capacity of the present single tubular cell. To achieve this, the diameter of the individual tubular cell will be substantially increased in order 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 diameter increase with a practical pressure boundary while operating at either 2,500 or 6,500 psi, Avâlence has partnered with a composite cylinder manufacturer, HyPerComp Engineering Inc. They will develop a custom designed containment vessel/cathode using their composite technology expertise that will allow an increase in the diameter of the individual electrolysis cell, enable operation at 2,500 psi and above, and reduce the cell weight and cost relative to conventional metal containment (similar to what is seen today with composite storage tanks used on vehicles). 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, Avâlence is proposing to build a quarter-scale pilot plant to be composed of 20 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 the National Renewable Energy Laboratory.
for verification testing over the last three months of this nominal 30 month project. The final result of the project will be a commercially operating 30 kg/day pilot plant integrated with a wind turbine and/or photovoltaic array, and delivering hydrogen gas at pressure directly 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 the technology for commercialization.

**Results**

In order to minimize project risk, a decision was made to demonstrate 6,500 psi operation in existing Avâlence technology prior to and as a step towards designing and building the large cell prototype. A number of findings resulted from this action. While it was shown that as expected, that the basic electrochemistry work, some issues arose need to be addressed going forward.

- It was found that that the 80 mm membrane created a larger voltage drop between the anode and cathode and therefore resulted in decreased efficiency. Table 2 lists the energy requirement per kg of hydrogen produced for both the 40 and 80 mm membrane tests.

<table>
<thead>
<tr>
<th>Polysulfone Membrane Thickness</th>
<th>Energy Used in Electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 mm</td>
<td>62 kWh/kg</td>
</tr>
<tr>
<td>80 mm</td>
<td>67 kWh/kg</td>
</tr>
</tbody>
</table>

- At high pressure, all leak paths also become more of an issue. As a result:
  - Pipe threads had to be removed from the cell design.
  - Multiple attempts were made before finalizing the design of the Parker dielectric hoses.
  - Internal cell seals have been redesigned on the head of legacy cells; and the new design concept is being used on the large cell.

- In achieving the goal of 6,500 psi operation, it was found that the present standard cell design requires periodic depressurization and electrolyte mixing to maintain cell performance and gas purity over the long term. Gas bubbles being formed are very small (almost invisible) and the velocity of bubbles is low, causing masking of the electrodes. As a result, high-pressure operation, which results in reduced buoyancy and smaller bubbles makes gravity based sweeping problematic at higher (design point) rates. A further issue is that since velocity is lower, dwell time in cells increases. This by itself can impact impurity, because there is more time to react with any electrolyte contaminants and greater time for any side electrolysis reactions (hoses) to accumulate.
impurity. Also, since diffusion is either steady or increasing with pressure, the additional dwell time amplifies any impurity as a result of diffusion. To address all of these issues, it is proposed that a different, constant recirculation approach may eliminate the depressurization cycle need and therefore increase production availability, oxygen side purity, and production efficiency. The electrolyte will be circulated to cool the system and to sweep the electrodes of gas bubbles to maintain gas production rates (current density). Additional components required for recirculation such as pumps and blowers actually simplify other parts of the system such as passive level control, water addition, and cell-to-cell electrolyte balancing, which become essentially automatic (see Figure 3).

Other findings include:

- Electrical isolation hoses need to be eliminated in order to move the Y-axis intercept on purity to above 99% (see Figure 1).
- Structural issues can be addressed using a conventional design of an overwrap to the metallic inner pressure vessel (see Table 3).
- Gas production rates are achievable as long as masking does not block electrode surface.
- High surface area cathode treatment can be employed to increase production rate.

### Conclusions

- Avâlence has shown that the biggest challenge of 6,500 psi with no compressor can be met.
- A robust large cell design is complete, ready to build/test.
- The technology is valid:
  - structurally (composites exit criteria)
  - electrochemically (2.1 v, 1,800 A exit criteria)
  - thermally (derived)
  - economically (DOE goal met @ 1,000 units/yr exit criteria)

- We feel that demonstration of the large cell nested operation is very low risk.
- We feel that demonstration of composite overwrap to achieve containment is also very low risk.

### Future Directions

- Demonstrate large diameter cell operation at 1,000 psi.
- Test long-term 6,500 psi operation approaches:
  - Using existing small cell apparatus.
  - Purified gas “recirculation/dilution” approach as required to achieve the lower explosive limit (see Figure 3).
  - Neutral electrolyte chamber approach – membrane related effort.

### TABLE 3. Composite Shell Design

<table>
<thead>
<tr>
<th>Specification for Composite Overwrapped Pressure Vessel for Electrolysis Cell</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design Number</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum Burst Pressure</td>
<td>5625</td>
<td>14625</td>
</tr>
<tr>
<td>Target Average Burst Pressure</td>
<td>8000</td>
<td>20000</td>
</tr>
<tr>
<td>Overall Length</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>Liner Material</td>
<td>316L</td>
<td>316L</td>
</tr>
<tr>
<td>Liner OD</td>
<td>8.25</td>
<td>8.25</td>
</tr>
<tr>
<td>Liner Sidewall Thickness</td>
<td>0.12</td>
<td>0.31</td>
</tr>
<tr>
<td>Pressure Vessel ID</td>
<td>8.01</td>
<td>7.63</td>
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<tr>
<td>Liner Dome Config.</td>
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<tr>
<td>Port Configuration</td>
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<tr>
<td>Required Port OD</td>
<td>4.625</td>
<td>4.625</td>
</tr>
<tr>
<td>Fiber Overwrap Material</td>
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<td></td>
</tr>
<tr>
<td>Resin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Composite Hoop Thickness</td>
<td>0.086</td>
<td>0.258</td>
</tr>
<tr>
<td>Carbon Composite Helical Thickness</td>
<td>0.11</td>
<td>0.33</td>
</tr>
<tr>
<td>Carbon Composite High Angle Helical Thickness</td>
<td>0.038</td>
<td>0.114</td>
</tr>
<tr>
<td>Overall Carbon Composite Thickness</td>
<td>0.234</td>
<td>0.702</td>
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<tr>
<td>Pressure Vessel OD</td>
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II.E.2 PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane

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Contract Number: DE-FG36-08GO18065

Subcontractors:
• Virginia Polytechnic Institute and University, Blacksburg, VA
• Parker Hannifin Ltd domnick hunter Division, Hemel Hempstead, United Kingdom

Project Start Date: May 1, 2008
Project End Date: April 30, 2012

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

GES Progress toward Meeting DOE Targets for Distributed Electrolysis

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<th>Characteristics</th>
<th>Units</th>
<th>2012/2017 Targets</th>
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*Using H2A model rev 2.1.1. A cost of $1.80 is included for H2 compression, storage, and delivery

LHV - lower heating value

Accomplishments

- Membrane
  - Demonstrated enhanced dimensionally stable membrane (DSM™) performance (>Nafion® [1] 1135 membrane)
  - Completed 1,000-hour life-test with DSM™ (@ 80°C)
  - DSM™ operating lifetime estimated at 55,000 hours
  - Reduced membrane support cost by one-order of magnitude

- Cell-Separator
  - Demonstrated reduced hydrogen embrittlement in titanium/carbon cell-separator
  - Projected longevity of the carbon/titanium cell-separators (> 60,000 hours)

- Preliminary Electrolyzer Stack and System Design
  - Completed electrolyzer stack and system design utilizing low-cost components
  - Completed process and instrumentation diagram, process flow diagram (PFD), system control diagrams and layout drawings
  - Completed extensive safety review of electrolyzer system
  - Completed modeling of electrolyzer capital and operating costs; performed economic analysis using the DOE H2A model illustrating cost-reductions.

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Introduction

The Department of Energy (DOE) has identified hydrogen production by electrolysis of water at forecourt stations as a critical technology for transition to the hydrogen economy, and as the hydrogen economy matures, for hydrogen production at centralized locations using renewable energy sources. 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-H\textsubscript{2}, considerably higher than the DOE target of $3.70/kg-H\textsubscript{2} by 2012 [2]. 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, the capital costs of electrolyzer stacks and systems, and the high cost of hydrogen compression, storage, and delivery.

GES has developed PEM-based electrolyzer technology that operates at differential pressure for producing hydrogen at moderate to high pressure directly in the electrolyzer stack, while oxygen is evolved at near-atmospheric pressure. In this system, liquid water, which is a reactant as well as coolant, is introduced into the oxygen side at near atmospheric pressure. The goals of the project are to reduce the cost of the stack and system, improve electrolyzer efficiency, and to demonstrate electrolyzer operation at moderate pressure.

Approach

To reduce the cost of PEM-based electrolyzers, GES is improving electrolyzer stack efficiency and reducing stack cost through development of an advanced low-cost, high strength, membrane using a perforated polyimide support imbibed with perfluorosulfonic acid (PFSA) ionomer. GES is also reducing stack capital cost and increasing stack life through development of a long-life bipolar stack cell-separator, decreasing stack costs by initiating scale-up to a larger active area, and reducing the system capital cost by applying commercial production methods to 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-H\textsubscript{2}/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 DOE cost targets for hydrogen production, assuming high-volume production. This will provide competitively priced hydrogen for delivery at forecourt stations to enable transition to the hydrogen economy.

Results

**DSM™ Membrane Performance:** To improve electrolyzer efficiency, GES has developed 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 (DSM™) due to the membrane support that minimizes changes in dimensions (swelling/contraction) under high-pressure operation and with changes in water content. The support structure utilized in the development of the DSM™ consists of a polyimide (Kapton®) base film with a definable open pattern. Two separate techniques were employed in the fabrication of the DSM™ support. This includes membranes fabricated with a laser-drilled support (L-DSM™) and those with a recently developed low-cost chemically etched support (C-DSM™), Figure 1. The support structures are then imbibed with 850 and 1100 equivalent weight (EW) PFSA ionomer to a thickness of 3 mil (0.003”).

Polarization scans of the DSM™ were conducted through a current density range of up to 3000 mA/cm², a differential pressure of 300 psid, a temperature of 80°C, and with similar cathode and anode electrode structures. Results were compared to Nafion® 1135, Figure 2. During testing, both L-DSM™ and C-DSM™ exceeded the criterion for performance: each membrane exhibited lower cell voltages and thus higher cell efficiencies than that of a Nafion® 1135 membrane. In a direct comparison of DSM™ support structures imbibed with 1100 EW PFSA ionomer, L-DSM™ slightly outperforms C-DSM™. At an operating current density of 1,500 mA/cm², the performance of the L-DSM™ is 1.72 V, C-DSM™: 1.75 V. The slight loss in performance
of the C-DSM™ is attributed to the larger landing width within the chemically etched support structure resulting in an increase of the proton-transport path and thus restricting the proton-transport kinetics. The loss in performance of the C-DSM™ is overcome using a lower EW PFSA ionomer, namely 850 EW. It has been shown that the performance of the “low-cost” C-DSM™ (850 EW) is equivalent to that of the L-DSM™ (1100 EW) as noted:

L-DSM (1100 EW) = C-DSM (850 EW) > C-DSM (1100 EW)

Durability of the DSM™ was also demonstrated in full-size 160-cm² active area hardware via fluoride-release-rate (FRR) measurements at constant current operation. Since PFSA ionomer is used as the membrane material and in the binder for the catalyst layer, the loss of fluoride is used as a measurement of membrane degradation. An FRR rate of 3.7 μg F⁻ ion/hr or less than 10 micrograms F⁻ ion/L (<10 ppb) was present in the cathode effluent (electro-osmotically transported water) at the end of the 1,000-hour life test. Based on electrolysis FRR results, the lifetime of the DSM™ is projected to be between 45,000 and 55,000 hours, which exceed the durability requirements of the electrolyzer system. In addition to its durability, the DSM™ exhibits high cell efficiencies in the range of 75% LHV (88.8% higher heating value) at an operating current density of 1,500 mA/cm².

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 has been achieved by 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 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. 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.

Preliminary Electrolyzer Stack and System Design: As a result of the component and membrane development conducted in this project, the overall projected capital cost of the electrolyzer stack has decreased from greater than $2,500/kW in 2001 to $463/kW in 2010, with a further projected decrease to <$400/kW by 2012. In addition to the use of low-cost cell-separators, the completed preliminary stack design shown in Figure 3 includes several modifications to the previous hardware; (1) an increase in cell active area
from 160 to 290 cm², effectively reducing the number of cells required to produce a given amount of hydrogen, thus reducing the stack manufacturing labor and the materials scrap rate, (2) an overall decrease in parts count per cell (from 41 to 11), (3) a 75% reduction in catalyst loadings, (4) molded thermoplastic cell frames resulting in a cost reduction of 95% for this component alone, and (5) the use of a pressurized dome that encloses the electrolyzer stack to conform to the regulatory code requirements pertinent to hydrogen generators.

Our subcontractor, Parker Hannifin Ltd. (Parker) has completed the preliminary system design which includes the PFD, the P&ID, and the control logic diagrams. The dimension of the electrolyzer system shown in Figure 4 is roughly 6’ x 6’ x 6.5’. The layout is effectively broken into three zones, namely the oxygen (O₂) compartment, the hydrogen (H₂) compartment, and the controller section. The O₂ compartment contains the oxygen gas-phase separator, a circulating liquid pump, and the deionized water feed tank; the H₂ compartment, encloses the high- and low-pressure hydrogen gas-phase separators, heat exchanger, cooling fans, and various flow valves. The refrigeration unit, a component of the H₂-dryer that is used to cool H₂ gas prior to entering the dryer, is located below the controller and adjacent the electronic power supply. Nitrogen (N₂) tanks provide nitrogen gas for filling the dome and for purging the electrolyzer stack during start-up and shut-down.

**Conclusions and Future Directions**

Significant progress has been made in DSM™ membrane development. GES has demonstrated membrane reproducibility and durability as well as a significant improvement in electrolyzer cell efficiency that exceeds the DOE’s 2017 target. 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 balance-of-plant components efficiency. The future objectives (by company) are to:

- **Parker Hannifin**
  - Continue fabrication and evaluation of key system components
  - Complete critical design review
  - Fabricate and operate deliverable system

- **GES**
  - Fabricate scaled-up ‘short stack’ prototype (0.1 kg-H₂/hr)
    - Scale-up DSM™ (to 290-cm²)
    - Scale-up Cell-Separators (to 290-cm²)
  - Operate short stacks at GES for 1,000 hours
  - Assist in system start-up at Parker facilities
  - Receive and install operating system at GES
  - Add cells to stack to increase capacity to 0.5 kg-H₂/hr
  - Verify stack/system performance
  - Demonstrate prototype system at NREL

- **Virginia Polytechnic Institute**
  - Complete fabrication of alternative hydrocarbon membrane
  - Evaluate 100-hour durability

**FY 2010 Publications/Presentations**


**References**

1. Nafion® and Kapton® are registered trademarks of E.I. du Pont de Nemours and Company
II.E.3 Renewable Electrolysis Integrated System Development and Testing

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Subcontractors:  
• Engineering Procurement & Construction, Denver, CO  
• Spectrum Automation, Denver, CO  
Project Start Date: September, 2003  
Project End Date: September 30, 2012

Objectives

• Model and evaluate the potential of using hydrogen as an energy storage mechanism when coupled to renewable electricity sources at utility scales.  
• Quantify efficiency and capital cost improvements achieved by designing and building integrated power electronics to more closely couple wind turbines and photovoltaic arrays to the electrolyzer stacks.  
• Test and characterize the impacts on commercial electrolyzer systems to accommodate the varying energy from wind turbines and photovoltaic arrays coupled directly to the hydrogen-producing electrolyzer stack.  
• Work closely with 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.  
• Characterize and evaluate performance improvements of system-level integration and optimization opportunities for renewable-energy-based electrolysis production facilities.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration (RD&D) 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 objectives of this work includes the development of integrated power electronics and control theory to couple renewable electricity sources with the electrolyzer stack. This work can help reduce the capital cost and improve the efficiency to reduce the cost of renewable hydrogen production 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

• Completed the hydrogen-based energy storage analysis and companion energy storage benchmarking study.  
• Installed, commissioned and operated 13 kg/day polymer exchange membrane (PEM) electrolyzer at the wind-to-hydrogen demonstration project (loan from the U.S. Army):  
  – Relocated both small (2.2 kg/day) PEM electrolyzers to adjacent Hydrogen Test Facility to upgrade with additional 10-cell stack for further testing.
• Completed the extensive process to obtain approval to run in unattended mode of operation:
  – Operated both the PEM and alkaline systems for longer duration run-times in unattended mode.
  – In March alone achieved about 120 hours of operation of the integrated energy system test bed producing over 40 kg of hydrogen.
  – Product fuel from testing used in hydrogen-powered vehicles.
• Installed and began testing upgraded PEM electrolyzer with additional 10-cell stack electrically in series with original 20-cell stack:
  – Conducted comparison testing of 10 kW photovoltaic (PV) array directly coupled with electrolyzer stack with power converter between array and stack.
• Authors from NREL and Natural Resources Canada published book chapter as part of the 18th World Hydrogen Energy Conference.
• Installed, commissioned and began operating 5 kW PEM fuel cell in the integrated renewable energy system.

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 peak demand. Xcel Energy and NREL have collaborated to design, install, and operate the Wind-to-Hydrogen (Wind2H2) project, which demonstrates how to make and use hydrogen with renewable energy without producing greenhouse gases or other harmful byproducts.

The Wind2H2 project is helping industry 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 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 electrolysers commercially available today are designed for grid-connected operation; therefore, they incorporate power electronics to convert alternating current (AC) from the grid to direct current (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. By designing and incorporating dedicated power converters that allow wind turbines and photovoltaic arrays to be more closely coupled to electrolyzer stacks, energy transfer within the system can be improved and costs lowered.

Approach

This RD&D project examines the design and optimization of electrolysers, power electronics, fuel cells, and energy storage system components to integrate renewables and electrolysers to improve the efficiency, cost, and robustness of these systems. The cost of the resulting hydrogen 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 and storage 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 on large MW-scale systems for utilities.
• Developing and optimizing advanced controls, subsystems, and power electronics to reduce electrolyzer capital cost and improve system efficiency.

Results

Experimental Findings

Direct Coupling versus Power Converter: NREL designed, installed and tested an additional 10-cell stack in a system with an existing 20-cell PEM stack. The original 7 kW rated electrolyzer could produce 2.2 kilograms of hydrogen per day. After the 10-cell upgrade, the modified PEM system requires 10 kW of electricity and produces 50% more product. More
importantly, the added ½-stack shifted the electrical operating point of the combined stacks to better align with the maximum power point of NREL's 10 kW PV array. The improved alignment allowed for a more optimal direct coupling of the array to the stack pitted against the NREL-designed power converter utilizing an algorithm for maximum power point tracking (MPPT).

NREL produced hydrogen with power provided from the 10 kW PV array, comparing power transfer from a directly-coupled array to power transfer to the stack using NREL's MPPT power converter. This testing showed that direct-coupling outperformed power electronics utilizing MPPT when irradiances were below 500 W/m² (see Figure 1).

These findings provide useful insight into future integrated system designs. Electrolyzer stack voltage is a function of temperature, stack current and age. While the PV array maximum power point varies with temperature, irradiance and age. Passively keeping these two operating points aligned and optimal would be challenging as both systems vary over their normal operating ranges. Finally, time-of-day influences irradiance from the sun and configurations can be selected based on their performance for the irradiance level. As all of these parameters drive the operating points of the source and stack it seems reasonable to employ a situational approach to energy transfer. In this case, during the morning and evenings when the irradiance is below 500 W/m² switch to the direct coupling configuration. Also, during cloudy or stormy periods when the irradiance drops below the transition point power the stack in a direct-coupled mode. All other times when the irradiance is greater than 500 W/m² the power converter utilizing MPPT will transfer more energy from the array to the electrolyzer stack.

**Long Duration Testing:** NREL completed the installation, commissioning and started operation of an H-series (13 kg/day) PEM electrolyzer on loan from the U.S. Army. This will enable the side-by-side comparison testing of similarly sized alkaline and PEM electrolyzer technologies. Both smaller S-series system were relocated from the wind-to-hydrogen demonstration project to NREL’s Hydrogen Test Facility. One of the two smaller PEM systems is the source of the previously described direct coupling versus MPPT power converter testing.

The NREL and Xcel Energy wind-to-hydrogen demonstration project has been conducting daily operations since 2006. Originally developed as a platform for research, demonstration, evaluation, and testing, the Wind2H2 system has recently undergone significant modifications to enable operations in an unattended mode, thereby allowing longer duration system testing. To run the Wind2H2 system in an unattended mode, new monitoring and control systems were developed and an extensive safety review and verification of these new systems was completed.

Since March 2010 (Figure 2) the wind-to-hydrogen system has been approved for long-duration unattended operation. However, also in March 2010 the alkaline electrolyzer, from Teledyne Energy Systems, displayed symptoms of severe gas cross-over within the stack. A replacement stack has been ordered and the existing stack will be returned for failure analysis. The PEM system has now been operated overnight and all the way through weekends to keep up with the demand of NREL’s leased 12-passenger hydrogen-fueled internal combustion engine shuttle.

Long-duration testing showed the system could operate safely without operator attendance. Long-duration operation will continue for demonstration purposes while the wind-to-hydrogen system will also continue to be used for research and evaluation.

**Analysis**

NREL conducted a study of the life-cycle costs associated with hydrogen-based energy storage systems, and benchmarked these costs against competing energy storage systems including pumped hydro energy storage, compressed air energy storage, and battery storage. The study included full sets of analyses of hydrogen-based energy storage systems, including PEM fuel cell-based systems and hydrogen expansion-combustion turbine based systems. The study found that hydrogen-based systems were competitive with battery-based systems, with hydrogen expansion-combustion turbine systems providing stored electricity for as little as 17 cents/kWh (Figure 3).

The goal of this analysis was to develop a cost survey of the most-promising and/or mature energy storage technologies and compare them with several configurations employing hydrogen as the energy carrier. A simple energy arbitrage scenario was developed for a mid-sized energy storage system consisting of a 300-
MWh nominal storage capacity that is charged during off-peak hours (18 hours per day on weekdays and all day on weekends) and discharged at a rate of 50 MW for 6 peak hours on weekdays. The full report can be found at http://www.nrel.gov/docs/fy10osti/46719.pdf.

**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 of hydrogen production. 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 control algorithms developed at NREL showed significant improvements in energy transfer within the system.

The experimental results from the direct-coupling versus power converter testing between the PV array and
combined PEM electrolyzer stacks provide a valuable starting point for higher voltage testing. These results establish gains in the energy transfer between renewable resources and the hydrogen-producing electrolyzer stacks as a function of the sun's irradiance.

Long-duration testing of the Wind2H2 system will continue. The new H-series PEM electrolyzer was instrumented with stack voltage and current sensors. This enables long duration testing of two (of three) PEM stacks under a wind-based stack current profile while the third stack operates at constant current. Stack voltage monitoring over long duration provides decay rates to confirm industry reports of constant current operation and enables comparison of multiple stacks receiving current based on varying wind profile. The alkaline stack will be replaced and operated under the same wind profile. Stack decay rates will be compared between the varying and constant current stacks.

NREL will test and evaluate the 5 kW fuel cell system that has been integrated into the Wind2H2 system. Hydrogen produced during long-duration system testing will be used to provide fuel for the 5 kW fuel cell. Such testing will demonstrate the use of a fuel cell in an integrated, hydrogen-based energy storage system. As part of this evaluation, NREL will characterize the performance of the fuel cell in terms of turn-down rate, turn-on time, and system efficiency at power levels below the maximum power output to better understand the real-world aspects of using fuel cells in hydrogen-based energy storage systems.

NREL will also continue to model and analyze the potential of hydrogen-based energy storage systems, including analysis of dual-use energy storage systems. These systems use hydrogen for energy storage and fuel for vehicles. The analysis will include the impact of carbon taxes and carbon policies on hydrogen-based energy storage and compressed air energy storage.

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.

**FY 2010 Publications/Presentations**


**References**

II.E.4 High-Performance, Low-Cost Hydrogen Generation from Renewable Energy

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<th>2012 Target</th>
<th>2017 Target</th>
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<td>Hydrogen Cost</td>
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<td>74</td>
<td>65</td>
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Note: Estimates are based on H2A v2.1, for electrolysis only (compression-storage-delivery not included). Model assumes $0.05/kWh.

Accomplishments

- A new flow field design resulted in a 20% cost savings, reductions in part count and assembly time, improved cell robustness and is ready for production validation and commercial release.
- Additional alternative flow field materials are being evaluated to provide an additional 15 to 20% cost reduction in the near future.
- Demonstrated a new catalyst formulation and application technique through the successful operation of prototype electrolyzer cells containing 55% less precious metal in the catalyst layers.
- A comprehensive electrolyzer cell model has been created at Penn State and is currently being validated against physical test data.

Introduction

This project addresses the DOE Hydrogen Program objective for distributed production of hydrogen from proton exchange membrane (PEM) water electrolysis. The DOE technical targets for hydrogen cost as well as electrolyzer efficiency and capital cost will be directly addressed through the advancement of key components and design parameters. Currently, a significant portion of the electrolyzer system capital cost comes from the cell stack(s). When added together, the flow fields and membrane electrode assemblies (MEAs) constitute over half of the total cell stack cost (Figure 1). Significant cost reductions of these components as demonstrated with this research are required in order to reach the targets. Further optimization of cell stack components

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Contract Number: DE-EE000276

Subcontractors:
• Entegris, Inc., Chaska, MN
• The Electrochemical Engine Center at Penn State, University Park, PA

Project Start Date: September 1, 2009
Project End Date: February 28, 2011

Project Objectives

- Improve electrolyzer cell stack manufacturability through:
  - Consolidation of components
  - Incorporation of alternative materials
  - Improved electrical efficiency
- Reduce cost in electrode fabrication through:
  - Reduction in precious metal content
  - Alternative catalyst application methods
- Quantify the impact of these design changes through utilization of the H2A model.

Technical Barriers

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

(G) Capital Cost
(H) System Efficiency
(J) Renewable Electricity Generation Integration
results in efficiency gains at the system level and ultimately a reduction in the cost to produce hydrogen.

**Approach**

The scope of work for this project allowed for research and development in several key areas relating to cell stack cost reduction. Topics included: 1) flow field design, 2) catalyst formulation, and 3) computational performance modeling. Advancements in flow field design are intended to be advantageous for low-cost, high-volume manufacturing. Alternatives to the current flow field design include composite bipolar plates or unitized flow fields which consolidate parts and reduce the amount of required precious metal plating. Material testing samples and prototype flow fields will be fabricated and tested for compatibility with the corrosive environment known to exist within operating electrolyzer cells. Higher efficiency oxygen evolution catalysts are of interest because the oxygen evolution reaction is inefficient and therefore requires high catalyst loadings to achieve reasonable operational voltages at the desired current densities. Improving catalyst utilization can substantially reduce the cost of the MEA by reducing the noble metal content in the catalyst layers. Novel electrode structures will be constructed using alternate synthesis techniques and characterized for performance and durability. Computational modeling of an electrolyzer cell will allow for optimization studies to be performed around flow field material and architecture. Cell performance can be quantified in ways not typically possible with standard physical test experiments. Validation of all of the previously mentioned design changes will be achieved through cost analysis based on the H2A model.

**Results**

During this project, significant near-term electrolyzer cell cost reductions were identified through the testing of non-metal flow field components (Figure 2). The use of alternative conductive materials has been shown to provide comparable electrochemical performance when compared to legacy designs while allowing for the consolidation of components and the use of manufacturing methods more suitable for high volume production. Additional materials are still being evaluated that could present a further cost reduction thanks to their ability to be injection-molded in a full-scale production scenario. It should be noted that the operating potential of electrolyzer cells is typically above 2.0 V while water, oxygen and hydrogen gasses are also present at various pressures and temperatures. The challenge with alternative materials is to ensure that they can withstand these highly corrosive conditions contained within an operational electrolyzer cell while also maintaining low electrical resistance.

Specially developed emersion tests have allowed for the evaluation of several materials and coating options within the described environment. These tests indicate that while coatings can effectively protect materials from corrosion, small cracks or discontinuities in the coating may be allowing a gradual corrosion of the substrate material. Completed test runs have been limited to 500 hours, therefore, it will be necessary to perform additional longer term tests in order to better quantify the rate of corrosion. If the rate of corrosion is significant, process improvements will be required in order to ensure continuous coverage of the substrate material. Remaining testing of alternative materials will be focused on evaluating the impact of the electrical resistivity of prototype flow fields on cell potential during operation.

Significant advancements have been made in the development of an optimized catalyst formulation and application technique. This work has demonstrated a 55% reduction in the amount of precious metal used in the catalyst layers of the MEA. As a result, the cost of the MEA can be reduced and will in turn create cost savings at the cell stack and total system level. These improvements save cost and improve quality.
while maintaining cell potential performance when compared to existing commercial cell stacks operating at standard conditions (Figure 3). In order to achieve this, a mathematical model was developed and refined to accurately predict the final catalyst loading from the beginning of the formulation and application process. Using the model, it was possible to perform a concise matrix of experiments and quickly determine the lower limits of catalyst loading with respect to desired cell performance. The selected application technique represents an improvement over existing production techniques in that it allows for improved accuracy and uniformity while also enabling higher speed throughput.

A comprehensive computational model of an electrolyzer cell has been developed at Penn State and is capable of predicting performance parameters based on the geometry of the flow fields and specified operating conditions. Calculated parameters include overall cell potential, distribution of potential and current density distribution, as well as, volume fractions of water, oxygen and hydrogen in various regions of the cell. Results can be plotted in as colored gradients superimposed over three-dimensional models or as more traditional plots such as polarization curves (Figure 4). This custom-developed code merges traditional two phase flow modeling with a specialized electrochemical model. Variables common to both sets of governing equations create linkages between the sections of the model and improve the accuracy of the results.

Design parameters and operational data from a baseline design have been provided to Penn State for the purpose of validating the model. Once the predicted results are confirmed to be consistent with actual data over a larger range of conditions, the model can reliably be used for parametric analysis of electrolyzer cell designs. Cell component architecture can be refined in light of model performance predictions and the relative impact of design parameters on overall efficiency can be understood. It is anticipated that improved water distribution within the cell will allow for better thermal management. The minimization of coolant flow could reduce demands on the system such as the pump flow and pressure head requirements which can lead to reductions in capital cost and gains in system efficiency.

**Conclusions and Future Directions**

- Tests have shown that alternative conductive materials can remain stable in the corrosive environment of operational electrolyzer cells for tests up to 500 hours, however, much longer term testing is required to ensure stability beyond the 30,000 hour minimum operational life of Proton Energy Systems cell stacks.
- Cost reductions can be made by controlling the catalyst formulation process and through advanced application techniques. The next step is to implement the formulation and application processes developed during this project into Proton’s commercial production design.
- Electrolyzer cell performance can be predicted with the use of a comprehensive computational model. No future work is planned at this time but the next step would be for Penn State to develop an executable program which could interface directly with computer aided drafting and design models and provide upfront electrolyzer simulation capability.
II.F.1 R&D Status for the Cu-Cl Thermochemical Cycle-2010

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Start Date:  June 2006
Projected End Date:  September 2015

Objectives

The strategic objective is to develop a robust process for producing hydrogen using the Cu-Cl thermochemical cycle. This year’s objective is to facilitate the development of the electrolyzer capable of long-term operation. The long-term goal remains an integrated laboratory-scale demonstration for the Cu-Cl cycle.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell 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 proposed target for the cost of hydrogen production is $6.00 per gasoline gallon equivalent (gge) H₂.

Accomplishments

- Initiated a development and testing program for new membrane materials for the CuCl electrolyzer.
- Collaborated with the Atomic Energy of Canada Ltd. (AECL) and five Canadian universities funded by the Ontario Research Foundation.
- Demonstrated high yields from the hydrolysis reactor with lower steam usage. Lowering the steam requirement improves the process efficiency.
- Developed a method for quantifying the amount of Cu₂OCl₂ produced from the hydrolysis reactor.

Introduction

The U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (DOE-EERE) is 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. The lower temperature option for this cycle is attractive to DOE-EERE because the solar power tower provides heat near 550°C and is near commercialization. The three reactions in the Cu-Cl cycle are shown in the following. The experimentally verified temperatures for the two thermal reactions (hydrolysis and decomposition) are within the range of the solar power tower’s process heat.

\[
\begin{align*}
\text{CuCl}_2 + H_2O & \rightleftharpoons \text{Cu}_2OCl_2 + 2HCl(g) \quad \text{Hydrolysis,} \; \sim375°C \\
\text{Cu}_2OCl_2 \rightleftharpoons 2\text{CuCl} \; \text{Decomposition,} \; 450-550°C \\
2\text{CuCl} + 2HCl & \rightleftharpoons \text{CuCl}_2 + H_2 \; \text{Electrolysis,} \; \sim100°C
\end{align*}
\]

Based on preliminary experimental and modeling work, the Cu-Cl thermochemical cycle was chosen for further development for the following reasons:

- A maximum cycle temperature of \(\sim550°C\) has been verified.
- All reactions have been demonstrated at laboratory scale.
- No catalysts are needed for thermal reactions and no catalyst is needed for the anode in the electrolyzer.
- Conceptual process design is based on commercially practiced technologies.
- Preliminary mass and energy balanced flowsheet showed promising efficiency and the corresponding H2A showed estimated hydrogen production costs were within the proposed DOE target.

While the cycle has the attributes listed above, there are significant challenges in the electrolysis reaction and in the hydrolysis reaction. Copper crossover/cell degradation is observed in the former and a large excess of steam is required for complete conversion in the latter.
**Approach**

In the early electrolysis experiments, copper crossover was observed with both anion and cation exchange membranes. Copper crossover represents a potential showstopper as it degrades the electrolyzer’s performance and prevents long-term operation of the electrolyzer at a stable cell voltage. A membrane development project has been initiated to identify and test promising membrane materials for the CuCl electrolyzer. Three types of cation exchange membranes are being tested in the first phase of this work: (1) commercial membranes such as Nafion® and CMX, (2) Nafion® coated with a low permeability layer for larger ions, and (3) new materials such as the polysulfone membranes, which can also be modified to obtain the desired cation selectivity and which were able to reduce sulfur crossover in the hybrid sulfur electrolyzer [1]. Screening tests include diffusivity, water uptake, conductivity, and ion exchange capacity measurements in high acid environments and water over a range of temperatures. The most promising samples will be tested for chemical stability and durability in electrolyzers at AECL and Pennsylvania State University (PSU). In the second phase of the work, tests will be conducted at elevated temperature and solutions with varying concentrations of CuCl, CuCl₂, and HCl. Since the electrolyzer tests are by definition long-term tests, the use of screening tests, which take a shorter time, should expedite the search for the ‘best’ membrane.

The challenge for the hydrolysis reaction was that the reactor used a large excess of steam to convert all of the CuCl₂ to Cu₂OCl₂. This high steam demand adversely impacts the efficiency of the cycle and the cost of hydrogen production. The goal of the current research was to verify the model’s prediction that subatmospheric pressure operation would reduce steam demand. At one bar, a steam to CuCl₂ molar ratio of 20-23 was required for >97% conversion experimentally, somewhat higher than the model’s value of 17. However, at 0.25 bar, the model predicts a steam to CuCl₂ molar ratio of only 7 is needed for complete conversion. A low-cost, commercially used method to obtain a partial vacuum, i.e., an aspirator or ejector, was tested. Since CuCl has been found in all of the hydrolysis products, experiments to determine the mechanism of CuCl formation were also planned. Possible mechanisms for the formation of CuCl are the decomposition of CuCl₂ or Cu₂OCl₂, or a combination of both. CuCl₂ decomposition results in the formation of Cl₂ and CuCl, while the decomposition of Cu₂OCl₂ results in CuCl and oxygen. The corrosive nature of the gaseous products prevents measurement of the mechanism and kinetics by standard techniques. However, experiments following changes in the environment around the Cu ion will provide this information. Synchrotron radiation allows this type of measurement and is available at the Advanced Photon Source at Argonne National Laboratory. Extended X-ray absorption fine structure analysis has been a key technique for determining the substitution of O with Cl or vice versa in the first coordination sphere of the copper species [1]. X-ray absorption near-edge spectroscopy (XANES) at Cu K-edge would allow us to determine the coordination geometry of Cu in the samples. The XANES spectra of the Cu species of interest have been reported in literature to be very distinctive [2] and therefore a method to obtain quantitative information on the composition of the samples during reaction. A matrix of experiments has been designed to measure CuCl₂ and Cu₂OCl₂ decomposition as a function of temperature and time and to measure the formation of Cu₂OCl₂ as a function of time, temperature, and steam to CuCl₂ molar ratio.

**Results**

**Membrane Development**

The membrane development project is new and is a collaborative effort involving several institutions. Argonne National Laboratory is preparing low permeability membranes for the anode by applying low-permeability coatings on commercial Nafion® 115 membrane. The coatings consist of either (a) substituted aromatic hydrocarbons or (b) a non-aromatic that forms a flexible network through the pores to inhibit the transport of copper ions without sacrificing the ion exchange capacity of the precursor Nafion® membrane. These membranes are then processed according to published literature. Polymer chemists at PSU and Sandia National Laboratories are developing polysulfone membranes, whose selectivity can be tuned by the choice and number of side groups [3,4]. Electrolysis experiments are conducted at PSU and AECL.

Membrane samples are now being examined. Diffusivity measurements of Cu species through the membranes are being used as the primary screening technique. The diffusion cell consists of two compartments separated by a membrane and is shown in Figure 1. The solute-rich side contains the solution of CuCl₂ dissolved in a hydrochloric acid solution and the solvent-rich side, either a solution of HCl or water. The diffusion of copper species into the solvent-rich side versus time is measured by following the change in concentration of the Cu species on the solvent-rich side.

The concentrations of Cu species are being determined by measuring the absorbance using ultraviolet-visual spectroscopy and correlating it with the absorbance of standards prepared by dissolving a known amount of CuCl₂ into the desired solution, in this case 10.2 MHCl. Standards spanned CuCl₂ concentrations from 25 to 1,000 ppm. The maximum absorbance was
measured at 380 nm. The HCl concentration for both the solute-rich and solvent-rich sides is 10.2 M because these conditions were used by AECL in their longest duration test.

Figure 2 shows the results of the diffusivity measurements of Nafion®, Nafion® with three polymeric coatings, and two samples of s-Radel, a polysulfone-type membrane. As can be seen, the new membranes have lower diffusivity with respect to copper than does Nafion®. Based on these results, new membranes are being modified to further reduce transport of Cu species.

Conductivity measurements are in progress as are measurements of the ion exchange capacity and water uptake. Samples have been sent to PSU and AECL for testing copper crossover in their electrolysers. Higher temperature tests are either in progress or will be started shortly.

Hydrolysis Reaction

The model as well as Le Chatelier’s Principle shows that reduced pressure operation should result in lower steam demand for complete conversion to the desired products in the hydrolysis reaction. An aspirator, a relatively low-cost method to obtain a partial vacuum, was added to the exit of the hydrolysis reactor. A schematic of the set-up and details of the experimental method are described elsewhere [5,6]. Experiments were conducted at 0.4, 0.7 and 1 bar. The amount of CuOCl₂ in the products was quantified using oxygen evolution from the decomposition of the solid products. The amount of O₂ produced was calibrated using a known amount of Cu to form CuO in presence of 3% O₂/He. The yield of CuOCl₂ was calculated based on the ratio of the measured O₂ to the theoretical value. The amount of CuCl was measured using a wet chemistry method.

Figure 3 shows the amount of CuCl and Cu₂OCl₂ formed at the three pressures. At 0.4 and 0.7 bar, the amount of CuCl formed is significantly lower than that formed at 1 bar at all steam to CuCl₂ molar ratios. The maximum amount of CuOCl₂, about 98%, is formed at a steam to CuCl₂ ratio of 15, a noteworthy reduction from the 20-25 used in the tests at 1 bar. From a practical standpoint, the observed increase in Cu₂OCl₂ formation at reduced pressure is consistent with the modeling results, where a favorable effect of low pressure was predicted. However, the decrease in CuCl formation was not predicted. Assuming that CuCl forms due to thermal decomposition of CuCl₂ or Cu₂OCl₂ or both, it is unclear why decreasing the pressure inhibits this decomposition. This effect maybe associated with the relative rates of the hydrolysis and decomposition reactions and the hydrodynamics of the experimental reactor. If the decomposition reaction rates are much slower at 375°C than the hydrolysis rate, the formation of CuCl should critically depend on the residence time, which is determined by particle size and flow conditions in the reactor. Additional details of this analysis are published elsewhere [5]. This analysis demonstrates the critical need for the kinetic and mechanistic studies of these reactions.

Figure 3 also shows the results of reduced pressure operation for other steam to CuCl₂ molar ratios. The amount of CuOCl₂ formed with a steam-to-Cu ratio of 11 is relatively low at <80% while the amount of CuCl was 4%. Thus a significant amount of CuCl remained, indicating insufficient mixing and/or residence time. Further optimization of the operating parameters is required.
Electrolysis Reaction

The ultimate test of the membrane development work is a demonstration of its performance in the electrolyzer. Early tests showed large increases in cell voltage within one hour of operation. Scanning electron microscopy showed copper deposits in the membrane or on the cathode. A recently completed electrolyzer test at AECL is shown in Figure 4. The two tests were run under identical conditions, 10.2 M HCl, 0.5 M CuCl and a Nafion® membrane. The reason for the differences in the results is under study. Nevertheless, these results are a significant improvement over the earlier tests as the cell voltage was stable for 72-96 hours and was near our target voltage of 0.7 V. The new membranes should provide longer duration cell performance since they have lower copper diffusivity.

Large-Laboratory Demonstration of Cycle

Collaborators at the University of Ontario Institute of Technology are planning an integrated demonstration of the Cu-Cl cycle. Large laboratory-scale reactors and ancillary equipment have been purchased and set up in a newly refurbished building. Cold testing is ongoing. As part of the collaboration, Argonne National Laboratory will study the decomposition of CuCl₂ and Cu₂OCl₂ and the hydrolysis of CuCl₂ as a function of time and temperature using synchrotron radiation. Kinetic data are needed to set operating conditions in these larger scale reactors and for further scale-up.

Conclusions

Several types of membranes have been prepared. These include Nafion® with low selectivity coatings, modified polysulfones, known as s-Radel, and a higher temperature version, known as EXSDAPP. Thus far, the diffusivities of the first two types have been measured. The results show that the new membranes are less permeable to Cu species than Nafion® and that the modifications have been successful. Based on these results further modifications are being made to further decrease the diffusivity of Cu species and to improve stability at elevated temperatures. Other characterization tests are ongoing. Electrolyzer tests will start as soon as the larger membranes required for the electrolyzers are prepared.

Operation of the hydrolysis reactor at reduced pressure provides an engineering method for reducing the steam demand. Further work is required to optimize conditions. The results of the present experiments indicated the need for measurement of the kinetics and mechanisms of the hydrolysis and the decomposition reactions of CuCl₂ and Cu₂OCl₂. Experiments to obtain these data are planned.

Future Directions

- Continue membrane development and testing that includes diffusivity measurements and characterization tests, i.e., ion exchange capacity, conductivity and water uptake.
- Change composition on the solute-rich side by adding CuCl to the CuCl₂ and HCl solutions.
- Modify the equipment for elevated temperature use and test the most promising membranes at 60-80°C.
- Investigate the use of other types of proton exchange membranes as needed.
• Continue testing of the most promising membranes in the electrolyzers at AECL and PSU and assess long-term chemical stability and durability.
• Continue the investigation of engineering methods to reduce copper crossover, including flow rates, anolyte and catholyte concentrations, temperature, etc.
• Continue synchrotron radiation experiments that monitor the nearest neighbors of Cu(II) species as a function of temperature and time to obtain mechanistic and kinetic information for CuCl₂ and Cu₂OCl₂ decomposition and CuCl₂ hydrolysis.
• Identify and test potential materials of construction.

FY 2010 Publications/Presentations

Publications


Presentations


References

II.F.2 Solar High-Temperature Water-Splitting Cycle with Quantum Boost

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Contract Number: DE-FG36-07GO17002

Subcontractors:
• University of Central Florida, Florida Solar Energy Center (FSEC), Cocoa, FL
• Electrosynthesis Co. (ESC), Inc., Lancaster, NY

Project Start Date: September 1, 2007
Project End Date: August 31, 2014

Objectives

• Demonstrate a cost-effective high-temperature water splitting cycle for hydrogen production using concentrated solar energy.

• Evaluate photocatalytic and electrolytic options for generating hydrogen that meet DOE’s solar high temperature H₂ production efficiency and cost goals.

• Confirm the feasibility of the selected cycle via bench-scale experiments.

• Determine the economic prospects of the selected cycle using the Aspen Plus™ chemical process model and H2A economic analysis program.

• Demonstrate a fully-integrated pilot-scale solar H₂ production unit.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the

Fuel Cell 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>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>U.S. DOE Targets</th>
<th>Project Status</th>
</tr>
</thead>
<tbody>
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<td>Solar-Driven High-Temperature TCWSC Hydrogen Production Cost</td>
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<td>10.00 6.00 3.00</td>
<td>$5.98/5.05 *</td>
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<tr>
<td>Heliostat Capital Cost (installed cost)</td>
<td>$/m²</td>
<td>180 140 80</td>
<td>97²</td>
</tr>
<tr>
<td>Process Energy Efficiency</td>
<td>%</td>
<td>25 30 &gt;35</td>
<td>19.3</td>
</tr>
</tbody>
</table>

* Electrolytic/photocatalytic system projected costs based on revised H2A analysis.

² Based on SAIC glass-reinforced concrete structure with 10 sq.m. area and low production quantity.

³ 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 imports (electricity or heat) required for the process.

4 Electrolytic sulfur-ammonia (SA) thermochemical water-splitting cycle efficiency based on the most recent Aspen + flow sheet analysis.

Accomplishments

• Quantitative hydrogen production using an electrolytic cell with efficient sulfite oxidation was verified.

• The voltage of the electrolytic cell was reduced from 1.2 V to less than 1.0 V by increasing temperature/pressure, controlling pH and improving cell design.

• A short-term electrolytic cell test achieved 0.63 V at 186 mA/sq.cm using a proprietary new design/catalyst.
The basic feasibility of the all-(liquid/gas) K$_2$SO$_4$/K$_2$S$_2$O$_7$ chemistry for the high-temperature oxygen evolution sub-cycle using potassium sulfate has been demonstrated, but more lab testing is needed.

A mass balance on the oxygen evolution half cycle was performed using three sources of data; theoretical, thermogravimetric analysis (TGA) measurements and reactor experiments.

A preliminary economic analysis based on the previously fabricated half-scale prototype glass-reinforced concrete (GRC) heliostat indicates that the cost can be reduced from $126/m^2$ to $90/m^2$.

Using the Aspen Plus™ Process Design and Analysis model, trade-off studies were performed to optimize the overall plant configuration, e.g.:

- Electrical heating of the sulfur trioxide reactor was shown to be not cost-effective compared to direct solar heating.
- Electrical production from steam and ammonia in the process was shown to be sufficient to power the electrolytic process.
- Drying the aqueous ammonium sulfate material to solid form was shown to have little or no advantage over using it in aquaeous form.

Using the H2A economic model, the hydrogen production costs were determined to be $5.98/kg for the electrolytic SA cycle with K$_2$SO$_4$/K$_2$S$_2$O$_7$ sub-cycle.

Introduction

The source of hydrogen must be sustainable and the process to produce hydrogen must be efficient and thus cost-effective compared to conventional energy. The thermo-chemical production of hydrogen by splitting water with solar energy is a sustainable and renewable method of producing hydrogen. The process must be proven to be efficient and cost-effective. 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. The spectrum of sun light contains ultraviolet and visible photons that are very energetic and able to trigger photocatalytic reactions. In the photocatalytic SA cycle, the photonic portion of the solar spectrum is used directly to accomplish the hydrogen evolution step of the cycle. This means that less energy is needed in the high-temperature oxygen production part of the cycle.

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 mixture to prevent unwanted back-reaction to ZnO. An example of the latter 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 the working reagent (thus sulfur-ammonia, or “SA,” cycle) to attain a 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 the Aspen Plus™ 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 have been considered 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 the cycle has been validated in closed-loop operation in the lab, it will be scaled up and tested on-sun.

Results

Cycle Evaluation and Analysis

In previous years, significant work was performed on the photo-catalytic SA cycle. During the past year, efforts have been redirected to the electrolytic SA cycle. The electrolytic SA cycle is summarized in the following equations:

1. $\text{SO}_2(g) + 2\text{NH}_4(g) + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_3$ (1 – chem. absorption) 25°C
2. $(\text{NH}_4)_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{H}_2$ (2 – electrolytic) 80°C
3. $(\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4 \rightarrow \text{K}_2\text{S}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$ (5 – solar thermal) 400°C
4. $\text{K}_2\text{S}_2\text{O}_7 \rightarrow \text{K}_2\text{SO}_4 + \text{SO}_2$ (6 – solar thermal) 550°C
5. $\text{SO}_2 + \frac{1}{2} \text{O}_2$ (7 – solar thermal) 850°C

An example of the latter 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.
The electrolytic oxidation of the ammonium sulfite solution occurs above ambient temperature at reasonably low pressures. Reactions (3) and (4) form a sub-cycle by which potassium sulfate is reacted with ammonium sulfate in the low-temperature reactor, to form potassium thiocyanate. That is then fed to the medium-temperature reactor where it is decomposed to SO₂ and K₂SO₄ again, closing the sub-cycle. The potassium sulfate and thiocyanate form a miscible liquid melt that facilitates the separations and the movement of the chemicals in reactions (3) and (4). The oxygen production step (5) occurs at high temperature over a catalyst. Separation of the oxygen from SO₂ occurs when they are mixed with water in reaction (1). The net cycle reaction represented by reactions 1-5 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. Figure 1 depicts the high-temperature reactions in a pictorial fashion.

Electro-Oxidation of Aqueous Ammonium Sulfite Solutions

Optimization of the electrolytic process continued at both ESC and FSEC. FSEC developed a proprietary catalyst and briefly demonstrated a divided cell at 0.63 V and 186 mA/cm². In a further development, an electrolytic cell with no Naftion® separator was also run. ESC tested operation of cells at elevated temperature and showed that the voltage could be reduced below 1.0 V in a conventional electrolytic cell by operating at elevated pressure and temperature. Figure 2 shows results of electrolysis runs at elevated temperatures.

High-Temperature Cycle Step Evaluation

Evaluation of the all-liquid/gas high-temperature cycle steps continued. As shown in Figure 3, TGA experiments were conducted to show the evolution of ammonia and water vapor, followed by evolution of sulfur trioxide at a higher temperature. A potential difficulty is the small temperature differences between these evolutions, which may make separation of the products more difficult. A mass balance was also successfully conducted to check that the experimental results matched the analytical predictions, as shown in Figure 4.

Solar Field Optimization

The solar field configuration continued to be updated as the thermochemical system evolved. The primary present activity is to incorporate the all-liquid K₂SO₄/K₂S₂O₇ system. A two-receiver heliostat field design has been created to separate the low-temperature and high-temperature receivers. For the highest temperature oxygen evolution process, consideration is being given to using dish concentrators in addition to the heliostat field for the other thermal processes. Control optimization to best use the variable solar resource was also performed.

Heliostat Cost Reduction

The half-scale prototype glass-reinforced concrete heliostat was successfully tested and evaluated, and design features to be carried over to a full-scale unit were identified. The cost of heliostats in low production was updated, with the results shown in Table 2. The estimated production cost is less than $100/m², a reduction of over 25% from present-day heliostat costs.
TABLE 2. Cost of Low Production Heliostat

<table>
<thead>
<tr>
<th>System Component</th>
<th>Cost per Square Meter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete Structures</td>
<td>$13.31</td>
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<tr>
<td>Mirrors</td>
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<tr>
<td>Control Electronics</td>
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<tr>
<td>Drive components</td>
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<tr>
<td>Other components</td>
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<tr>
<td>Total</td>
<td>$96.75</td>
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</table>

Economic Analysis

The H2A economic model for the photocatalytic SA process with separate heliostat and photoreactor fields was updated. The resulting cost for hydrogen was found to be $5.05/kg, but the system solar efficiency was only 5.2% due to the large land area needed. The cost analysis of the electrolytic SA cycle was completed, with a resulting cost of $5.98/kg and an overall system efficiency of 19.3%. The H2A results are summarized in Table 3.
The H2A cost analysis program was also used along with Aspen Plus™ calculations to perform trade-off analyses on different configurations and process designs. In particular, the following trade-off analyses were performed:

- Using solar thermal vs. electricity to heat the reactor for the 900°C reaction to reduce SO₃ to SO₂ and O₂. It was determined that the solar thermal heat would provide higher efficiency.
- Reducing the aqueous ammonium sulfate to solid form before feeding to the low-temperature reactors. Drying the ammonium sulfate led to a lower system capital cost, but required more purchase of electricity from the grid. The cost of hydrogen was practically the same for both approaches ($6.21 vs. $5.98).

### Conclusions and Future Directions

In summary:

- Significant progress was made in reducing the cell voltage and increasing the current density of the electrolytic cell.
- Initial evaluation of the all-liquid/gas high-temperature oxygen generation cycle steps appears to prove the subcycle feasibility.

- GRC continues to show promise to reduce heliostat cost substantially.
- Based on the work performed to date, it appears that the electrolytic SA cycle has the potential to meet DOE’s near- and long-term H₂ production cost and efficiency goals.

Activities planned for the upcoming year include:

- Perform a thermodynamic analysis of the overall SA cycle to recheck earlier results, provide data to verify the cycle performance and ascertain if previous work by others may preclude the need to perform certain tasks. The complete SA cycle will be modeled using Aspen Plus™ to verify that the cycle can be closed and provide data to document the chemical plant analysis.
- Completion of optimization of the electrolytic process and cell. This will include identification of catalysts that will reduce the over-potential at the anode and allow operation at high current densities, and determining approaches to recombine anolyte and catholyte streams to control and maintain fixed pH.
- Complete evaluation of the K₂SO₄ oxygen subcycle reactions, including reaction kinetics.
- Finalization of the thermal reactor/receiver designs including materials specification and testing.
- Finalization of the solar field configuration and design to match the final chemical plant requirements.
- Continue to update H2A economic analyses to document the potential cost of hydrogen from the SA cycle.

After completion of phase 1, the next phase of the project will involve laboratory validation of the closed-loop SA cycle leading to on-sun hydrogen production demonstration.

### Special Recognitions & Awards/Patents Issued


### FY 2010 Publications/Presentations


II.F.3 Solar-Thermal Atomic Layer Deposition Ferrite-Based Water Splitting Cycles

Objectives

- Use H2A analysis to provide guidance for conceptual process design that is cost-effective.
- Conceptualize a scalable central solar reactor/receiver per H2A guidance on economics.
- Develop/demonstrate suitable materials for robust redox/thermochemical cycling.
- Develop an overall plan to take the technology to the point of demonstration in five years.

Technical Targets

The technical targets for solar-driven thermochemical conversion are summarized in Table 1. The projected thermal efficiency for the developed process is 54.6% based on lower heating value (LHV), thus exceeding the >35% requirement for the 2025 case. For a solar-to-receiver annual average efficiency of 40.2%, the overall solar-to-H₂ efficiency is estimated at 21.9% (LHV). Furthermore, the $6/kg H₂ plant gate cost for the Central 100,000 kg H₂/day facility 2015 case should be easily achieved for the $126.50/m² installed heliostat cost. The $3/kg H₂ plant gate cost for 2025 for a $90/m² installed heliostat field may be achievable (details below).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2015 Target</th>
<th>2025 Target</th>
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</thead>
<tbody>
<tr>
<td>Plant Gate H₂ Cost</td>
<td>$/gge H₂</td>
<td>$6</td>
<td>$3</td>
</tr>
<tr>
<td>Installed Heliostat Capital Cost</td>
<td>$/m²</td>
<td>$126.50</td>
<td>$90</td>
</tr>
<tr>
<td>Process Energy Efficiency (thermal)</td>
<td>%</td>
<td>30</td>
<td>&gt;35</td>
</tr>
</tbody>
</table>

TABLE 1. Progress towards Meeting Technical Targets for Solar-Driven High-Temperature Thermochemical Hydrogen Production

gge – gasoline gallon equivalent

Accomplishments

- Discovered that a ferrite/alumina-based materials system provides for a hercynite intermediate that can be thermally reduced between 1,200 and 1,450°C without high temperature sintering/deactivation issues.
- Demonstrated that <5 nm thin ferrite films can be synthesized by atomic layer deposition (ALD) and provide for significant opportunities to reduce diffusional resistances and promote radiation-driven heat transfer; both potentially providing for rapid redox cycling.
- Designed a multi-tube absorbing fixed-bed cavity reactor/receiver that provides for efficient internal heat recuperation and the potential for rapid cycling; mitigates erosion and complications associated with transporting solids.
- Carried out process design/economic evaluation indicating that ALD of ferrite materials on 100 m²/g supports cycling every 5 minutes will meet the DOE cost targets in 2015 and most likely in 2025 as well.
Developed a 5-year plan to develop materials, build a prototype device for testing and design a demonstration facility.

Introduction

The direct thermolysis to split water (H₂O → H₂ + 1/2O₂) requires materials operating at T > 3,500°C and methods to separate the H₂ and O₂ gases at high temperature [1]. This seemingly impossible task can be overcome by implementing a two-step thermochemical water splitting cycle in which a ferrite spinel material (MFe₂O₄; M=Co, Ni) can be thermally reduced using concentrated sunlight to release O₂ and the reduced ferrite then subsequently oxidized (redox cycle) with steam producing H₂ [2-4], recovering the original spinel structure in the process. It has recently been demonstrated at the University of Colorado that thin film cobalt ferrites can be deposited by ALD onto high surface area alumina (Al₂O₃) supports and that a redox cycle through a hercynite (FeAl₂O₄) pathway (Reduction: MFe₂O₄ + 3Al₂O₃ + solar energy → MAl₂O₄ + 2FeAl₂O₄ + 0.5 O₂; Oxidation: MAl₂O₄ + 2FeAl₂O₄ + H₂O → MFe₂O₄ + 3Al₂O₃ + H₂) can be cycled repeatedly and at lower temperatures than the conventional ferrite materials [5].

Approach

The primary scientific barrier to successful implementation of a solar-thermal water splitting process is access to a robust active material for efficiently and rapidly carrying out redox cycles producing H₂. Further, the key engineering barrier to successful implementation is demonstration of a large-scale solar reactor concept that allows for rapid redox cycling taking advantage of highly active thin film materials while providing for highly efficient usage of delivered solar energy. The key scientific challenges to successfully overcoming the primary scientific barrier are:

1. Identify/synthesize high surface area active materials with favorable transport properties.
2. Identify/demonstrate suitable interfacial substrate materials to facilitate rapid redox cycling.
3. Combine the active/substrate materials into a characteristic volume sample and demonstrate robust cycling to split water, particularly if able to operate the reduction in air.

High surface area active ferrite materials (MFe₃₋ₓO₄; M=Co, Ni) were synthesized using ALD to deposit nanometer thick films onto nanosized particles [6-9]. Nanoparticle substrates were placed in fluidized bed reactors and coated (Figure 1) with Fe₂O₃, CoO, and NiO thin films using self-limiting surface chemistry.

![Ultra-thin Films (2 to 10 nm)](image)

**FIGURE 1.** Thin Film Deposition of Ferrite Materials
vi metalloocene \([\text{C}_5\text{H}_5\text{M}; \text{M} = \text{Fe}, \text{Co}, \text{Ni}]\) and \(\text{O}_2\) precursors. The approach recommended is to design the nm thick ferrite films and to deposit them on high surface area (100 \(\text{m}^2/\text{g}\)) support materials.

**Results**

Unlike the conventional cobalt ferrite process that requires \(T > 1,200^\circ\text{C}\) to release \(\text{O}_2\) and is then plagued by a deactivating liquid solution “slag” phase at \(-1,525^\circ\text{C}\), the “spinel/hercynite” cycle requires reduction temperatures of only \(T > 900^\circ\text{C}\) and does not have a “slag” phase present for \(T < 1,600^\circ\text{C}\). Furthermore, nano-thick \(\text{MFe}_2\text{O}_4\) films deposited by ALD mitigate both the typical M/steam diffusional resistances and the slow conduction heat transfer that plague bulk ferrite materials. Instead, the ALD thin films provide for an opportunity to drive the redox cycle quickly using fast solar radiation heat transfer and fast mass transfer. As shown in Figure 2, the thin film “spinel/hercynite” cycle can produce significant quantities of \(\text{H}_2\) for reduction temperatures as low as \(1,200^\circ\text{C}\), while the conventional ferrite cycle requires a reduction temperature of at least \(1,450^\circ\text{C}\) (within \(75^\circ\text{C}\) of the “slag” liquid solution phase) in order to produce sufficient \(\text{H}_2\). Likewise, oxidation can be carried out for \(T > 1,200^\circ\text{C}\), providing an opportunity to drive a thermochemical cycle in which redox \(\Delta T < 300^\circ\text{C}\), thus, simplifying the recuperation of heat during redox steps. These phenomena are predicted by free energy minimization thermodynamics calculations as well [5].

A conceptualized prototype thermochemical redox receiver/reactor is shown in Figure 3. The reactor consists of a cavity-receiver, i.e. a well-insulated enclosure with a small opening – the aperture – for the access of concentrated solar radiation. Because of multiple inner reflections, the cavity-receiver is able to capture efficiently incoming concentrated solar energy. To some extent, the aperture size may be reduced with the help of non-imaging secondary concentrators, e.g. compound parabolic concentrators, placed at the receiver’s aperture in tandem with the primary concentrating system.

The cavity-receiver will contain an even number of closed-end SiC tubes. Each tube will contain a second open end SiC tube with a porous SiC plug at the base. Active high surface area and porous ferrite material, \(\text{M}_x\text{Fe}_{3-x}\text{O}_4\) in the form of catalyst honeycomb support, foams, reticulate material, etc. for the redox reactions will be packed in the annular region between the two tubes to allow for efficient heat and mass transfer and, consequently, fast overall kinetics. The active material will be deposited on a high surface area supporting alumina (\(\text{Al}_2\text{O}_3\)) substrate material in which the substrate takes part in the redox reaction (e.g. \(\text{FeAl}_2\text{O}_4\), hercynite).

![Graph](image-url)

**FIGURE 2.** “Hercynite” Cycle Compared to Standard Ferrite Cycle Performance – Theory and Experiment
The inner tube will be packed with media providing surface area for improved heat transfer to drive the vaporization of water to steam.

The redox cycle will be effected at temperatures T_R for the reduction step and T_O for the oxidation step (T_R > T_O). At a given instant, half of the tubes will be operated in the reduction mode at T_R while the remaining half will be operated in the oxidation mode at T_O. When the reactions reach completion, the operational modes will be switched. The temperatures T_R and T_O will be controlled by the endothermicity of the reaction during the reduction step and by the flow of H_2O during the oxidation step, respectively. Arrangement of the tubes inside of the cavityreceiver is a key aspect and will be such that they are arranged symmetrically in such a manner as to achieve the desired temperatures (T_R or T_O) under thermal equilibrium. Concentrated solar radiation entering the cavityreceiver and radiation emitted by the hot tubes undergoes absorption and multiple reflections. The net thermal energy absorbed by the tubes is transferred to the reaction site by combined conduction, convection, and radiation heat transfer. With such an arrangement, the sensible heat of the solids components during the switching of modes is transferred among tubes and kept inside the cavity, achieving high internal recuperation of heat. The sensible heat of the hot gaseous streams exiting the cavityreceiver will be recovered via heat exchangers and used to generate steam and preheat the cold gaseous streams to the operating temperatures.

Process/heliostat field design considerations coupled with H2A analysis indicated that 100,000 kg H_2/yr can be produced using five towers (250 m tall each) on a total of 237 acres of land. Each receiver provides for 250 MWthermal power. A net solar concentration of 4,000 suns is delivered to the receiver with a 40.2% annual average efficiency. This combined with the 54.6% LHV thermal efficiency provides for an overall solar-to-H_2 efficiency of 21.9%. A total of 2,376 GWhr annually drives the process. In order to achieve the 2015 H2A cost target of $6/kg H_2, ferrite must be produced for <$2,600/kg (Figure 4).
To achieve the 2025 cost target of $3/kg H\textsubscript{2}, ferrite must be produced for <$571/kg. Since the current cost of ALD precursors is $240/kg ferrite, cost targets appear reasonable, although 2025 is somewhat of a stretch. This design calls for redox cycling averaging 144 cycles/day.

**Conclusions and Future Directions**

- ALD films are advantageous in terms of fast redox cycling.
- The “hercynite” cycle operates in the solar thermal sweet spot of 1,200 to 1,450°C where fast radiation heat transfer dominates, but where containment issues are mitigated; forgiving chemistry with no sintering/deactivating liquid solution phase.
- Future work should demonstrate redox cycling over thousands of cycles in order to validate materials robustness.

**FY 2010 Publications**


**References**


II.G.1 Photoelectrochemical Hydrogen Production: DOE PEC Working Group Overview

Objectives

The DOE 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

(Y) Materials Efficiency
(Z) Materials Durability
(AA) PEC Device and System Auxiliary Material
(AB) Bulk Materials Synthesis
(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 sub-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].

The DOE PEC Working Group utilizes 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 continued in the development of the Working Group’s “Tool Chest” of materials theory, synthesis, characterization and analysis techniques; and this enhanced “Tool Chest” has been

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2003 Status</th>
<th>2006 Status</th>
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<tr>
<td>Plant solar-to-hydrogen efficiency</td>
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<td>not available</td>
<td>8</td>
<td>10</td>
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<tr>
<td>Plant durability</td>
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<td>not available</td>
<td>1000</td>
<td>5000</td>
</tr>
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</table>
instrumental in the development and optimization of important PEC materials classes. In nano-structured molybdenum disulfide photocatalyst materials systems, for example, band-gaps up to 1.8 eV have been demonstrated for the first time, with important implications for efficient PEC production. Progress has also continued in other PEC materials classes falling within the DOE-defined “useable” band-gap range. Important new results have been achieved in tungsten-trioxide, iron-oxide, silicon-carbide, copper-chalcoprites, and the III-V materials classes, among others. DOE PEC Working Group efforts are ongoing to render these potentially “useable” materials for high-efficiency PEC hydrogen production. General accomplishments of the PEC Working Group, detailed further in following sections, can be summarized broadly as follows:

- Successful development and application of new PEC “Tool Chest” capabilities.
- Advances in PEC Focus Materials Classes toward meeting DOE-PEC performance targets.
- 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 future energy economies 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. PEC semiconductors such as titanium-dioxide and other metal-oxides, for example, 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 2010 DOE Hydrogen Program Annual Merit Review held in Washington D.C. featured numerous 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 and analytical techniques to identify and develop the most promising materials classes to meet the PEC

FIGURE 1. PEC Working Group Members with current DOE financial support, including the 2010 DOE Hydrogen Program Annual Merit Review oral/poster presentation designations.
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 employing 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.

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 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 WS₂ and MoS₂ nanoparticle systems, and the development of breakthrough synthesis technologies to reduce the cost of high-performance crystalline semiconductors, such as GaAs/GaInP₂. Future progress in all these approaches is integrally tied to the DOE PEC Working Group’s continued development and deployment of its tool-chest capabilities, 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 have resulted in significant progress, including:

- Significant Progress in Establishing PEC Testing Standards [6,7]
  - First revision drafts of 16 protocol documents completed.
  - Web site set up to facilitate international review/revision process.

- Important Advances in PEC Characterizations [8,9]: Project PD051
  - Ultraviolet/soft X-ray/electron spectroscopic tools for evaluating optoelectronic and chemical properties of PEC materials' surfaces, near-surfaces and bulk fully operational.
  - “Solid And Liquid Spectroscopic Analysis” characterization facility installed at the Lawrence Berkeley National Laboratory Beamline 8.0 Advanced Light Source for the in situ evaluation of PEC semiconductor/electrolyte interfaces (as illustrated in Figure 2).

- New Advances in PEC Materials Theory [10,11,12]: Projects PD052, PD058
  - First principle models of the PEC interface constructed based on III-V semiconductors, exploring effects of O, H and OH termination (as illustrated in Figure 3a).
Important correlations between surface morphology and interaction with interfacial water molecules established.

Theoretical band structures of new PEC materials classes investigated (as illustrated in Figure 3b).

- First Phase of PEC Hydrogen Production Techno-economic Analyses Completed [13]
- Incorporating performance and processing cost feedback from the broader materials R&D efforts, coordinated through Directed Technologies, Incorporated.
- Sensitivity analyses indicating hydrogen production costs as low as $1.86/kg hydrogen for some PEC systems configurations based on available plant technologies, and using projected high-performance PEC semiconductor materials.

Continued feedback between the theory, synthesis, characterization and analysis among PEC Working Group participants is providing fundamental insights needed to promote technical breakthroughs in a broad spectrum of promising PEC materials classes. The Working Group serves to organize, focus, and track scientific research progress in PEC R&D. This approach over the past year has resulted in important progress toward DOE PEC Materials & Device Targets. Examples include:

- Successful first-time demonstration of bandgap tailoring in photoactive MoS2 nanoparticles at Stanford University [14,15]: Project PD033
  - Nanoparticle sizes ranging from 25 down to 5 nm have exhibited band-gaps ranging from 1.0–1.8 eV (as shown in Figure 4a).
  - Initial exploration of photocatalyst nanorods, in collaboration with University of Louisville (as shown in Figure 4b).

- Identification of thin-film device configurations based on current chalcopyrite and silicon compound materials at MVSSystems Incorporated and the University of Hawaii with potential for meeting DOE Performance Targets [16,17]: Projects PD053, PD055
  - Identified complex multi-junction device having >5% STH using current copper gallium diselenide materials.
  - PEC interfacial barrier identified as limit to >10% STH tandem.
  - New theory and characterization tools to be used to address the interface barrier problem for meeting DOE performance targets.

- Identification of crystalline semiconductor device configurations based on current III-V materials with >15% STH conversion efficiency at the National Renewable Energy Laboratory [18]: Project PD035

In addition, notable progress also has continued over the range of PEC materials classes under investigation by the PEC Working Group, including progress in:

- Tungsten-oxide and related modified compounds [19-21]: Project PD054
- Iron-oxide and related modified compounds [22,23]: Project PD034
- Amorphous silicon-carbide based photoelectrodes [24,25]: Project PD053
- Copper indium gallium diselenide based photoelectrode systems [26,27]: Project PD055
Conclusions and Future Directions

The DOE’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. 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.
  – Further discovery and optimization of viable PEC semiconductor materials.
  – Integration of best available PEC materials into optimal device and system configurations.

• Continued Expansion of Collaboration Efforts: Nationally and Internationally
  – DOE PEC Working Group expansion.

The ultimate aim is to make the materials and device advances necessary for high-efficiency, low-cost PEC hydrogen production.

Special Recognitions & Awards/Patents Issued


Publications/Presentations

1. The publication list of the U.S. DOE PEC Working Group Members is extensive. The reader is referred to the progress reports of the 2010 DOE AMR presentations of the Working Group Participants (including presentations PD 033, 034, 035, 051, 052, 053, 054, 055, 058, 061 and 062) for a comprehensive list of publications.

References


7. www2.eere.energy.gov/hydrogenandfuelcells/pec_standards_review.html#standards.


II.G.2 Nanostructured MoS₂ and WS₂ for the Solar Production of Hydrogen

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 three-dimensional double-gyroid network.
- Explore and optimize bandgap and bandedge position as a function of size and architecture for water splitting.
- Study photo-generated 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 Fuel Cell Technologies 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 FCT Multi-Year RD&D Plan:

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
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<td>Plant solar-to-hydrogen efficiency</td>
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<tr>
<td>Plant durability</td>
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</tr>
</tbody>
</table>

Accomplishments

- Achieved low temperature (150°C) sulfidization of molybdenum/MoO₃ to produce MoS₂.
- Synthesized tungsten nanoparticles and air-stable nanoscaled MoS₂ nanoparticles in various sizes ranging from 5-25 nm.
- Achieved quantum confinement of MoS₂ nanoparticles with indirect bandgaps up to 1.8 eV.
- Electrochemical testing of the MoS₂ nanoparticles supported on fluorine-doped tin oxide revealed activity for the hydrogen evolution reaction with Tafel slopes of ~200 mV/decade.
- Developed a macroporous indium tin oxide support to allow vertical integration of nanoparticles for increased absorption.
- Synthesized quantum confined nanowebs of MoS₂ with bandgaps up to 1.6 eV.
- Synthesized Nb doped MoS₂ films that produced cathodic photocurrent.
- Produced highly stable nanoscaled double-gyroid RuO₂ counter electrodes for efficient oxygen evolution with over 19 times the exchange current density of a comparable thin film.
- Developed nanoscaled alumina templates for nanowire synthesis with mean pore diameter of 15 nm.
• Investigated sulfidization of MoO$_3$ nanowires up to 700°C without significant sintering in collaboration with Prof. Mahendra Sunkara at the University of Louisville, Kentucky.

Introduction

PEC water splitting for hydrogen production was first demonstrated by Fujishima and Honda in 1972 using titanium dioxide (TiO$_2$) [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, the best absorbers to date are often hindered by other issues such as poor charge transport [11], slow kinetics for the hydrogen evolution reaction or oxygen evolution reaction [12], and/or poor stability [13,14]. Thus, no material system exists that can yet be considered as a wide-scale deployable solution. The world record PEC device with 12.4% solar-to-hydrogen efficiency was developed by Khaselev and Turner in 1998 [14], but it exhibited significant material instability and extremely high cost [15,16]. 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 [17-20], which enables absorption of a significant portion of the solar spectrum. However, this value is too small to provide the photovoltage necessary to split water, which requires a minimum thermodynamic potential of 1.23 eV in addition to the overpotentials required to drive the kinetics of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The minimum bandgap value will likely lie in the range of ~1.8-2.0 eV [21]. Nanostructuring materials can result in an effect known as quantum confinement [20,22,23], 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 HER [24]. This translates into a smaller required bandgap and higher theoretical efficiency.

Furthermore, controlling the material conductivity has important consequences on its PEC properties. By focusing on the development of MoS$_2$ and WS$_2$ as photocathodes (rather than photoanodes), the possibility of photo-oxidizing the sulfide is minimized and stability can be improved since photogenerated electrons drive the HER at the semiconductor-electrolyte interface while oxidizing holes flow to the counterelectrode to drive the OER [25-29]. One approach to develop a material that exhibits photocathodic behavior with minimum input bias is to increase its work function by the addition of dopants. In the case of MoS$_2$, doping with niobium can produce a p-type semiconductor [30] that is more likely to behave as a photocathode. Consequently, a photocathode that drives the HER requires a counterelectrode that efficiently drives the OER. Ruthenium dioxide (RuO$_2$) is a material known to exhibit high conductivity, chemical and thermal stability [31-35] and catalytic activity for the OER [34-36]. By nanostructuring RuO$_2$ in a double-gyroid geometry [37] it is possible to improve its catalytic ability even further [38].

Results

Our efforts within the project have focused on the development of MoS$_2$, since it represents a material with a rich history of catalysis and photoactivity [23,39-41]. We achieved 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).

Synthesis of supported MoS$_2$ nanoparticles in various sizes was accomplished using a reverse micelle encapsulation method [42-44]. The low temperature sulfidization process minimized nanoparticle sintering. The nanoparticles were imaged using atomic force microscopy as shown in Figure 1. Scanning electron microscopy (SEM) revealed size distributions ranging from 5-25 nm. Despite their small size, these nanoparticles are resistant to oxidation from exposure to air, as confirmed using XPS shown in Figure 2. The same reverse micelle encapsulation method was used to synthesize tungsten nanoparticles, which are currently under further development.

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 indirect bandgaps are shown in Figure 3.
During attempts to synthesize MoS$_2$ nanoparticles, we found that using a highly hydrophilic precursor (MoCl$_3$ instead of Mo(OCOCH$_3$)$_2$) could disrupt the micelle network and form an interconnected web morphology. These nanowebs still exhibited a quantum confined blueshift in the absorption onset up to 1.6 eV, slightly less than the blueshift seen with nanoparticles. One reason for this may be because of a greater degree of electron delocalization in the interconnected structures.

In order to obtain measurable photocurrent from the MoS$_2$ nanoparticles, they must first be supported in a structure that allows them to absorb a significant number of photons. This is difficult to achieve with a sub-monolayer of nanoparticles supported on a planar surface due to the short absorption path length. One approach is to develop a macroporous transparent conducting oxide which enables the vertical integration of nanoparticles to increase absorption path length without sacrificing absorption or limiting the diffusion of reactants and products to the active sites. Using this approach, we synthesized a macroporous indium tin oxide support structure, and are currently optimizing its conductivity.

While MoS$_2$ crystals in nature can be found to intrinsically have either n-type or p-type conductivity, leading them towards photoanodic or photocathodic behavior, we synthesized a p-type photocathodic MoS$_2$ by doping with Nb. Activity was assessed using photocurrent measurements under a negative applied bias in a PEC cell. The observed photocurrent was cathodic and increased with greater negative applied bias.

As part of the effort to develop photocathodes of sulfides, it is necessary to produce counter-electrodes that efficiently drive the oxygen evolution reaction. Using an electrochemical deposition technique followed by a heat treatment, we produced RuO$_2$ films that exhibit a 320 mV earlier onset for oxygen evolution compared to Pt. The films demonstrated 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$_2$SO$_4$ solution. To develop even more active RuO$_2$, we used a silica template made with a poly(ethylene oxide)-poly(propylene oxide)-alkane tri-...
block copolymer surfactant [37,45,46] to form a double-gyroid RuO$_2$ structure. In comparison to the thin film of RuO$_2$, which produced an exchange current density of $3.67 \times 10^{-9}$ A/cm$^2$ for the OER, the double-gyroid RuO$_2$ structure produced an exchange current density of $7.11 \times 10^{-8}$ A/cm$^2$, over 19 times greater than the thin film.

To synthesize nanowires, we have focused on the development of anodic alumina templates [47-51]. Using this technique, we have synthesized templates with 13 nm pores, as imaged by SEM, and are continuing to optimize the synthesis towards even smaller pore sizes. We are also working to synthesize double-gyroid MoS$_2$ structures using the same silica template developed for the double-gyroid RuO$_2$. We plan to fill the templates and develop the inverse Mo and W structures using an electrodeposition technique optimized in our laboratory.

We are also working in close collaboration with Mahendra Sunkara, Professor of Chemical Engineering at the University of Louisville, Kentucky. Using a hot-wire chemical vapor deposition technique, Sunkara has successfully formed vertical nanowires of MoO$_3$. We convert the nanowires to MoS$_2$ using our sulfidization furnace and study their physical and PEC properties as a function of sulfidization temperature. Once sulfidized, the nanowires change in color from transparent blue to an extremely opaque black with imperceptible amounts of reflection and transmission, indicating very high levels of photon absorption, as confirmed by UV-Vis. SEM reveals that our sulfidization process results in minimal sintering of the nanowires, even up to 700°C. Transmission electron microscopy shows the formation of polycrystalline layers of MoS$_2$, which is further confirmed by X-ray diffraction. We are continuing to work on the development of substrates that can withstand the effects of higher sulfidization temperatures, yet retain the necessary conductivity and electrochemical inertness for PEC testing.

**Conclusions and Future Directions**

We have made significant progress in developing nanostructured MoS$_2$ for PEC water splitting, with the most significant results being summarized as follows:

- Synthesized air stable MoS$_2$ nanoparticles in various sizes that exhibit a size-dependent quantum confinement up to 1.8 eV.
- Developed a highly porous nano-scale double-gyroid structure of RuO$_2$ with very high activity for the OER.
- Synthesized air stable MoS$_2$ nanowires in collaboration with the University of Louisville that show extremely high photon absorption.

Our work on this project continues with the development of substrates that will enable PEC testing of nanostructured MoS$_2$. In order to achieve this goal, we will:

- Optimize the conductivity and transmissivity of the indium tin oxide macroporous network upon which we will support quantum confined MoS$_2$ nanoparticles. This will allow vertical stacking of the nanoparticles for improved photon absorption, while retaining the required conductivity for the photogenerated electrons and holes.
- Investigate the use of molybdenum foil and other metals as substrates for MoS$_2$ nanowires. Unlike the nanoparticles, the nanowires are already excellent absorbers of light, and simply need a substrate that can withstand the sulfidization process and retain good conductivity.

Upon achieving photoresponse from our nanostructures, we will proceed with a full battery of PEC studies, including the determination of the flat-band potential using:

- Illuminated open circuit potential
- Mott-Schottky
- Photocurrent onset

The flat-band potential 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 other PEC measurements on the supported nanostructures, including:

- Monochromatic photoresponse to obtain the incident photon-to-current conversion efficiency.
- Photoresponse under an applied bias to obtain the applied bias photon-to-current conversion efficiency.
• Photoresponse under zero applied bias to obtain the solar-to-hydrogen conversion efficiency.
• Assessing the hydrogen and oxygen products in the headspace to obtain the Faradaic efficiency for water-splitting by gas chromatography.

These studies will help to elucidate fundamental charge transport and interfacial properties of our materials and enable an improved degree of scientific understanding necessary to meet the goals set forth in Table 1. These techniques are explained in further detail in one of our recently published articles that outline proper methods, definitions, and protocols for developing materials for PEC hydrogen production [52].

Lastly, work is underway to further develop the anodic alumina templates, as well as the nanoporous double-gyroid networks. The templates will enable the development of MoS2 and WS2 nanowires and double-gyroid networks using an electrodeposition process. Although initial efforts have focused on MoS2, work is already underway to develop WS2 nanostructures. WS2 is an important avenue of study due to its structural and electronic similarities to MoS2. By studying both MoS2 and WS2 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 2010 Presentations**


**References**


46. L. Bollmann, V.N. Urade and H.W. Hillhouse: Controlling interfacial curvature in nanoporous silica films formed by evaporation-induced self-assembly from nonionic.

II.G.3 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material for PEC production of bulk hydrogen from water – a clean, renewable route to

Objectives

- A focus on the use of abundant and non-toxic elements in the development of improved photoelectrocatalyst 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 photoelectrochemical (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.

Technical Barriers

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

Technical Targets

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
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<th>2007 Target</th>
<th>Achieved 2008</th>
<th>2013 Target</th>
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</tr>
</tbody>
</table>

NA - not applicable

Accomplishments

- Investigation of iron oxide electrodes with different levels of Ti doping by spray pyrolysis.
- Investigation of the PEC performance of Ti-doped hematite photoanode with oriented crystallography and different Ti%.
- Synthesis of bulk Ga$_{1-x}$Mo$_x$P (x ≤ 0.1) powders and deposition of cocatalyst.
- Exploration of the PEC activity of Ga$_{1-x}$Mo$_x$P (x ≤ 0.1) powders for hydrogen iodide (HI) and hydrogen bromide (HBr) splitting.
- Investigation of surface modification/passivation of InP wafer for increased corrosion resistance during HI and HBr splitting using simulated solar radiation.

Introduction

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material for PEC 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/vacance band energies relative to H⁺ and O₂ 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 solar-to-hydrogen efficiency and durability: 2006, 4%; 2013, 8% and 1,000 hrs; 2018, 10% and 5,000 hrs.

Hematite (α-Fe₂O₃) has many potential advantages for hydrogen photoproduction. It has a bandgap of 2.2-2.3 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]. However, 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 lower conduction band-edge relative to the redox level of H⁺/H₂. Our hypothesis is that by deliberately doping hematite with selected heteroatoms [6] (e.g. Ti) and controlling the growth dimensions, crystal orientation and facets exposed, these limitations may be overcome. Phosphides have a narrow bandgap (~1.3 eV), which can utilize most of the visible light radiation, and a higher conduction band potential relative to the redox level of H⁺/H₂, which is preferable for hydrogen production using solar energy [7,8]. By surface modification and back contact engineering, a respectable incident photon conversion efficiency (IPCE) and chemical stability can be achieved in strong acid electrolyte.

Approach

The approach of this project involves the application of spray pyrolysis and solid state reaction methods to synthesize and optimize PEC materials and systems for cost-effective hydrogen production. This presents a systematic 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, InP, and GaP. Iron oxide thin films doped with various amount of titanium have been synthesized by rapid spray pyrolysis of Fe(CO)₅ and TiCl₄, and screened by investigation of their PEC performance using a high through-put screening system. Gallium molybdenum phosphate powders were prepared through solid state reaction involving alloying of a stoichiometric amount of Ga₂O₃ and Mo metal through high temperature calcination. The resulting alloy was treated with H₃PO₄ and calcined in air at 500°C for 24 h and further reduced in H₂ flow at 875°C for 20 h. Pt nanoparticles were deposited on the powder samples which were then dispersed in 0.5 M HI or HBr solution in sealed vials. The PEC performance of these slurry systems were then tested in a high-throughput PEC reactor.

In parallel to our research on particulate phosphide systems, the PEC performance of n- and p-type InP wafers with ohmic contacts in HI and HBr systems were also investigated. Various passivation treatments were implemented in order to minimize the dark (corrosion) current of InP in the acidic solutions. Moreover, using the planar electrodes of InP would allow for determination of IPCE and PEC properties of InP in any electrolyte of interest. The ultimate results from these experiments enable one to select the best working conditions for any particular synthesized transition metal phosphide in a PEC particle system. Sulfur passivation was achieved by treatment of InP wafer with 7% aqueous (NH₄)₂S with added elemental sulfur (saturated solution) [9].

Results

Hematite photoanodes with various Ti doping densities were prepared by spray pyrolysis of Fe(CO)₅ and TiCl₄ and their PEC performance in water splitting was investigated. The feature size of the thin films increases from 10 nm to larger than 300 nm with an increase of Ti from 0-35% (Figure 1a-e). Orientated crystallography was observed in all the thin films as prepared with different Ti%, as shown in the X-ray diffraction (XRD) patterns (Figure 1f). The IPCE of the thin films at 0.4 and 0.6 V vs. Ag/AgCl was plotted as a function of Ti% in Figure 2a, which shows the highest IPCE of 27.5% at 400 nm from sample with Ti% of ~0.78%. With the increase of Ti%, the IPCE decreases. All samples show a low IPCE at 0.2 V vs. Ag/AgCl, which was ascribed to the higher density of trap states and the presence of the magnetite crystal phase when titanium was used in higher concentrations (7.17% and 34.5). Calcination at 500°C diminished the amount of magnetite present in these two samples and improved the performance of the Ti-doped hematite thin films at 0.2 and 0.4 V vs Ag/AgCl except the sample with 34.9% of Ti. The pure hematite sample shows almost no photoelectrocatalytic activity both before and after 500°C calcinations. This indicates that the poor performance of this thin film is not related to its crystallinity.

The PEC H₂ production from HI splitting on bulk GaₓMoᵧP and Pt/GaₓMoᵧP (x≤0.1) particles is shown in Figure 3a and b. The improvement of the performance by deposition of cocatalyst (Pt nanoparticles) is significant. The GaₓMoᵧ₀.₀Po.₀P sample with and without Pt cocatalyst in HI splitting...
the best performance. The Ga$_{1-x}$Mo$_x$P samples also showed a high activity in HBr splitting, a much more valuable reaction than pure hydrogen production. Figure 3c shows the performance of the Ga$_{0.95}$Mo$_{0.05}$P sample in both HBr and HI over the course of 50 hours continuously. The efficiency of HBr splitting is approximately half of HI splitting.

Intensive hydrogen evolution from p-InP wafer surface was observed in 0.5 M HI solution under 100 mW/cm$^2$ white light illumination. The efficient hydrogen production was confirmed by the IPCE and photocurrent measurements in a two electrode configuration under no applied bias. The IPCE of this p-InP in 0.5 M HI yields an average value of ca. 35% in a wide range of visible light from 500-900 nm, Figure 4a. A short-circuit photocurrent of 10 mA/cm$^2$ was also observed under 1 sun illumination, Figure 4b. The abrupt change of photocurrent as shown in Figure 4b is attributed to the bubbling of hydrogen. In addition, our experimental data has shown that n-InP is a promising candidate for HBr splitting even in the absence of any cocatalyst. However, compared to our obtained results in HI, the photocurrent recorded in HBr electrolyte is in the range of 0.5–1.0 mA/cm$^2$.

One of the main flaws of n- and p-InP in HI and particularly HBr solutions is the relatively high dark (corrosion) current. Undoubtedly, one of the main requirements of any potential material to function as a sustainable and stable photocatalyst is to exhibit an acceptable corrosion rate. Thus, a great deal of effort in our laboratory has been devoted to the investigation of efficient chemical passivation to minimize the corrosion rate with no adverse impact on the photoactivity of the material. To date, sulfur passivation of n-InP has been the most effective passivation treatment, remarkably minimizing the corrosion rate of n-InP in
The dark current over the course of 1 week in solution and three 16 h light periods (100 mW/cm²) remained constant at about 0.1 µA/cm². Untreated samples display dark current on the order of 200 µA/cm² after a single light cycle. The main advantage of this treatment is the possibility of application of this treatment to our slurry phosphide systems such as Ga₁₋ₓM₀ₓP with no need to apply any external bias.

Conclusions and Future Directions

• The methodology of combinatorial material science has been applied to expedite the discovery of improved photocatalytic materials for hydrogen production.
A spray pyrolysis system has been used to synthesize Ti-doped iron oxide thin films with various Ti concentration and orientated cryptography. The Ti-doped iron oxide thin films show a remarkable improvement in efficiency for PEC water splitting compared to undoped samples.

Surface modification by saturated aqueous ammonium sulfide solution has been successfully applied to passivate InP wafer for PEC use in strong acid electrolyte.

Ga$_{1-x}$Mo$_x$P ($x \leq 0.1$) powders have been prepared and shown high activity in HI and HBr splitting under visible light illumination with Pt cocatalyst.

Development of novel synthetic methods for nanoscale/nanostructured Ga$_{1-x}$Mo$_x$P ($x \leq 0.1$) powders.

Synthesis of Ga$_{1-x}$M$_x$P (M = Ni, W, Fe) powders and PEC performance testing in HI and HBr splitting under visible light illumination with Pt cocatalyst.

**FY 2010 Publications/Presentations**


**References**


II.G.4 Semiconductor Materials for Photoelectrolysis

Objectives

Identify, synthesize, and characterize new semiconductor materials that have the capability of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device, either as a single absorber or as part of a high-efficiency multi-junction device.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Fuel Cell Technologies Program’s Multi-Year Research, Development, and Demonstration Plan (MYPP):

(Y) Materials efficiency
(Z) Materials durability
(AB) Bulk materials synthesis
(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% conversion efficiency
- 1,000 hr lifetime

Accomplishments

- In addressing the MYPP barrier Z, preliminary testing of CuGaSe2 (CGS) was completed. UNLV analysis of CGS samples that were subjected to PEC testing showed that biasing the material alters the chemical environment of Ga and immersion into an acidic electrolyte appears to remove a native SeO2 feature. Further analyses are necessary to determine how these changes might affect stability and performance.
- Our Stanford subcontractor synthesized tungsten nanoparticles and air-stable MoS2 nanoparticles in various sizes ranging from 5-25 nm and achieved quantum confinement of MoS2 nanoparticles with indirect bandgaps up to 1.8 eV.
- We characterized a-SiC, deposited by plasma-enhanced chemical vapor deposition (PECVD) to address barriers Y, Z, AB and AC. We determined a-Si/a-SiC hybrid photoelectrodes have poor efficiency when operated at zero bias and poor durability when moderate current (-3 mA/cm2) was applied. Removing the surface SiOx layer with an hydrofluorhydric acid (HF) etch can improve water splitting efficiency to just over 1%.
- In addressing barriers Y, Z, and AC we determined InxGa1-xN thin films have appropriate interfacial energetics for spontaneous water splitting, exhibit good durability, and can be incorporated into multi-junction absorber cells to improve photoconversion efficiency.
- We published a manuscript to the Journal of Materials Research on standardized PEC methods which was the culmination of a year-long effort with other members of the PEC working group. The document is intended to establish standard practices for reporting water splitting efficiencies within the PEC community.
- Stabilization of the GaInP2 electrolyte interface through electrochemical nitridation and thin oxide coating by atomic layer deposition show these strategies may be able to passivate the corrosion-prone surface. If these highly efficient materials (12.4% solar-to-hydrogen, STH) could be made more durable, the MYPP 2013 technical target or 10% efficiency for 1,000 hours would be satisfied.
- Density functional theory (DFT) calculations showed W would make a good n-type dopant in BiVO4 and efforts to incorporate W during synthesis are underway.
- We made a “no-go” decision on continued study of a-SiNx and Cu-W-O materials and a “go” decision on protective coatings and nitride treatments on high-efficiency III-V photoelectrodes.
Future Direction

- Continue to synthesize and characterize nitride materials (GaNP, GaInN, GaInPN) for higher efficiencies and longer lifetimes. Synthesize InGaN on conductive substrates.
- Investigate nitridation of III-V surfaces for corrosion passivation.
- Evaluate additional PEC semiconductor candidates in collaboration with others.
- Work with UNLV to correlate surface and near-surface spectroscopic results with test conditions to identify corrosion pathways and performance barriers related to surface composition.

Introduction

Photoelectrochemistry 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 electrode of the water-splitting system, and the other is an electrode in a separate compartment. The key is to find a semiconductor system that can efficiently and sustainably collect solar energy and direct it towards 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 stability under solar conditions and (iv) can be adapted to volume-manufacturing techniques.

Approach

Our approach has two thrusts, (i) the study of current material sets used in commercial solar cells as well as related materials, and (ii) the discovery of new semiconducting materials using advanced theoretical calculations to identify promising candidates, closely coupled with synthesis and state-of-the art characterization. The latter is in collaboration with NREL’s theory group.

Results

III-V Nitride Materials

We characterized InGaN alloy samples from Los Alamos National Laboratory grown by molecular beam epitaxy (MBE). InGaN is a promising emerging material with a bandgap between 0.7-3.4 eV, depending on the In:Ga ratio. Nitride materials have well documented stability in contact with electrolytes, therefore InGaN alloys may be stable and efficient photoelectrodes for PEC water splitting because of their chemical inertness and ability to absorb visible photons. These materials were characterized to determine bandgap, bandedge alignment, water-splitting efficiency, and stability. Samples were grown on sapphire substrates, which are electronically insulating. Contacts were applied to the periphery of the front surface in order to fabricate electrodes, a non-ideal configuration that results in poor carrier collection. Despite these non-ideal contacts, we were able to determine some basic material properties.

The samples had obvious visible absorption as evidenced by their colored appearance (Figure 1a). The material composition varied across the surface of the wafer due to issues with the gallium source within the MBE reactor. The bandedge positions were appropriate for water splitting according to Mott-Schottky measurements. Illuminated open-circuit measurements and photocurrent onset potential measurements indicated the flatband potential was too positive, i.e. the conduction bandedge was too low to drive the hydrogen evolution (reduction) half-reaction. Two-electrode measurements (Figure 1b), however, demonstrated zero-bias photocurrent, which we correlate with spontaneous water splitting. Though the InGaN was capable of zero-bias photocurrent, the efficiency was very low, generating 10s of μA/cm² instead of mA/cm² that would be expected of a material with a bandgap in the visible region. We believe the inconsistent bandedge analyses and low conversion efficiency is due to the long carrier collection distances due to the non-ideal contacts. Initial durability analysis showed moderate stability, but it is doubtful that the uneven spatial distribution of current replicated what an appropriately contacted material might experience. Realistic appraisals of efficiency and durability cannot be made until the contact geometry is modified to a more ideal vertical collection is achieved by using conductive substrates.

Thin-Film Amorphous SiN and SiC Systems (with MVSystems)

In collaboration with our industrial partner, MVSystems, Inc., who performed the material synthesis, we studied amorphous silicon nitride (a-SiN) and silicon carbide (a-SiC) samples grown by PECVD. PECVD is a scalable process that can yield low-cost photoelectrodes and although the instability of amorphous silicon (a-Si) makes it a non-ideal PEC material, stability might be achieved when synthesized as a nitride or carbide.

We characterized PECVD grown a-SiN, that was synthesized with an appropriate bandgap (~2.0 eV) for water splitting; however, the bandedges at the electrolyte semiconductor interface were not favorable.
for spontaneous water splitting. When assembled into a p-type device, a-SiNx electrodes can produce milliamps of photocurrent per square centimeter but only under a strong negative bias of -3 V. A 30 second 5% HF surface treatment damaged the film surface and did not significantly improve photocurrent onset potential. Holding the sample at -2.6 V vs. Pt-black counter electrode for 24 hours produced numerous pinholes in the a-SiNx film and allowed the passage of dark current from the conductive tin oxide substrate. Because of the questionable efficiency and durability of this material, a-SiNx has limited promise for PEC water splitting applications, and thus we made a “no-go” decision on continued study of this material.

The PEC performance (efficiency and durability) of a-Si(photovoltaic, PV)/a-SiC(PEC) was determined. These types of cells are known as a PEC/PV hybrid because they incorporate a photovoltaic absorber in series with a PEC absorber as a monolithic device. When these cells are fabricated into solid-state devices, the short-circuit current density under air mass (AM) 1.5 G illumination is about 4.5 mA/cm². When similar cells were tested in a PEC environment, the short-circuit (water splitting) current densities were below 1 mA/cm².

HF etching can improve the photocurrent by removing the insulating SiOx interfacial layer, but the effect is only temporary. We have been unable to identify an active catalyst to facilitate the hydrogen evolution reaction on the surface of these photocathodes. Our typical applications of platinum by electrodeposition or immersion in colloidal solutions have not been effective for these amorphous materials. Platinum applied by sputtering also led to diminished photocurrents.

The STH efficiencies achieved in pH 0, 5, 8, 10, and 14 under AM 1.5 G illumination were all lower than 0.25% when a platinum counter electrode was used. The use of a RuO₂ counter electrode in pH 0 sulfuric acid achieved the highest STH efficiency of about 1%, and was stable over the 20-hour test period. However, no bubbles were observed from the working electrode so the cathodic current could not be unambiguously attributed to water splitting. Our collaborators at the University of Hawaii observed that using an HF acid treatment, the overall efficiency could be as high as 1.6% (RuO₂ counter, in pH 0 phosphoric acid).

When a current of -3 mA/cm² was applied by external biasing, (the current that a 3.6% efficient electrode would generate) severe degradation of the surface was observed in less than 24 hours. The electrodes developed several pinholes that were visible without magnification that increased with extended testing (Figure 2).

For a-SiC coated a-Si to be considered for PEC water splitting devices, the efficiency and durability both must be improved.

Protection Strategies for High-Efficiency III-V Materials

Tandem cells based on p-GaInP₂/n/p-GaAs semiconductors have demonstrated over 10% STH, which exceeds the DOE near-term technical target, but are prone to corrosion during operation. The unprotected cells only last a few days in operation. Improving the durability to 1,000 hours could yield a
photoelectrode that satisfies both the efficiency and durability technical targets. This year we examined two different pathways for III-V photoelectrode passivation. One strategy is to use an electrolyte that has constituents that modify the semiconductor surface in a way that leads to protection. The other approach focuses on applying a protective coating through a chemical deposition process.

Initial results from our lab found that operating a p-GaInP₂ for 24 hours in a pH 1 NH₄NO₃ solution resulted in less surface degradation, as determined by optical microscopy and scanning electron microscopy (SEM), than running it in our standard 3M H₂SO₄ solution. Our hypothesis is that the passivation is due to electrochemical nitridation that occurs during the durability testing. X-ray photoelectron spectroscopy on a sample that had been run in the NH₄NO₃ solution found ammonia on the surface after rinsing the electrode with deionized water post durability testing. We are following up to determine if the difference in pH (3M H₂SO₄ pH = -0.5) plays a significant role. We are also investigating the origin of the ammonia, whether from the cation or anion, so we are testing in (NH₄)₂SO₄ and KNO₃. In addition we are performing durability analysis on tandem GaInP₂/GaAs electrodes to see if the protective effect is observed when the electrode is biased internally instead of via a potentiostat.

The second strategy for electrode passivation involves applying a thin coating that should provide protection. The coating must not significantly attenuate visible light, and be robust enough to protect the surface while not impeding electron flow to the electrolyte. Our first attempt was to coat p-type GaInP₂ with 20 nm of TiO₂ by atomic layer deposition (ALD). TiO₂ is a fairly stable oxide material that has a wide bandgap and is naturally a good (n-type) electron conductor. We cleaved GaInP₂ wafers and sent half of each one to our colleagues in the Sunkara group at the University of Louisville to have the oxide coating applied. We mounted the coated and uncoated samples into electrodes to compare their ability to generate photocurrent and determine their durability characteristics.

We were unable to determine if the coating attenuated photocurrent because there was high variability between individual electrodes from the same wafer, but some of the highest photocurrents were achieved on coated electrodes. For durability analysis, the electrodes were operated for 22 hours at -5 mA/cm² in 1M KOH. We were unable to find significant differences in post-durability performance or variation in solubilized Ga in the testing solution. We believe the durability test conditions were not harsh enough to observe corrosion effects on either the coated or uncoated samples.

Visual analysis of the coated and uncoated samples did reveal differences after the durability testing. The uncoated samples displayed a degraded surface from their initially shiny and featureless appearance while the coated electrodes had areas where the coating had flaked off but otherwise appeared free from degradation. SEM imaging of a coated electrode showed that the TiO₂ film has fissures that probably contributed to its inability to adhere to the semiconductor surface (Figure 3). The fissures appear to be a native feature of the TiO₂ coating because they are evident in an area which was masked by epoxy during the testing. This result indicates a thicker coating may be required to achieve an uninterrupted film with the required stability.

Because of the promising results obtained so far, we made a “go” decision for continued study of both nitrided and ALD-coated III-V surfaces for corrosion remediation.
II.G Hydrogen Production / Photoelectrochemical

Chalcopyrites Materials based on Cu(In,Ga,Al)(S,Se,Te)₂

This year we continued potentiostatic (constant applied potential) durability analysis of CGS materials on fluorine-doped tin oxide substrates obtained from the University of Hawaii. In addition to samples sent to UNLV for synchrotron analysis (results reported by our subcontractor NREL project: subcontract NO. NFH-8-88502-01 under prime contract NO. DE-AC36-99GO10337) we performed our own surface and electrochemical analysis. Figure 4 illustrates how a pinhole can lead to cracking and delamination of the CGS thin film during durability.

Theory of Metal Oxide, Nitrides and Other Materials

BiVO₄ has attracted significant interest as a semiconducting material for the PEC decomposition of water. Our analysis of BiVO₄ by density functional theory indicated good electronic properties for this material such as high hole mobility and good band edge positions. For PEC applications, the semiconductor must be doped p-type or n-type to a reasonable carrier concentration in order to support current flow. Therefore, we studied the effect of doping of W in BiVO₄ using DFT.
We previously calculated that the valence band of BiVO_4 is derived from hybrid Bi lone pair 6s and O 2p states. Tungsten can have various ionized states in oxides. We find that if a W occupies a Bi site, W is shallow donor. From the calculated band structure and site projected density of states, it was found that the states introduced by W are in the conduction band, indicating that indeed W is a very shallow donor. In this case, W is 5+ and Bi is 3+, therefore W on Bi site results in double donors. Beside Bi sites, W may also occupy a V site where the states introduced by W are also in the conduction band, meaning W at V site is also a shallow donor. However, in this case, W is a single donor.

Our results conclude that W at either a Bi site or a V site is a shallow donor, suggesting W would be an excellent dopant for making n-type BiVO_4, and we will be pursuing the synthesis of this material for PEC testing.

**NREL Synthesis of Metal Oxide Alloy Thin Films**

We synthesized Cu-W oxide thin films by co-sputtering. In order to produce Cu-W oxide materials with tunable band gaps and avoid phase separation, amorphous Cu-W oxide films were synthesized. Considering the fundamental gap as direct, the band gaps for a series of samples with Cu to W ratios of 1:3, 1:1:1, and 2:2:1 were 2.63 eV, 2.05 eV, and 1.88 eV respectively. The trend of the bandgaps correlate well with values expected from the composition. The fundamental bandgaps correspond to the transition between Cu 5d-derived valence band and W 5d-derived conduction band.

Although these materials have optimal bandgap energies, they are unstable in both basic and acidic solutions. In light of their instability, we made a “no-go” decision on amorphous Cu-W oxide for PEC applications.

**Conclusions**

- InGaN shows promise for a single junction water splitting electrode with potential for high efficiency and durability if the contacts can be improved. Synthesis on conductive substrates should remedy this situation and these efforts are underway.
- Thin film a-Si carbides have the potential to be inexpensive water splitting electrodes if durability and efficiency can be improved.
- Protection of highly efficient, but corrosion prone photoelectrodes could result in a single material that meets the DOE technical targets for efficiency and durability. Results from GaInP cells with nitride treatments and thin oxide coatings suggest this route is viable.
- CGS appears to suffer mechanical stability, which could be overcome by synthesis modifications. CGS could potentially serve as the outer coating for a tandem cell and obtain high efficiency.
- DFT has indicated that W is a good dopant for BiVO_4 which we are currently synthesizing.

**FY 2010 Publications/Presentations**

**Papers**


**Presentations**


II.G.5 Characterization of Materials for Photoelectrochemical Hydrogen Production

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• National Renewable Energy Laboratory (NREL) project: subcontract #NFH-8-88502-01 under prime contract number DE-AC36-99GO10337

Project Start Date (UNLV project): October 1, 2004  
Project End Date (UNLV project): December 31, 2010 (no-cost extension)

Project Start Date (NREL project): May 6, 2008  
Project End Date (NREL project): May 5, 2011

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

(H) System Efficiency  
(K) Durability  
(G) Capital Cost

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

• Further studies of the impact of Mo doping/alloying in WO$_3$:Mo/WO$_3$ bilayer structures (with University of Hawaii/Hawaii Natural Energy Institute).
• Investigation of the band gap of a-SiC and its change after surface treatments (with MVSystems).
• Studies of PEC-tested and untested CuGaSe$_2$ samples (with University of Hawaii/Hawaii Natural Energy Institute and NREL).
• Completion of Fe$_2$O$_3$ thin film analysis (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 (XPS) and ultraviolet excitation to determine the occupied electronic states (core levels and valence electrons) and inverse photoemission 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 (XAS) spectroscopy, 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. Results are immediately shared with the collaboration partners and discussed in detail through powerpoint presentations, at phone conferences, and working group meetings. In the brevity of this report, we will focus on one materials class only, namely copper gallium diselenide (CGS) samples grown at the University of Hawaii and PEC-tested at NREL. Results for other material classes (tungsten trioxide, amorphous silicon carbide, and iron oxide) are shown in the annual review presentation.

To demonstrate the chemical insights that can be gained with our experimental tool chest (complementary to the electronic structure information described in last year's report for, e.g., WO$_3$ thin films), we will focus on five samples as described in Table I.

Figure 1 shows Se M-edge and S L-edge XES spectra of the CGS samples and of CdSO$_4$ (top spectrum) and Cu$_2$Se (bottom spectrum, showing a significant Se oxidation and sulfate contamination) references. Sample A (untested CGS) shows a dominant Se M$_{2,3}$ emission line at 143 eV and some weaker features at higher emission energies (three peaks from 152 to 157 eV and one broad peak around 162 eV). The latter are indicative of Se oxide formation and show that the untested CGS sample is weakly oxidized. In contrast, the emission spectrum of Sample B (CGS in H$_2$SO$_4$ electrolyte for 24 hours) is dominated by the sulfate and/or selenium oxide features. The sulfate formation is likely from residual sulfuric acid on the surface of the samples, while selenium oxide formation is likely due to the CGS exposure to the aqueous sulfuric acid solution. Note that the cross section for Se L$_{2,3}$ emissions is significantly larger than that for Se M$_{2,3}$ emission, and thus the observed features are more likely due to sulfate deposition.

The spectra of samples C–E at first glance appear to be similar to that of sample A, but upon closer
inspection significant differences are visible. In particular, the sulfate/selenium oxide peak intensity increases in the order D–C–E.

Additional analysis was performed on the spectrum of sample D in Figure 2 by subtracting the spectrum of sample A (weighted by 0.9) to account for the signal originating from the CGS substrate (difference spectrum shown in red). The difference spectrum is characteristic of sulfur emission (specifically sulfide) with a dominant peak at 146 eV. This suggests that a new sulfur-containing species is present on the surface of the tested sample. Note that this is not a sulfur oxide species, because the characteristic features at emission energies above 153 eV, are notably absent in the difference spectrum. As one possibility, we note that the difference spectrum is similar to that of a copper sulfide (e.g., Cu$_2$S, shown in the same figure, in green), but other sulfides might also play a role.

We thus find that the PEC testing influences the local Se environment at the surface. Additionally, we are able to detect S atoms adsorbed onto the CGS surface after PEC testing, in some cases as a sulfide and in others as a sulfur oxide. We find that the chemical structure of the samples (with respect to the local Se and S environments) varies between samples, and thus allow correlation with the PEC test parameters that were used.

The CGS samples described in Table I were also investigated with XPS at the UNLV lab to elucidate the chemical surface composition after testing. Survey scans of the three samples are shown in Figure 3. In the control sample A, copper, gallium, and selenium are observed (as expected). Significant surface contamination is also found, as indicated by the presence of oxygen and carbon. For the tested samples B and E, the same five elements are detected, but their relative intensities differ. For sample B, the signals ascribed to copper and selenium are enhanced, while the oxygen signal has decreased when compared to the control sample A. Sample E has similarly increased signals of copper and selenium, but the oxygen has decreased much less. Thus, even just based on the survey spectra, a qualitative comparison between the different tested and non-tested samples already reveals significant changes in surface composition.

Detailed spectra (with a smaller energy range and better resolution) of Cu, Ga, and Se core levels were acquired to monitor the chemical changes of the CGS surface as a function of PEC testing. In Figure 4a, the Cu 2p$_{3/2}$ region of all three samples is shown. The peak shape and energetic position of samples B (tested in dark) and E (tested in light) are very similar to that of sample A (untested). Although the copper signal in samples B and E has increased, the copper present on the surface of all three samples appear to be in the same chemical environment. In contrast, the Ga 2p$_{3/2}$ region (Figure 4b) of the untested sample (A) and the tested samples (B and E) are all at different binding energies. The tested samples are at higher binding energies (at about 1,119 eV), while the untested sample is at about 1,117 eV. The Ga 2p$_{3/2}$ (energetic) position of the tested samples is in agreement with reported Ga$_2$O$_3$ values [1]. At first glance, the tested samples (B and E) appear to be similar to each other, but upon
closer inspection, the spectral width of sample E is wider than that of sample B, and the peak maximum of sample B is at slightly higher binding energy. This is an initial indicator that the gallium on the surface of sample E may be in two different chemical environments, one of them possibly identical to that of sample B. We thus find that the details of PEC testing (in particular, dark vs. illuminated) do affect the chemical Ga environment on the surface. In the case for Se, the main peak (at about 53.5 eV) positions are about the same for all three samples. However, the untested sample (A) has an additional peak at higher binding energies which is in agreement with literature values of Se 3d in SeO₂ chemical environments [1], and which has also been previously found by our group on Cu(In,Ga)Se₂ surfaces [2]. This additional peak is absent in the tested samples. This absence could be due to the acid exposure of the samples, which etched away the oxide Se surface atoms.

From XPS, we thus find that the PEC testing influences the local chemical environment of the Se and Ga atoms at the surface. Such results give valuable insights into the atomic-scale effects on PEC candidate material surfaces under operating conditions and will contribute to a guided search for custom-tailored stable PEC materials.

Conclusions and Future Directions

In conclusion, development of the spectroscopic "tool chest" to give a comprehensive picture of the electronic and chemical structure has become a key component of the DOE PEC research and development efforts. Evaluating a variety of PEC candidate materials in view of their electronic and chemical properties has enhanced progress in many of the DOE PEC working group projects. Continued experiments within excellent collaboration structures with a large number of partners of the DOE PEC working group has been critical to recent progress, and is vital to future success in meeting DOE targets. As a result, future directions include:

- Continue the collaborations with our existing partners and bring new partners “on board”.
- 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 2010 Publications/Presentations


8. “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Chemistry and Geochemistry Department at the Colorado School of Mines, Golden, CO, September 25, 2009 (invited).


10. “Using soft x-rays to look into interfaces of energy conversion devices”, Materials Science & Engineering Colloquium (co-sponsored by ECE and Physics), Boston University, December 4, 2009 (invited).

11. “How x-ray and electron spectroscopies can help to tackle the energy problem”, Physics Department, Free University Berlin, Germany, January 20, 2010 (invited).


13. “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Department of Physics, Technical University of Denmark, March 12, 2010 (invited).


References


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 Production section 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

Technical Targets

This project is intended to provide a theoretical understanding of the performance of current PEC materials and provide feedback and guidance for performance improvement.

Accomplishments

- Studied theoretically the properties of Cu delafossite (CuXO₂, X= group-IIIA, or IIIB) materials for PEC water splitting.
- Proposed solution for enhancing the optical absorption for Cu delafossite through symmetry breaking.
- Investigated the effects of W doping in BiVO₄, a potential material for PEC water splitting.

Introduction

Cu delafossites, CuMO₂ (M = group-III elements), have received great attention in recent years due to their potential applications as electrodes for hydrogen production by PEC water splitting and transparent conductive oxides (TCOs) in optoelectronic devices [1,2]. The p-type conductivity and good hole mobility are what make the Cu delafossites so unique and more attractive in these applications than other metal oxides. For instance, due to their p-type nature, the Cu delafossites are resistive against oxidative corrosion. Some recent experimental studies demonstrated that Cu delafossites are stable in solution and are capable of H₂ evolution from water [1,2].

Among the two Cu delafossite families, [CuM⁷⁺O₂ (M⁷⁺=Al, Ga, In) and CuM⁶⁺O₂ (M⁶⁺=Sc, Y, La)], the CuM⁷⁺O₂ family (particularly M⁷⁺=Al) has mostly been considered for p-type TCOs. On the other hand, the focus on the CuM⁶⁺O₂ family has been limited and specifically on the application on H production by solar water splitting. Until now, there has been no solid understanding of which family is better suited for which of the applications.

Despite the similar structures, the CuM⁷⁺O₂ and CuM⁶⁺O₂ families exhibit significantly different electronic properties. The optical measurements indicate that the group-IIIA delafossite family has indirect bandgaps [3,4], and can hardly be doped p-type by extrinsic dopants [5]. On the other hand, the group-IIIB delafossite family has been exclusively reported to have direct wide bandgaps and can be doped by extrinsic dopants.

It is also important to note that the main difference between the requirements for PEC electrodes and TCOs is as follows: PEC electrodes require smaller bandgaps (in the visible region) and an appropriate band-edge alignment, whereas TCOs require larger bandgaps (in the ultraviolet region). We therefore needed to conduct...
a detailed comparative study on the electronic structure between the CuMIIIO₂ and CuMIIIBO₂ families so that these materials can be used for their best-suited applications in optoelectronic devices. Furthermore, we need to develop a method to enhance the optical absorption for the Cu delafossite families.

BiVO₄ has shown particular promise for water photodecomposition with the presence of both a low bandgap (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 effects of dopants on the electronic properties of BiVO₄ have not been well explored.

Approach

We have employed density functional theory (DFT) to study the electronic properties of the delafossite materials and BiVO₄. Generalized gradient approximation (GGA) to DFT and the projected augmented wave (PAW) basis as implemented in the Vienna ab initio simulation package (VASP) [8] are used. A plane-waves cut-off energy of 400 eV was used, and the ion positions were always relaxed until the force on each of them is 0.01 eV/Å or less. To correct the DFT+GGA underestimation of electron correlation of the cation d band, an $U_{\text{eff}} (U=7$ eV) parameter was added to the DFT Hamiltonian for all the valence Cu-d, Sc-d, and Y-d bands. No U was added for the group-IIIA elements because their filled 3d bands are fully occupied shallow core states, which is situated more than 15 eV below the top of the valence band (Al has no d-band). Also, we found that adding an additional U, for example, on the Ga-3d band resulted in a much smaller in-plane lattice a parameter compared to the experimental value. In the case of CuLaO₂, an empty and highly localized f-band is present just above the conduction-band minimum (CBM), and a localized band with d-character is seen in the lower edge of the conduction band. This overall presence of f on top of d character at the CBM makes it particularly sensitive on the choice of U parameter in the DFT+U scheme. In fact, we found that a small U value on the La d-band highly overestimates the bandgap relative to experiment. So, for CuLaO₂, no U potential has been used to La-5d. The choice of U parameter was not found to affect the relative stability of the hexagonal and rhombohedral delafossite structures. For BiVO₄, we found that U parameters were not needed.

Results

We first discuss the structure preferences for the group-IIIA and -IIIB delafossites. The delafossite structure can have either $P6/mmc$ ($#194$) or $R3m$ ($#166$) space-group symmetry, depending on the stacking sequencing of the O–M (M = group-IIIA and -IIIB) octahedron layers. Our total energy calculation revealed that group-IIIA delafossites prefer the rhombohedral group (R3m), whereas group-IIIB delafossites favor the hexagonal group (P6/mmc), which is in good agreement with experimental observation. In both symmetries, O and Cu form linear bonding structure along the c-axis, which is considered to be the main channel for the hole transport, whereas O–M bonds form distorted octahedra.

Figure 1 shows the calculated band structure for the group-IIIA and group-IIIB delafossites in rhombohedral and hexagonal structures, respectively. Our results reveal that although the CuMIIIO₂ and CuMIIIBO₂ delafossites have a similar local structure environment, they have very different electronic properties. Comparing the band structures for the CuMIIIO₂ and CuMIIIBO₂ delafossites, we find that the nature of the valence band is similar for both group-IIIA and -IIIB families. As mentioned earlier, the valence-band maximums (VBMs) are mainly composed of Cu-d and O-p orbitals. However, for hexagonal CuMIIIO₂ band structures (lower panel in Figure 1), the occurrence of the VBM at the H point is no longer observable in all cases. For example, for CuScO₂, the VBM is still at H-point, but for CuYO₂ and CuLaO₂, the VBM appears to be at the Γ point. Larger variations are seen between the CBM of the group-IIIA and group-IIIB delafossites.

**FIGURE 1.** Calculated electronic band structure of group-IIIA (upper panel) and group-IIIB (lower panel) delafossites along the high-symmetry lines of the first Brillouin zone.
The biggest difference is that at the $\Gamma$ point, the $s$-band-derived CBM in the Cu$^{III}$BO$_2$ family is not as deep as compared to that in the Cu$^{II}$BO$_2$ family. First, comparing the band structure of CuScO$_2$ and CuGaO$_2$, we clearly see the much lower CBM due to Ga-4s band in the later at $\Gamma$ point. For CuScO$_2$, the presence of unoccupied Cu-3$d$ states at the CBM ($\Gamma$ point) makes it much less dispersive. Secondly, for Ga, all its 3$d$ bands are occupied and are situated at much higher binding energy below the Fermi level, and they do not contribute much to the conduction band. At the L point, significant Ga-$s$ contribution along with $p$ character is seen for CuGaO$_2$. In contrast, for CuScO$_2$, the $d$ contribution is significant at the L point of the conduction band because of its partially filled Sc-3$d$ nature. In addition, unoccupied $f$ bands are present in the conduction band in CuLaO$_2$ which affect the CBM significantly. In principle, all the differences identified above can be attributed to the differences in electronic configurations between group-III and -IIIB elements. The detailed discussions can be found in Ref. [9]. Our results explain well the experimentally reported bandgap trends for Cu$^{III}$BO$_2$ delafossites.

We have also calculated the optical transition matrix elements for the band edges of group-IIIB delafossites at the special symmetry points as shown in Figure 1. Only the diagonal components (direct gap) of the momentum matrix were calculated, because the off-diagonal elements would not contribute significantly to optical absorption. In all cases, the transition between VBM and CBM at the $\Gamma$ point is forbidden (zero transition matrix elements), because of mainly $d$ character for both VBM and CBM and transition would result in a parity violation. Therefore, for the application for PEC water splitting, Cu delafossites have too weak absorption, particularly for visible light.

The zero contribution to the optical absorption at the $\Gamma$ point is due to the inversion symmetry of the delafossite structure. For efficient PEC water splitting, the optical absorption of Cu delafossites must be enhanced significantly. We found that significant band-structure modification can be achieved by isovalent alloying of Cu-based delafossites. This alloying significantly improves the optical absorption at lower energy because it reduces the crystal symmetry; thus, it lifts the parity-forbidden transition near the band edge, which exists in the pure delafossite compounds. Moreover, the bandgap of the quaternary delafossite alloy can be further tuned through alloy composition and ordering, thus improving the flexibility in designing delafossite-based PEC photo-electrodes. Figure 2 shows a few examples of mixed Cu delafossites. Figure 2(a) shows the structure of Cu(Y,Ga)O$_2$, where Ga substituted at Y site with a 1:1 ratio. The crystal structure (type-I), Ga- and Y-based octahedrons are separated by the O-Cu-O chain, i.e., Ga and Y are not present in the same octahedron layers. Figure 2(b) shows the structure (type-II) with the same composition of the structure shown in Figure 2(a). However, Ga and Y are present in the same octahedron layers. Figure 2(c) shows the structure of Cu(Y,Ga,In)O$_2$, where the ratio of Y:Ga:In is 2:1:1.

Figure 3 shows the calculated optical absorption coefficient for the three isovalent alloys. For comparison, the optical absorption coefficient of pure CuYO$_2$ is also given. Due to this mixed nature of the CBM, the transition matrix element is no longer zero. However, the matrix element is still not very large because for this isovalent alloy, the wavefunction mixing is relatively small. Nevertheless, the breakdown of the inversion symmetry should help to improve the near-band-edge absorption. The 50%-50% alloy, however, has an indirect bandgap with its VBM away from $\Gamma$, which may not be desirable for PEC application. However, this can be remedied by further band engineering, e.g., by reducing the Ga concentration. The absorption onset
of the type-II alloy is slightly lower in energy; however, the absorption increase is faster for the type-I layer structure, and both show remarkable improvements over bulk CuYO\textsubscript{2}. The direct bandgap for Cu(Y,Ga,In)O\textsubscript{2} at Γ point is 1.725 eV. Close inspection of the absorption curve also shows the onset of absorption at the same energy. This indicates that first, the bandgap is reduced further from the type-I and type-II alloys, and second, the absorption at the Γ point is not suppressed.

BiVO\textsubscript{4} is a promising photocatalyst for hydrogen generation, with demonstrated experimental potential in terms of bandgap, stability, and conductivity. Recent experiments have shown that doping of W can significantly enhance the PEC performance of BiVO\textsubscript{4}. Therefore, we have calculated the doping effects of W in BiVO\textsubscript{4}.

Figure 4 shows our preliminary results of doping of W in BiVO\textsubscript{4}. Figure 4(a) shows the calculated band structure of a BiVO\textsubscript{4} supercell with one W at a V site. We found that the band structure is very similar to that of pure BiVO\textsubscript{4}, indicating that substitutional W at V sites do not create any deep level in the bandgap and the W’s states are much higher in energy than the CBM. This is seen in the site projected density-of-state plot shown in Figure 4(b). These results indicate strongly that substitutional W atoms at V sites are degenerate donors, which are the most preferred donor states. We have also considered substitutional W atoms at Bi sites. We found that they are also shallow donors. However, our preliminary results indicate that W prefers the V site more than Bi due to better atomic size matching.

**Conclusions and Future Directions**

We have calculated the electronic structure of Cu delafossites and W doping in BiVO\textsubscript{4} using DFT. We have provided a detailed understanding on the different electronic structure for group-IIIA and group-IIIB delafossites. We have understood why the Cu delafossites have insufficient optical absorption in the visible-light regime, and we have demonstrated that significant bandgap modification can be achieved by isovalent alloying of Cu-based delafossites. This alloying significantly improves the optical absorption at lower energy because it reduces the crystal symmetry, thus lifting the parity-forbidden transition near the band edge, which exists in the pure delafossite compounds. Moreover, the bandgap of the quaternary delafossite alloy can be further tuned through alloy composition and ordering, thus improving the flexibility in designing delafossite-based PEC photo-electrodes. Our preliminary results have shown that W doping in BiVO\textsubscript{4} may enhance the n-type conductivity. In future study, we will provide a detailed understanding of defect physics in BiVO\textsubscript{4}, including the formation energies and transition energies of intrinsic and extrinsic defects.

Future directions will include the following:

- Perform a detailed study of defect physics in BiVO\textsubscript{4}.
- 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, and sulfides.

**FY 2010 Publications/Presentations**

II.G Hydrogen Production / Photoelectrochemical


**References**


II.G.7 Progress in the Study of Amorphous Silicon Carbide (a-SiC) as a Photoelectrode in Photoelectrochemical (PEC) Cells

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-H_2 plant production cost by 2010 and $5/kg by 2015. Table 1 shows detailed milestones year by year.

TABLE 1. Progress towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production using Amorphous Silicon Carbide-Based (a-SiC) Compound Films

<table>
<thead>
<tr>
<th>Task #</th>
<th>Milestone Note</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year 1</td>
<td>Material photocurrent ≥ 3 mA/cm². Achieved</td>
<td>≥ 100 hours</td>
</tr>
<tr>
<td>Year 2</td>
<td>Material photocurrent ≥ 4 mA/cm². Achieved</td>
<td>≥ 200 hours</td>
</tr>
<tr>
<td></td>
<td>Device STH efficiency ≥ 5%</td>
<td>32% Achieved</td>
</tr>
<tr>
<td>Year 3</td>
<td>Device STH efficiency ≥ 6.15% over 300 hours</td>
<td></td>
</tr>
<tr>
<td>Year 4</td>
<td>Device STH efficiency ≥ 7.5% over 500 hours</td>
<td></td>
</tr>
</tbody>
</table>

Accomplishments

- Improvement in a 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:
  - Photocurrent of a solid-state PV/a-SiC/indium tin oxide (ITO) (illuminated through ITO) device exhibited ~5 mA/cm².
  - Photocurrent of an actual PV/a-SiC PEC device increased to 1.26 mA/cm², or equivalent to a STH efficiency of ~1.6%.
  - Good durability in pH_2 buffered electrolyte for up to 200 hours.

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 Fuel Cell Technologies
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 mA/cm² and with sufficient durability to meet the lifetime requirement is 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 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 (June 2009–June 2010), 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 of amorphous silicon carbide-based compound films is detailed in the following subsections.

During this project period, further improvement of the PEC performance of the hybrid PV/a-SiC device has been made. Figure 1 shows a schematic diagram for the solid-state version of the hybrid PEC device, with ITO as the top contact. Using this configuration, we aimed to optimize both the a-SiC photoelectrode and the a-Si tandem solar cell beneath the photoelectrode. Under AM1.5 Global spectrum, we have so far achieved a photocurrent of ~4.2 mA/cm² (at 1.23 V), indicating a potential STH efficiency of >5%.

In actual hybrid PV/a-SiC devices, due to existence of interfacial barrier at a-SiC/electrolyte interface, extraction of photocurrent is found to be severely suppressed, leading to a very low photocurrent of <1 mA/cm² (see Annual Report 2009). To overcome the over-potential loss, we have performed a wide variety of surface modifications on the hybrid device, including hydrofluoric acid (HF) etch (to remove thin SiOₓ on the surface) and metal nanoparticle treatment. As a result, photocurrent of the hybrid device is increased. Figure 2(a) shows current vs. potential characteristics of devices performed before and after HF etching. The testing conditions were: set-up - 2-electrode; light source - AM1.5G (calibrated with a reference cell); counter
electrode: RuO$_2$ (ruthenium oxide); electrolyte: pH$_2$ buffer + Triton-X; HF etch: using HF 5% for 1.5 minutes. It is seen that photocurrent at zero potential reaches ~1.3 mA/cm$^2$, or an equivalent STH efficiency of ~1.6%.

In addition, we also performed surface treatment on the a-SiC photoelectrode and the hybrid PV/a-SiC device using metal nanoparticles, including platinum (Pt), gold/palladium (Au/Pd) and titanium (Ti). Figure 2(b) shows a scanning electron microscope photo image on a Ti nanoparticle coated sample. The metal nanoparticle layer was fabricated using sputtering method, and the size of nanoparticles is of a few nanometers. We have observed that the metal with lower metal function (e.g., Ti) is more effective in enhancing photocurrent than those metals with high work function (e.g., Pt, Au/Pd). This behavior is probably due to the surface barrier caused by the high work function metals. Work is currently underway to understand the mechanism, and to explore other surface modification methods in order to further enhance the photocurrent.

We have also made progress in further increasing the durability of the hybrid devices, which exhibits good durability for up to 200 hours. Figure 3 shows the current vs. potential characteristics of a hybrid device, measured during the course of the durability test. Compared with the initial current density-voltage (J-V) curve (black), the dark current shows virtually no increase, indicating no corrosion on the device; whereas the photocurrent shows a slight increase, possibly due to changes in the surface structure (the mechanism behind these changes is not well understood). The surface of the device shows a color change but remains largely smooth (not shown here).

**Conclusions and Future Directions**

This 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 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, surface treatments (a-SiC, CGSe, WO$_3$), bilayer formation (WO$_3$) and new device integration schemes (CGSe and WO$_3$). Bulk modifications were also investigated, such as partial copper replacement with silver to form ACIGSe film to modify energy band position. Resulting interface and bulk energy band positions will be characterized using advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.
FY 2010 Publications/Presentations


II.G.8 Progress in the Study of Tungsten Oxide Compounds as Photoelectrodes in Photoelectrochemical Cells

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Contract Number: DE-FG56-07GO17105
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, synthetic 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-chalcopyritecompound 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 Fuel Cell 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 Synthesis

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. Progress Towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production with Tungsten Oxide-Based Compound Films.

<table>
<thead>
<tr>
<th>Task #</th>
<th>Milestone</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year 1</td>
<td>Material photocurrent ≥ 3 mA/cm²</td>
<td>Achieved</td>
</tr>
<tr>
<td></td>
<td>Durability ≥ 100 hours</td>
<td>Achieved</td>
</tr>
<tr>
<td>Year 2</td>
<td>Material photocurrent ≥ 4 mA/cm²</td>
<td>90% (3.6 mA/cm²) with bilayer</td>
</tr>
<tr>
<td></td>
<td>Durability ≥ 200 hours</td>
<td>50% (100-hours so far tested)</td>
</tr>
<tr>
<td></td>
<td>Device STH efficiency ≥ 5%</td>
<td>62% demonstrated</td>
</tr>
<tr>
<td></td>
<td>GO/NO-GO decision evaluated (End of 2010)</td>
<td></td>
</tr>
<tr>
<td>Year 3</td>
<td>Device STH efficiency ≥ 6.15% over 300 hours</td>
<td></td>
</tr>
<tr>
<td>Year 4</td>
<td>Device STH efficiency ≥ 7.5% over 500 hours</td>
<td></td>
</tr>
</tbody>
</table>

Accomplishments

- Foreign element incorporation into WO₃ lattice using house-made sputtering targets.
- Successful fabrication of RuO₂ nanoparticles and nanorods onto tungsten oxide thin films with improved catalytic activity (up to 20%).
- Evaluation of new integration using highly textured substrates to increase photocurrent density.
**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 2009–June 2010), 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. Specific progress in developing tungsten oxide-based compound films is detailed in the following subsections.

In our general approach, each component of the PEC electrode is addressed, from the absorber (bulk) to the surface energetics (near-surface) and catalysis (surface). This year, progress was achieved toward foreign element incorporation to reduce tungsten oxide bandgap. Here, we proposed to fabricate in our laboratory our own sputtering targets made of blended powders. With this method, the amount of both WO₃ and foreign elements can be easily controlled, leading to a much easier elaboration process when compared to co-sputtering techniques. Preliminary tests were done with WO₃ nanopowder only. After compaction and sintering at 1,200°C for 3 hours, the solid WO₃ body (2-inch diameter disc) was transferred to the sputtering chamber and several depositions were performed. Initial results indicated that WO₃ optoelectronic properties (optical transmission and bandgap) were easier to control when compared to initial process where a pure tungsten target is used. Photo-electro-chemical tests pointed out also that comparable performances were obtained with this method. In a second phase, powder blends were sintered to form new sputtering targets. Since nitrogen has been evaluated as possible foreign element candidate to decrease WO₃ bandgap, our research was initially focused on nitride-based powder. A top-view scanning electron microscopy (SEM) micrograph of a WO₃:BN (95 wt% / 5 wt%) is presented in Figure 1. Again, a very good powder sintering is observed (coalesced grains), leading to a solid body. Depositions of WO₃:BN materials are currently being performed to define optimum process parameters.

Research on tungsten oxide surface catalytic treatment continued and major improvements on RuO₂ nanoparticles and nanorods synthesis were achieved. Preliminary research in our laboratory on reactively sputtered RuO₂ thin films already demonstrated high catalytic activity for oxygen evolution reaction, where O₂ was generated with overpotential as low as 0.2 V. Nanoparticles (4-8 nm in diameter) were synthesized on WO₃ thin film using similar reactive sputtering process (Ru pure target, O₂/Ar ambient, 250°C). Current vs.
voltage characteristics measured on WO₃ PEC electrode covered or not with RuO₂ nanoparticles are presented in Figure 2. No modification of both the dark current and saturated photocurrent was observed in this experiment. However, one can notice that the presence of RuO₂ nanoparticles on WO₃ thin films yield a better “fill-factor” when compared to the WO₃ witness sample, with a photocurrent increase of about 20% at 1.2 V vs. the saturated calomel electrode. Current research is focused on ruthenium oxide nanorods (120 nm long, 20 nm wide) synthesis. It is believed that extended contact area between nanorods and the electrolyte could improve charge carriers injection at the WO₃/electrolyte interface.

Finally, the possible use of highly textured substrates (HTS) in PEC applications to increase the photocurrent density was evaluated in our laboratory. With this technique, the developed area is expected to be larger than the projected one, increasing the overall photocurrent density (normalized to the sample area). HTS used were obtained by anisotropic etching of silicon wafers using potassium hydroxide (KOH) solution. Because of orientation-dependant etching ([110]>[100]>[111]), KOH treatment leads to a textured Si substrate made of pyramids with base width ranging from 5 to 20 µm. Tungsten oxide was then deposited on HTS using reactive sputtering technique. Figure 3 presents a cross-section SEM micrograph of one of this sample. The PEC performances of WO₃ thin films deposited on HTS are presented in Figure 4. Also presented in this graph are the PEC performances measured on a WO₃ deposited on flat silicon substrate (control sample). To allow a direct comparison, photocurrent density values were normalized to the maximum photocurrent density measured in the case of a flat silicon substrate at 2.5 V vs. SCE. First, one can directly observe the net photocurrent density increase when HTS are used. It is also interesting to note that a higher fill factor is achieved with HTS. Thus, it is believed that, in addition to the geometric factor, the HTS enable better harvesting of incoming normal irradiance, either by limiting the surface reflection or simply by increasing the optical path in the tungsten oxide thin film.
Conclusions and Future Directions

This 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 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 performance. New surface modification techniques were investigated, surface treatments (a-SiC, CGSe, WO$_3$), bilayer formation (WO$_3$) and new device integration schemes (CGSe and WO$_3$). Bulk modifications were also investigated, such as partial copper replacement with silver to form ACIGSe film to modify energy band position. Resulting interface and bulk energy band positions will be characterized using advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.

FY 2010 Publications/Presentations


II.G.9 Progress in the Study of Copper Chalcopyrites as Photoelectrodes in Photoelectrochemical Cells

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DOE Project Officer: David Peterson
Phone: (303) 275-4956
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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, 2011

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 Fuel Cell 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-$5/kg by 2015. Table 1 shows detailed milestones year by year.

TABLE 1. Progress towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production with Copper Chalcopyrite-based Materials

<table>
<thead>
<tr>
<th>Task #</th>
<th>Milestone</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year 1</td>
<td>Material photocurrent ≥ 3 mA/cm²</td>
<td>Achieved</td>
</tr>
<tr>
<td></td>
<td>Durability ≥ 100 hours</td>
<td>10%</td>
</tr>
<tr>
<td>Year 2</td>
<td>Material photocurrent ≥ 4 mA/cm²</td>
<td>Achieved</td>
</tr>
<tr>
<td></td>
<td>Durability ≥ 200 hours</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>Device STH efficiency ≥ 5%</td>
<td>*Pending Fabrication</td>
</tr>
<tr>
<td></td>
<td>Go/No-Go decision evaluated (End of 2010)</td>
<td></td>
</tr>
<tr>
<td>Year 3</td>
<td>Device STH efficiency ≥ 6.15% over 300 hours</td>
<td></td>
</tr>
<tr>
<td>Year 4</td>
<td>Device STH efficiency ≥ 7.5% over 500 hours</td>
<td></td>
</tr>
</tbody>
</table>

*Components are available that, combined numerically, can achieve 5% STH efficiency

Accomplishments

• Material photocurrents are in excess of goals.
• Surface and bulk modifications are improving feasibility of completed device.
• Planned device can achieve 5% STH efficiency.
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 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 CIGSe, CGSe, etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) are 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

Progress in the study of copper chalcopyrite-based thin films of the formula \( (\text{Cu} \text{Ag}_{1-x}) \text{In}_{y} \text{Ga}_{1-y} \text{Se}_{1-z} \) for PEC water splitting this period has been focused on device integration. While copper chalcopyrite-based films are capable of high photocurrents, band misalignments currently preclude current extraction without superfluous external voltages. This particular problem has been addressed through bulk, surface and device modifications.

The typical baseline absorber film is CuGaSe₂ (CGSe), which has the highest attainable bandgap in the Cu(InₓGa₁₋ₓ)Se₂ system of ~1.68 eV. CGSe is capable of high photocurrents but only at an impractically high external voltage bias. Bulk modification has led to the best cells produced in this material class which are CuInGaS (CIGS) films (fabricated at the Helmholtz Zentrum Berlin in 2009). While performing well, these “sulfide” cells are still inadequate for a monolithically integrated hybrid (photovoltaic [PV]/PEC) photoelectrode (HPE) device shown in Figure 1 where voltage is supplied by underlying PV cells harvesting passed sub-bandgap photons.

Bulk modification was also pursued by replacing Cu with Ag, which can raise the bandgap and more properly align the band edges. Films were fabricated with a formula of Ag(InₓGa₁₋ₓ)Se₂ (AIGSe) with a bandgap only slightly lower than CGSe showing an expected n-type conduction, which is not ideal but, with a sufficient voltage, photocurrents nearly as high as that in typical CGSe films (~15 mA/cm²) could be extracted from AIGSe films (Figure 2). These films showed that Cu replacement with Ag did indeed move the band edges, but full replacement moved them an extreme amount beyond our desired levels. Further tests exploring partial replacement of Cu with Ag will
Surface modifications were also performed with PdAu nanoparticles sputtered onto the surface of CGSe films. The results, shown in Figure 3, show an improvement in the “fill factor”, however, onset voltage remains unchanged. These surface treatments can be used to extract a few more mA/cm² of any as-fabricated film in this material class.

Currently unable to monolithically integrated devices, Figure 4 shows a co-planar HPE device. The DOE goal of 5% STH can be theoretically (from numerical calculations) achieved using available materials. This device is of course impractical, however it develops a pathway towards creating a viable device. Work is underway to both fabricate these cells as standalone devices and improve upon their design.

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, surface treatments (a-SiC, CGSe, WO₃), bilayer formation (WO₃) and new device integration schemes (CGSe and WO₃). Bulk modifications were also investigated, such as partial copper replacement with silver to form CAIGSe film to modify energy band position. Resulting interface and bulk energy band positions will be characterized using advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.

FY 2010 Publications/Presentations


II.G.10 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Contract Number: DE-FG36-05GO15028
Subcontractors:
• University of Toledo, Toledo, OH
• National Renewable Energy Laboratory (NREL), Golden, CO

Project Start Date: April 1, 2005
Project End Date: December 31, 2011

Objectives
• To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin-film silicon (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 Photoelectrochemical Hydrogen Production section (3.1.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYPP):
(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 this project towards achieving the DOE MYPP technical targets for PEC production of hydrogen for 2015 is:

<table>
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<th>Characteristic</th>
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TCCR = transparent, conducting and corrosion-resistant; PAS = photoactive semiconductor; PV = photovoltaic

Accomplishments
• A 12”×12” substrate-type PEC cell model was fabricated and has been tested twice so far, however leaks exist in the framework.
• TCCR coatings and H₂ evolution catalysts were developed (Task 1).
For use as TCCR material In$_2$O$_3$-Fe$_2$O$_3$ work was completed and published in the Journal of Materials Research.

Large-area electroplating of porous Ni as H$_2$ evolution catalyst has been developed using precursor salts in order to improve and optimize the porous structure of the films for improved performance.

Facilities for large-area processing of substrate-type PEC cells have been established; processes for PEC components are under development (Task 5).

The effect of back reflector on amorphous silicon (a-Si) photoelectrodes was studied and material properties were optimized.

The current collection grid for a-Si photoelectrodes, which will incorporate a PAS layer, was optimized considering optimal bus bar thickness.

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**Introduction**

This project 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 (μc-Si) as the narrow band gap absorber material.

In this project 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/μc-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/μc-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.

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**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.

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**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 completion of work on fabricating and characterizing In$_2$O$_3$-Fe$_2$O$_3$ films; results and findings were published in the Journal of Materials Research. The TCCR films were deposited using radio-frequency magnetron sputter deposition in argon and oxygen using multiple sputter guns simultaneously. From the completed work, the results indicate that samples made at 250°C with 30 W of In and 100 W of InFe$_2$O$_4$ and a sputter deposition time of ninety minutes produced optimal results.

Under Task 2 a method for large-area electroplating of porous Ni used as H$_2$-evolution catalyst has been developed. Over the past year work has focused on the addition of precursor salts such as zinc chloride, zinc nitrate, and copper sulfate to the plating solution in order to improve micro- and macro-structures of the porous nickel films. The method uses the co-deposition of Ni and Zn (or another precursor metal) onto the back-side of tf-Si photoelectrodes; after Ni/Zn electrodeposition Zn is leached out leaving a porous Ni-structure behind. At this stage of research, zinc chloride shows the best results, which is shown in Table 2. The goal of electroplated nickel project is to develop materials that meet or exceed the performance of the industry standard of platinum-coated nickel. Table 2 is presented to show results from our latest experiments to improve upon the standard that we have developed previously in our lab.

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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. Thin film Si-based PEC cells employ preferentially back reflectors for re-directing unabsorbed incident light back through
the semiconductor layer enhancing the solar-to-hydrogen conversion efficiency of the device. A study was conducted addressing the long-term reliability of the back-reflector: tests conducted in a high humidity environment were used for evaluating the device stability. The fill factor for devices employing different back-reflector films were measured after numerous hours of highly accelerated stress test exposure. The experimental variable in this study is the composition of the back-reflector the tf-Si material is deposited onto. We tested numerous back-reflector compositions and we identified a specific composition providing the best stability under hot and humid conditions, which will translate into improved long-term reliability of PEC cells. We are planning to use this back-reflector for fabricating large-area PEC systems.

Conclusions and Future Directions

The proposed future work will include:

- Continue optimization of present oxide materials suitable for TCCR coatings:
  - Material class studies will be focusing on In$_2$O$_3$-Co$_2$O$_3$.
- Continue optimization of present oxide materials suitable for PAS coatings:
  - Material class studies will be focusing on Fe$_2$O$_3$-WO$_3$.
- 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 (1 ft×1 ft) 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 analysis and energy analysis for the PEC systems for hydrogen production.

FY 2010 Publications/Presentations


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II.G.11 Photoelectrochemical Generation of Hydrogen*

Technical Targets

- Solar-to-hydrogen (STH) efficiency: 10% by 2015 by developing photoanodes having efficient light absorption in the visible range and a long-term corrosion resistance.
- Hydrogen production cost: $3.00/gge (approximately 1 kg of H₂) by 2018 by optimizing the generation process and the storage of hydrogen.

Accomplishments

- Plasma treatments of photoanodes for (a) minimizing charge carrier traps and contaminants, (b) doping the photoanode surface with nitrogen, and (c) creating oxygen vacancies for achieving high photocurrent density.
- Optimization of the surface structure of the nanotubes to improve light absorption.
- Use of layered electrodes of titanium disilicide (TiSi₂) and titanium dioxide (TiO₂) for light absorption in the visible range.
- Development of processes for synthesizing layered patterned nanotubular electrodes.
- Increased photocurrent density by more than 80% by plasma treatments and enhanced light absorption by 55% with modified nanotubular structure.
- Patent application and publication of papers reporting our work.

Introduction

During the last four decades, PEC production of hydrogen has been intensively investigated due to the advantages of the PEC method: (1) potential for direct conversion of sunlight for generating pure hydrogen, (2) high quantum efficiency of several semiconductors over nearly the entire spectrum of solar radiation, (3) possible application of inexpensive and environmentally safe materials for large scale operation, and (4) relatively low capital and operating costs.

The current barriers that prevent commercialization of the PEC technology for hydrogen production are: (1) lack of semiconducting materials that will have two essential properties: (a) bandgap for harvesting sunlight from 360 to 860 nm in wavelength for splitting water into hydrogen and oxygen and (b) high corrosion resistance of the semiconducting photoanodes during electrolysis of water, and (2) poor transfer efficiency of the photo-generated charge carriers at the interface between the solid electrode and the liquid electrolyte.
No single or compound semiconductor photoanode has been found which satisfy these critical requirements [1-3]. Several nanostructural designs have emerged as are the choices of materials, but an efficient process with optimal photo-conversion efficiency is yet to be realized for commercialization of the PEC process. The aim of our project is to engineer chemically stable photoanodes which will have a bandgap with high light absorption efficiency and yet straddle the reduction and oxidation chemical potentials of water and meet the DOE goals for hydrogen production.

**Approach**

To address the current barriers, our approach is to develop a hybrid nanostructured photoanode comprised of thin-film layers of TiO₂ covering nanotubes of TiSi₂. The latter has a high efficiency in light absorption covering the visible solar spectrum. The layered nanotubular electrodes can be arranged in a patterned array for trapping sunlight, providing large effective area for electrolysis, and corrosion protection by the titania film.

The photoactive materials from the silicide and titania family have the potential to overcome deficiencies of single metal oxide photoanodes. While the nanostructure greatly improves the reaction surface area and light absorption, the efficiency of the charge carrier transport and the corrosion resistance need to be investigated for different heterostructures including layered films, nanotubes and nanoparticles.

Interfacial charge carrier transfer phenomena govern the PEC-based hydrogen generation process. While the role of surface and interface states in the charge carrier transport and the necessity for matched lattice structure in using heterostructured semiconductors (such as TiO₂ and TiSi₂) have been reported in the literature, the chemical and physical control mechanisms for mitigating the losses due to the presence of charge carrier traps and minimization of photocorrosion of the electrodes are yet to be established. Fundamental studies are needed in the design of the PEC process, including the synthesis of nanostructured photoanodes to provide the desired bandgap, surface structure, and corrosion resistance. Optimization of operational parameters such as the optical system for collecting sunlight, collection, storage of hydrogen, and the control system for monitoring the safety and production efficiency of the process needs to be pursued. Our experimental studies are aimed to: (1) remove surface contaminants [3-8] and surface states that act as charge carrier traps, (2) apply plasma surface modification [9-11], using a reactor as shown in Figure 1, for surface cleaning as well as for surface doping of the photoanodes with n-type dopants (N), (3) optimize the structure of the nanotubes by varying anodization voltage for increasing light absorption, (4) use layered electrodes of TiSi₂ and TiO₂, and (5) evaluate surface-modified nanostructured layered photoanodes for photoelectrochemical generation of hydrogen.

**Experimental Studies**

TiO₂ semiconductor has been extensively used for PEC-based hydrogen production. It has an ionic crystal structure and its surface lattice oxygen ions are not surrounded by Ti cations on a clean surface. These surface oxygen atoms act as donor surface states in the gap region above the valence band edge. These donor states can increase the production of photogenerated electrons in the visible range but the donor states at the surface act as efficient traps for the holes and reduces the PEC oxidation of water. Similarly, the adsorbates on the electrode surface can form chemical bonds with the atoms of surface contaminants forming extrinsic surface states. We have used helium plasma treatment for minimizing the density of these extrinsic surface states which improved the charge carrier transport significantly.

As the surface adsorbates [9-13] were removed by helium plasma cleaning, the surface atoms of TiO₂ are exposed. The dangling bonds of the metal and the oxygen atoms on the surface give rise to acceptor and donor states respectively. For an n-type semiconductor like TiO₂, it is desirable to have vacant acceptor states to increase the barrier height φ. Nitrogen plasma treatment was used to increase vacant acceptor states and the barrier height enhancing the migration of holes from the electrode surface to the electrolyte for oxidizing water.

A self-assembled vertically ordered nanotubular TiO₂ array, which has been considered to be an ideal architecture for photoelectrolysis, was synthesized and used in this study. The development of nanotubular electrode structure resulted in a significant improvement of electron conduction, rapid diffusion of holes for oxidation, and an increase of the effective surface area of the photoanodes. The nanotubular structure increases the effective surface area for light absorption.
as well as for photocatalysis, however, nanostructured surface increases the density of surface states which can affect photoactivity either positively or negatively depending upon if these sites are electron traps or hole traps. Minimizing the surface density of the hole traps is essential for oxidizing water with n-type photoanodes. We used nitrogen plasma for minimizing the hole traps.

Recent studies report that TiSi₂ (a) has a significant absorption of light over most of the AM 1.5 solar energy spectrum ranging from 1.4 eV (λ≈860 nm) to 3.4 eV (λ≈360 nm), (b) is photoactive in generating hydrogen by splitting water, but (c) has a low photocorrosion resistance. Our experiments showed light absorption of TiSi₂ micro-particles in the visible range of the solar spectrum providing a photocurrent density of 3.0 mA/cm² when we used TiSi₂ particles along with TiO₂ nanotubular photoanode. We are investigating different structures of TiSi₂ photoanodes covered by a thin TiO₂ film to maximize light absorption while protecting the electrodes against photocorrosion.

The test photoanodes prepared for evaluating the photoelectrolytic properties were annealed under both oxygen and nitrogen atmospheres achieve crystallization of TiO₂ in its anatase form.

The PEC apparatus used for measuring photocurrent density of the test photoanodes under dark and illuminated conditions consisted of (1) a potentiostat/galvanostat electrochemical instrument model 283, (2) a Xenon lamp (30 mW), (3) a 60 mm-diameter quarts optical window, and (4) a reference electrode (Ag/AgCl) placed close to the photoanode. The electrolyte used was 1M potassium hydroxide (pH~14) + deionized water solution.

**Results**

X-ray photoelectron spectroscopy (XPS) analysis indicated the incorporation of N in titania lattice structure of the photoanode surface. As shown in Figure 2, the narrow scan N 1s spectrum is demonstrated at 400 and 396 eV, which has been ascribed to the presence of nitrogen in the lattice structure either as substitutional dopants for O, or as interstitial dopants in the TiO₂ crystal structure.

Nitrogen plasma treatment of titania photoanodes resulted in 80% increase in photocurrent density as shown in Figure 3. Plasma surface cleaning with helium plasma and surface doping by nitrogen plasma increased photocurrent density of titania nanotubular electrodes.

Stepped-voltage anodization was used to synthesize titania nanotubes of variable diameters. Photocurrent density vs bias voltage plotted for samples anodized at different voltages. Annealing of the photoanodes was modified. The results (Figure 4) showed enhanced light absorption and increased photocurrent density by 55%. Several deposition processes for developing heterojunction TiO₂/TiSi₂ photoanodes have been
studied; an e-beam deposition system has been installed for depositing thin films of different photoanode materials. An electrospray system has been designed and constructed for electrostatic coating of \( \text{TiSi}_2 \) particles with nanoparticles of \( \text{TiO}_2 \).

**Conclusions and Future Directions**

Our experimental studies with plasma surface treatments with helium and nitrogen gas show clearly an increase of photoanode current density compared with the untreated surface of the electrodes. The nitrogen plasma treatment increased acceptor surface states and improved performance of the \( \text{TiO}_2 \) photoanodes. Surface cleaning of the photoanode by low-temperature helium plasma treatment removed a major fraction of the contaminants (adsorbates) from the surface.

The present work reports the importance of systematic investigations of (1) the geometric structure of the nanotube arrays, (2) the plasma treatment process for surface doping of \( \text{TiO}_2 \) nanotubular photoanode with \( \text{N} \) for increasing oxygen vacancies and (3) annealing process for crystallization for improving photocatalytic generation of hydrogen from water. The test results show promising aspects of tuning several parameters involved in PEC processes in improving conversion efficiency.

**Plan for Future Studies**

- Develop patterned nanotubular layered \( \text{TiSi}_2 \) and \( \text{TiO}_2 \) photoanodes.
- Study methods for (1) optimizing the film thickness (in the nm range, to improve tunneling) of \( \text{TiO}_2 \) (2) matching the crystalline structures of the layered semiconductors and (3) reducing the interface states in the heterojunction semiconductors and the electrolyte by passivating the surfaces involved.
- Characterize interfacial states between the \( \text{TiSi}_2/\text{TiO}_2 \)/electrolyte junction by determining the optical absorption spectrum, durability and photocurrent density.
- Develop multi-junction (\( \text{TiSi}_2 \) and \( \text{TiO}_2 \)) nanotubular electrodes to enhance the absorption of solar radiation in the visible range. Measure light absorption vs. \( \lambda \).
- Measure photocurrent conversion efficiency (incident photon conversion efficiency vs \( \lambda \), corrosion resistance, and photo-generated carrier concentration decay rate by using a radio frequency conductivity probe.
- Optimize the PEC process for developing layered photoanodes and minimize the density of interfacial charge carrier traps by hydrogen plasma passivation followed by nitrogen plasma treatments.

**FY 2010 Publications/Presentations**

**Patent Application**


**Publications**


**Conference Abstracts**

References

II.G.12 Characterization and Optimization of Photoelectrode Surfaces for Solar-to-Chemical Fuel Conversion

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Project Start Date: March 1, 2010
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Understand the underlying mechanism of surface corrosion of semiconductor-based photoelectrochemical (PEC) cells.
- Understand the dynamics of water dissociation and hydrogen evolution at the water-photoelectrode interface.
- Understand the electronic properties of the water-electrode interface.
- Identify the relationship between corrosion and catalysis.

Technical Barriers

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

(Y) Materials Efficiency (Photoelectrochemical Hydrogen Production)
(Z) Materials Durability (Photoelectrochemical Hydrogen Production)

Technical Targets

This project is conducting fundamental theoretical studies of mechanisms of corrosion and catalysis in III-V semiconductor-based photoelectrode materials for PEC hydrogen production. Insights gained from these studies will be applied toward the optimization and design of semiconductor materials that meet the following DOE 2013 PEC hydrogen production targets:

- Usable semiconductor bandgap: 2.3 eV
- Chemical conversion process efficiency: 10%
- Plant solar-to-hydrogen efficiency: 8%
- Plant durability: 1,000 hrs.

Accomplishments

- Discovered that spontaneous dissociative adsorption of water could be observed in simulations of oxide-decorated InP(001) surfaces.
- Discovered that oxide reactivity can be categorized generally according to oxygen bond topology.
- Isolated possible mechanism for water dissociation on oxide surfaces with In–O–In bond topology.
- Determined that hydroxide bridges are more stable than oxides, and demonstrated that conversion between hydroxide topologies is facilitated by hydrogen-bond network in water.
- Isolated two possible mechanisms for corrosion nucleation in InP(001), both of which will be tested further for compatibility with experimental measurements.

Introduction

Development of efficient processes for the carbon-free production of hydrogen is key to sustainable realization of a future hydrogen economy. One particularly promising approach is to use sunlight to catalyze direct evolution of hydrogen from water in a PEC cell. Semiconductor-based PEC devices are particularly attractive, thanks to a relatively simple device design and a wealth of data available for engineering efficient photon harvesting [1]. Results have demonstrated that one can achieve solar-to-fuel conversion efficiency in excess of the 2013 DOE targets (>12% using a tandem GaAs/GaInP₂ cell); however, this has come at the expense of short device lifetime due to fast degradation of the electrode [2]. Further progress has been hindered by a poor understanding of the fundamental hydrogen evolution processes operating at the electrode-water interface. Our research addresses this need from a theoretical perspective, leveraging realistic ab-initio simulations to determine the key mechanisms governing corrosion and catalysis at the water-semiconductor interface.
Approach

Further progress in semiconductor-based PEC photoelectrodes requires in-depth understanding of the complex relationship between surface stability and catalytic activity. This in turn relies on knowledge of the fundamental nature of the electrode-water interface, and of the chemical pathways explored during surface-active hydrogen evolution. As such, we have been carrying out finite-temperature ab-initio molecular dynamics simulations and energetics calculations based on density functional theory to understand the chemical, structural, and electronic properties of water/electrode interfaces under equilibrium conditions, as well as to understand the competing chemical reaction pathways visited during photocatalysis. Our approach uses InP(001), which has known water-splitting activity, as a model semiconductor electrode. Currently, our chief interest is in investigating the role of oxygen at the semiconductor surface, in response to experimental observations of high oxygen contaminant concentration in the samples evaluated by our collaborators in J. Turner’s group at the National Renewable Energy Laboratory [3] and suggestions that this oxide may play a key role in motivating both the surface photocorrosion and the catalytic water splitting reaction [4,5]. Accordingly, we are evaluating the stability and reactivity of the InP(001) surfaces in the presence of oxide and hydroxide species, correlating results to oxide topology and surface morphology. In each instance, the role of the surrounding water is also assessed.

Results

To evaluate the role of oxygen contaminants in the reactivity and stability of the InP(001) surfaces, we extracted low-energy oxide configurations by adsorbing atomic oxygen on high-symmetry sites of an initially unreconstructed In-rich surface slab. The atoms were then allowed to relax to their local-minimum configuration. Atop, hollow, and both bridge sites were tested at single-monolayer coverage limit, giving rise to several relaxed oxide structures. All tested configurations show that incorporation of oxygen is strongly thermodynamically favored with respect to the clean surface in the presence of gaseous O₂ (by an average of 2.5 eV per oxygen atom), in agreement with experimental observations of high surface oxygen contamination. Several of the tested configurations resulted in the oxygen in the subsurface layer rather than the surface layer. These generally feature oxygen simultaneously bonded to one indium and one phosphorous. Surface oxygens, on the other hand, generally bridge two indium atoms. Oxygen is more stable in the subsurface than on the surface (by 0.5 eV per oxygen, on average), reflecting the strength of the In–O–P complex with respect to In–O–In.

To test whether oxide formation affects reactivity for water dissociation, single water molecules were adsorbed near the oxygen sites on each of the morphologies. In each case, oxygen bond topology proves an excellent predictor of gas-phase dissociative adsorption of water: oxygen sites in In–O–P bonds bind water weakly and do not encourage dissociation, whereas sites in In–O–In bonds promote spontaneous dissociative adsorption. For morphologies containing both types of oxide bonds, reactivity depends on the specific dissociation site. To illustrate this point, the results of water adsorption on three representative oxide surfaces are shown in Figure 1.

Figure 1 indicates that the result of water reaction with certain bridge oxide structures is local surface hydroxylation. Accordingly, we also examined hydroxylated InP(001) surfaces, generated by placing OH in high-symmetry sites. Only three unique relaxed configurations were found for OH coverage, although we are currently mining additional morphologies for further study. Hydroxide formation is thermodynamically favored with respect to oxide formation (by an average of 1.3 eV per oxygen). This reflects the thermodynamic driving force for the dissociation of water on the reactive oxide surfaces, which results in surface hydroxylation. Interestingly, the bridge configuration, which was the least stable oxide configuration we tested, proved the most stable hydroxide configuration.

![Figure 1](image)

**FIGURE 1.** Result of gas-phase water molecule adsorption on representative oxide-contaminated In-rich InP(001) surfaces. For oxides consisting exclusively of In-O-P oxygen bond topologies (a), the water molecule does not dissociate. For oxides consisting exclusively of In-O-In oxygen bond topologies (b), the water molecule dissociates, resulting in local surface hydroxylation. For oxides containing both In-O-P and In-O-In oxygen bond topologies (c and d), dissociation of the water molecule does not occur if adsorption is near the In-O-P site (c), whereas dissociation does occur if adsorption is near the In-O-In site (d). Color scheme: hydrogen = small white spheres; oxygen = small dark red spheres; phosphorous = medium gold spheres; indium = large green spheres.
We have also been running ab initio molecular dynamics calculations of the full semiconductor-water interface to examine the influence of dynamics on the reactivity and stability of the surface. In order to isolate the two oxide bond topologies and examine them individually, we have been running two oxide surface simulations, one using a low-energy configuration with 100% In–O–P bond topology and the other using a higher-energy bridge-site configuration with 100% In–O–In bond topology. For the hydroxide surface, we have been running only one simulation (bridge-site hydroxide), recognizing the fact that the shallow free energy surface should mean realization of the other morphologies in the course of the dynamics.

As expected, the In–O–In surface oxide demonstrated much higher reactivity than the In–O–P subsurface oxide. The mechanism of dissociative water adsorption on the reactive In–O–In oxide is depicted in Figure 2. The reaction begins with the adsorption of a water molecule on a surface indium site to form a bond between the water oxygen (O1) and the indium. The water molecule is initially oriented such that one of the O1–H bonds lies generally parallel to the surface, with the other pointing upwards into the solution. The parallel-lying O1–H bond is thereby free to engage in hydrogen bonding with one of the surface oxygens (O2). The subsequent cleavage occurs via proton transfer across the O1–H· · ·O2 complex, such that the covalent and hydrogen bonds are exchanged. The result is the hydroxylation of two neighboring indium atoms, the first of which (the one to which the water O1 was originally bound) forms an atop-site hydroxide, and the second of which forms either an atop- or bridge-site hydroxide. In vacuum calculations, the atop and bridge sites were nearly isoenergetic. Therefore, the choice between the two is determined by the local structure visited during the dynamics and appears to be strongly dependent on number and strength of the hydrogen bonds formed with neighboring water molecules.

For many water cleavage events, the reaction culminates in two surface hydroxyl groups. However, there are also instances in which one oxygen atom further binds to a second-layer phosphorous and is pulled into the subsurface. This phenomenon can be seen in Figure 2e and f. Since subsurface oxygen that bridges In and P is not generally reactive, the choice the system makes could have significant consequences on further surface catalytic activity. In summary, there is a competition between three possibilities for the product hydroxide groups: first, formation of a bridge-site hydroxide configuration; second, formation of an atop-site hydroxide which strongly hydrogen-bonds with the solution; and third, a subsurface hydroxide that bridges In and P. Qualitatively, the choice between these three seems to be related to the nature of the surrounding hydrogen-bond network. To be pulled into the subsurface, the product oxygen must not be engaged in significant hydrogen bonding. On the other hand, to be converted into the atop hydroxyl configuration, a product oxygen must be engaged in very strong hydrogen bonding.

Although we start the simulation with all hydroxide groups in the bridge-site configuration, we quickly see conversion of several of these to the atop-site configuration, consistent with the zero-temperature predictions of facile exchange between the two. This exchange is bidirectional, indicating a dynamic equilibrium between the two configurations. As with the oxide simulations, whether a conversion takes

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FIGURE 2. Mechanism of water dissociation on a bridge-site oxide of In-rich InP(001). O1 and O2 refer to the oxygen atoms originally associated with the water molecule and the oxide surface, respectively. (a) and (b) O1 binds to indium, and a hydrogen bond is formed with O2. (c) The water molecule transfers a hydrogen across the O1–H· · ·O2 complex. (d) The In–O2 bond breaks. (e) and (f) Optionally, O2 is pulled below the surface to form a bond with P. Color scheme: white = hydrogen; dark red = oxygen; light green = In; medium gold = phosphorous. The thin purple lines represent hydrogen bonds.
place seems to largely depend on the structure of the hydrogen-bond network surrounding the hydroxide group. If the group is involved in strong hydrogen bonding, the atop-site configuration is preferred, whereas the converse is true for the bridge-site configuration.

Occasional dissociative adsorption of water is observed in the hydroxide simulations, although it is generally associated with temporary breaking of an O–H surface bond to form bridge-site In–O–In. Water cleavage then proceeds via an identical mechanism to that observed in the reactive In–O–In oxide (Figure 2). Since these local-oxide configurations are relatively rare, the rate of water dissociation is significantly slower than for the reactive oxide (almost an order of magnitude). In addition, hydrogen atoms can sometimes transfer from a water molecule in solution across a hydrogen bond to OH groups on the surface. This turns surface OH into an indium-adsorbed H₂O, which may then be released back into the solution to free up an indium for further reactions. This also leaves one OH in the solution for further surface reactions, such as the surface hydroxide-to-oxide conversion via further water dissociation. The suitability of this reaction depends on temporary stabilization via local fluctuations in the hydrogen-bond network.

Conclusions and Future Directions

- We investigated oxides and hydroxides of InP(001) and found that surface reactivity can be correlated with local oxygen bond topology.
- Our ab initio molecular dynamics simulations of the oxide- and hydroxide-decorated surfaces show possible mechanisms for corrosion and catalysis.
- Dynamics appear to be very important in understanding surface behavior, particularly in reference to the water structure at the interface. Further analysis of the water structure to identify the nature of these correlations is currently underway.
- These mechanisms will be tested further by running additional simulations, and the results will be compared with X-ray absorption spectroscopy spectra currently being obtained by our collaborator, Prof. Clemens Heske.
- We have yet to assess the effect of surface and solution treatments on stability and reactivity. These include modification of the water pH and inclusion of nitrogen additives.

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References

II.G.13 Photoelectrochemical Generation of Hydrogen from Water Using Visible Light Sensitive Ferro-Electric BiFeO$_3$ and Semiconductor Nanotubes*

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 photoelectrochemical (PEC) 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 incorporated in a single photo anode.
- Improve the durability of the material.
- Scale up the laboratory demonstration to production unit.

Technical Barriers

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

(Y) Materials Efficiency
(Z) Materials Durability

Technical Targets

This project investigates potential application of hybrid TiO$_2$ 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 bandgap: 2.3 eV by 2013
- Chemical conversion process efficiency: 10% by 2013
- Plant durability: 1,000 h by 2013

Approach

In this current project, utilization of hybrid metal (Ti, W, Fe, Ta) oxide nanotubular arrays for generation of hydrogen from water using sunlight is being studied. The metal oxide nanotubular arrays have been found to be robust, photo-corrosion resistant, and can be used efficiently to generate hydrogen and most importantly are active in the visible light portion of the solar spectrum. It is envisioned that the process will be efficient and economical in the production of solar hydrogen. The nanotubular arrays were prepared by electrochemical anodization of solid metal in different inorganic and organic electrolytes in the presence of fluoride ions. The effect of voltage, time, and solution chemistry on the size, uniformity, and self-assembly of nanotube formation was studied. It was found that materials prepared in organic solvents such as ethylene glycol by an ultrasonic assisted process were stable and form an efficient pattern of nanotubes that have excellent photo-efficiency. We have already developed processes to synthesize metal oxide nanotubes in inorganic, organic and ionic liquids as electrolytes. This process is also suitable to prepare mixed metal oxide nanotubes e.g. TiFe, TiMn and TiW. In addition to the...
preparation of metal oxide-based photoanodes, we have also shown that these nanotubes can work efficiently as a cathode by nanoparticle modification. In addition to the anodization process, we have also developed new mixed metal oxide compounds by sol-gel method. In this project, a highly efficient photoanode, a cathode, and a modified electrolyte will be integrated to design a PEC cell to generate hydrogen with at least 10% efficiency by 2013. The scale up process looks highly promising for large-scale hydrogen generation.

The hydrogen generation work was conducted using a hybrid metal oxide nanotubular or mixed metal oxide photoanode in alkaline solutions in the presence of simulated solar light. The material stability and photo-efficiency was determined as a function of time, electrochemical and analytical measurements. The photo-efficiency was determined by measuring current as well as volume of the hydrogen generated by gas chromatograph.

In the future our main focus for the research will be to understand:

- The formation mechanism and kinetics of metal oxide nanotubes prepared by various anodization methods and electrochemical solutions.
- Synthesis of visible light active metal oxide nanotubular photocatalysts for PEC applications and analysis of their various phases while annealing by X-ray diffraction (XRD) measurements followed by density functional theory (DFT) calculations.
- Synthesis of visible light active mixed metal oxide photocatalysts for PEC applications.
- Develop quantum dot sensitized nanotubular oxide hybrid photo-anodes based on DFT modeling.
- Stability of the catalysts for 1,000 h.

On the basis of fundamental and applied research, a scaled-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 designed a low-cost process for synthesis of nanostructured bismuth iron oxide (BiFeO$_3$) as a multiferroic material for PEC applications. The experimental band gap of BiFeO$_3$ was found to be 2.1 eV (Figure 1(I)). The synthesis conditions were optimized and it was found that a highly crystalline nanostructured material could be obtained when BiFeO$_3$ is annealed under N$_2$ at 600°C for 2 h (Figure 1(II)).
- BiFeO$_3$ was found to be an efficient photocatalyst generating hydrogen under AM 1.5 light illumination conditions in 1 (M) KOH as electrolyte (Figure 2).
The band structure and optical properties of BiFeO$_3$ were estimated using generalized gradient approximation with Hubbard-type interaction parameter and spin polarized approach (GGA+U-SP) approximation considering the unoccupied Fe 3d orbital state. The calculated band gap was 1.61 eV (Figure 3).

UNR has developed an innovative ultrasonically mediated fabrication process to synthesize crystalline tantalum oxynitride (TaON) nanotube (NT) arrays (Figure 4). TaON NTs have been synthesized by a two-step process, firstly by forming Ta$_2$O$_5$ NTs (anodizing Ta foil) followed by heating them in an atmosphere of flowing NH$_3$ at 700°C for 6 h. It should be mentioned here that TaON nanoparticles (NPs) are not formed when Ta$_2$O$_5$ NPs are heated at 700°C for 6 h under identical synthesis conditions as TaON NTs.

- TaON NTs have a band gap 2.07 eV (Figure 5(A)) and show excellent visible light activity (47%) compared to TiO$_2$ nanotubes (0.39%) (Figure 5(B)).
- The first principle computational calculations of Ta$_2$O$_5$ and TaON have been carried out based on DFT using plane wave assumption (Figure 6). The calculated band gaps are smaller than the experimentally determined values. In our current simulation, the calculated band gap of Ta$_2$O$_5$ is 3.6 eV, while the experimental value is 4 eV. The calculated band gap of TaON is about 1.9 eV.

Conclusions and Future Actions

In the past year, we have developed new metal oxide based mixed nanotube arrays. We have also got an expanded idea on the formation conditions of metal oxynitride NTs and metal oxynitride NPs. TaON NTs prepared by single nitridation and annealing step are found to be efficient photocatalysts for hydrogen generation by water splitting using visible part of the solar spectrum. Preliminary studies on BiFeO$_3$ as a multiferroic material for photocatalysis has shown positive results. Theoretical studies on bandgap calculations are in accordance with the experimentally determined values. 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 materials for PEC applications.
- Synthesis of photoanodes composed of multiferroic materials.
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


FY 2010 Publications/Presentations

4. “Ordered Titanium Dioxide Nanotubular Arrays As Photo Anodes for Hydrogen Generation”, Chapter 9, Solar Hydrogen and Nanotechnology, Edited by Lionel Vayssieres, 2010, Published by John Willey and Sons.
II.H.1 Maximizing Light Utilization Efficiency and Hydrogen Production in Microalgal Cultures

Objectives

- Minimize, or truncate, the chlorophyll antenna size in green algae to maximize photobiological solar conversion efficiency and H₂-production.
- Demonstrate that a truncated chlorophyll (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 Biological Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(AG) Light Utilization Efficiency

Technical Targets

The Fuel Cell Technologies Program Multi-Year 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.

Accomplishments

1. Published manuscript on the utility of the truncated light-harvesting chlorophyll antenna (*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.
2. Deposited two versions of the *tla1* truncated antenna mutant in the strains library of the Chlamydomonas Center (http://www.chlamy.org/), Accession Numbers CC-4169 and CC-4170. These *tla1* strains are openly available to the interested public.
3. 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, ±standard deviation). |
|-------------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Chl/cell mol x10⁻¹⁵                           | Wild Type       | *tla1*          | *tla2*          | *tlaR*          |
| Chl-PSII                                      | 222 ± 26        | 115 ± 36        | 80 ± 30         | 50 ± 30         |
| Chl-PSI                                       | 240 ± 4         | 160 ± 12        | 115 ± 10        | 105 ± 10        |
| Light Utilization Efficiency (Solar to Chemical) | ~3%            | ~10%           | ~15%           | ~25%           | ~30%           |

Long-Term Goal
TABLE 2. Progress achieved vs the DOE targets: Utilization Efficiency of Incident Solar Light Energy, $E_oE_r, \%$

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<thead>
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</thead>
<tbody>
<tr>
<td>Program Targets</td>
<td>3%</td>
<td>10%*</td>
<td>15%</td>
<td>20%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual Progress Achieved</td>
<td>3%</td>
<td>10%</td>
<td>tla1</td>
<td>15%</td>
<td>tla2</td>
<td>25% tlaR</td>
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</table>

*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 microalgae mutants with a truncated chlorophyll antenna size.

The rationale for this work 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 Fuel Cell Technologies Program. This objective is currently being approached through DNA insertional mutagenesis/screening and biochemical/molecular/genetic analyses of *Chlamydomonas reinhardtii* cells.

Results

The *tla*2 mutant plasmid insert site has been cloned and a gene of interest has been tentatively identified as causing the *tla*2 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*. Properties of the *tla* “truncated Chl antenna size” strains so far isolated are summarized in Tables 1 and 2, and Figure 3. The *tlaR* mutant has the smallest yet Chl antenna size known in green algae.

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.
- 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.

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References

II.H.2 Biological Systems for Hydrogen Photoproduction

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 Fuel Cell Technologies 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 Fuel Cell Technologies (FCT) Program Multi-Year Research, Development and Demonstration Plan:

(AI) Continuity of Photoproduction

(AH) Rate of Hydrogen Production

(AT) Feedstock Cost


Technical Targets

<table>
<thead>
<tr>
<th>TABLE 1. Photolytic Biological Hydrogen Production from Water</th>
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<tr>
<td>Characteristics</td>
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<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>Duration of Continuous Photoproduction</td>
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<tr>
<td>O₂ Tolerance (half-life in air)</td>
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N/A - not available

Accomplishments

- Extended the computational modeling techniques used to identify gas diffusion to the Desulfovibrio gigas [NiFe]-hydrogenase.
- Confirmed that the reduced state of the [FeFe]-hydrogenase is more tolerant to O₂ in vitro than the oxidized state; detected an “O₂-insensitive” state.
- Identified positive Chlamydomonas transformants transcribing the Ca1 hydrogenase gene.
- Simulated fusions between the petF ferredoxin and algal/clostridial hydrogenases to test optimal interactions and performed in vitro tests of fusions.
- Observed that increased thickness of the alginate film improves O₂ tolerance but decreases H₂-production rates.
- Designed adenosine triphosphate (ATP) synthase inducible mutants.
- Demonstrated that an anaerobic clostridial consortium ferments algal biomass, pure algal lipids, pure proteins and unpolymerized alginate.
- Optimized fermentative H₂ production from potato waste.
- Demonstrated sequential H₂ production from dark- and light-driven processes.

Introduction

Green algae can photoproduce H₂ using water as the source of electrons. This property requires the coordinated operation of the photosynthetic apparatus (splits water, producing O₂, electrons, and protons) and [FeFe]-hydrogenases (recombine protons and
electrons, producing $\text{H}_2$ gas). The catalytic center of [FeFe]-hydrogenases is composed of a unique 2Fe2S metal center that is sensitive to $\text{O}_2$, a by-product of photosynthetic water oxidation. This inactivation prevents sustained $\text{H}_2$ production by the organism in the light. The continuity of $\text{H}_2$ photoproduction is one of the major technical barriers to developing photobiological $\text{H}_2$-production systems, as listed in technical barrier AT.

A second major barrier to efficient algal $\text{H}_2$ photoproduction is the low rate of the reaction (technical barrier AH), which is dependent upon many factors: the competition for photosynthetic reductant between the $\text{H}_2$-production and the $\text{CO}_2$-fixation pathways; the down-regulation of photosynthetic electron transport from water under $\text{H}_2$-producing conditions; and the predominance of cyclic, unproductive electron transport over linear electron transfer under anaerobiosis.

Our current project addresses: (a) the $\text{O}_2$ sensitivity of $\text{H}_2$-producing algae and the low rates of $\text{H}_2$ production by using molecular engineering (both site-directed and random mutagenesis) to alleviate these barriers; (b) the further development of a platform, based on the induction of $\text{H}_2$ production by sulfur deprivation, to test biochemical and reactor engineering factors required to improve the rates and light-conversion efficiencies of algal $\text{H}_2$-photoproduction; and (c) the performance of different components of a proposed system that integrates fermentative with photobiological processes for more cost-effective, biological $\text{H}_2$ production. The latter addresses the technical barrier AT (feedstock cost in an integrated system).

**Approach**

**Task 1. Molecular Engineering of [FeFe]-hydrogenases**

This task has three objectives: (a) the engineering of increased $\text{O}_2$ tolerance in [FeFe]-hydrogenase through site-directed or random mutagenesis of region(s) that control $\text{O}_2$ access to the catalytic site; (b) the functional expression of clostridial [FeFe]-hydrogenases in *Chlamydomonas reinhardtii*; and (c) the evaluation of strategies for decreasing the competition between the $\text{CO}_2$-fixation and the $\text{H}_2$-production pathways, which are being implemented in cooperation with a research group at MIT. The efforts being conducted under the first objective have been guided by an extensive computational study of gas diffusion in the clostridial Cpl [FeFe]-hydrogenase, which identified four amino acids that form a “barrier” for $\text{O}_2$ migration into the catalytic site. Up until now, our experimental strategy had been to increase the energy required for $\text{O}_2$ to migrate through this barrier by changing its amino acid composition. Targets for mutagenesis were selected based on static and dynamic computational simulations of gas diffusion and identification of energy barriers. A random mutagenesis 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 $\text{O}_2$ 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 $\text{O}_2$-tolerant enzyme on the kinetics and metabolism of photo-hydrogen production.

In order to control the flow of photosynthetic reductant away from $\text{CO}_2$ fixation and towards $\text{H}_2$ photoproduction, we are working with Prof. Zhang’s research group at MIT to engineer fusions between ferredoxins, the final electron acceptor in photosynthesis, and the HYDA1 algal hydrogenase. This work should prove the hypothesis that it is possible to decrease the competition between these two electron transport pathways and thus increase $\text{H}_2$ photoproduction even in the presence of $\text{CO}_2$.

**Task 2. Optimization of the Sulfur-Deprivation Platform to Test the Performance of Various Algal Mutants**

With our collaborators at the University of California, Berkeley, we developed a method, based on depriving algal cultures of sulfate, to induce continuous $\text{H}_2$ 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 $\text{O}_2$-tolerant hydrogenase system (see Task 1) becomes available.

**Task 3. An Integrated Biological $\text{H}_2$-Production System**

The FCT Hydrogen Biological Production working group identified a novel system for biological $\text{H}_2$ 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 $\text{H}_2$-producing components in terms of limitations in their overall light-conversion efficiencies and substrate dependence. The two particular configurations being pursued at NREL...
involve: (a) stacked reactors of sulfur-deprived green algae and photosynthetic bacteria that produce H₂ in the light, followed by a fermentative component consisting of anaerobic bacteria that degrade the algal and photosynthetic bacteria biomass and produce H₂ and acetate as products. The latter is the source of reductant for H₂ production by the photosynthetic bacteria; and (b) fermentors that utilize potato waste to produce H₂ and organic acids, followed by organic acid-dependent photosynthetic H₂ production by photosynthetic purple non-sulfur bacteria.

**Results**

**Task 1. Molecular Engineering of [FeFe]-hydrogenases**

Our initial approach to engineer an O₂-tolerant [FeFe]-hydrogenase focused on *site-directed mutagenesis* of the amino acids that comprise a single barrier region controlling O₂ access from the hydrogenase’s central cavity to its catalytic site. One mutation of this region in the clostridial Ca1 [FeFe]-hydrogenase possessed high O₂ 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. This year, we showed that the ability of the enzyme to transition between redox states is critical for O₂ tolerance, and that hydrogenases isolated in the reduced state are more tolerant to O₂ than those isolated in the oxidized state. We also observed the presence of an apparently “O₂-insensitive” state that may be related to similar states described for *Desulfovibrio* [FeFe]-hydrogenases. We are preparing a manuscript describing these observations.

We also observed that, based on the recently published crystal structure of the algal hydrogenase by the Peters’ group, our targets for mutagenesis could interfere with the appropriate folding and assembly of the enzyme’s catalytic center, resulting mostly in inactive mutants, which agrees with our results. Thus, while considering different mutagenesis strategies for generation of O₂-tolerant Ca1 mutants, we also initiated efforts 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. Since Ca1 is already more O₂ tolerant than the algal hydrogenase, these studies will provide evidence that increased *in vitro* O₂ tolerance does result in increase *in vivo* tolerance. For these purposes, we introduced the Ca1 gene into the *C. reinhardtii* strain CC-849 genome and identified by polymerase chain reaction (PCR) transformants that show the presence of the entire Ca1 codon-optimized gene. The presence of the Ca1 transcript was demonstrated by reverse transcriptase polymerase chain reaction in at least one transformant, and it is anaerobically induced in a similar manner as expression of the endogenous *C. reinhardtii* HYDA1. Future efforts will be directed towards confirming that in these transformants the Ca1 protein is also expressed, localized and active. In addition, once Ca1 is confirmed to be active, preliminary O₂-sensitivity results will be confirmed and physiological characterization will be pursued.

In order to understand the partitioning of photosynthetic reductant among different metabolic pathways, we measured H₂ evolution and its competitive reaction, reduced nicotinamide adenine dinucleotide phosphate (NADPH) production (required for CO₂ fixation), in a series of *in vitro* reactions with purified thylakoids, Ferredoxin (Fd), FD/NADPH oxidoreductase (FNR) NADP⁺ and hydrogenases. In agreement with previous studies, we found that light-mediated H₂ evolution by algal hydrogenase with thylakoid membranes is blocked in the presence of FNR, Fd and oxidized NADP. When free hydrogenase was replaced with a Fd-hydrogenase fusion, H₂ was evolved at near maximal rates with NADPH as a co-product. Some of the NADPH was also recycled back into H₂. This tunable, catalytic complex led to partitioning of photosynthetic electron transport to H₂ even under conditions that support CO₂ fixation and will be investigated as a way to improve light-conversion efficiencies in algae under photosynthetic growth for scale-up development.

**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 the discoveries that: (a) a decrease in film thickness improves maximum specific rates and yields of H₂ production under anaerobic conditions but decreases H₂ production rates under aerobic conditions due to protection from O₂ inactivation; (b) the addition of acetate to alginate-immobilized algal cells stimulates H₂ production; (c) alginate-immobilized ATP synthase mutants show increased H₂ production under both low and high illumination, as predicted from uncoupled preparations; and (d) new ATP synthase mutants have been designed and are being introduced in *C. reinhardtii* behind an inducible promoter to allows us to regulate its expression.

**Task 3. An Integrated Biological H₂-Production System**

We demonstrated that our anaerobic bacterial consortium metabolizes algal biomass with a H₂/glucose ratio higher than 4, suggesting that components other than carbohydrates are being utilized. This
hypothesis was confirmed by the observation that the same consortium is capable of degrading pure algal lipid and protein. Finally, we demonstrated that the consortium also metabolizes un-polymerized alginate, thus underlining its usefulness in consuming residual immobilized algal biomass from an integrated photobiochemical/fermentative H₂-production system.

Working with a different integrated system that links fermentation of potato waste to photosynthetic H₂ production by purple non-sulfur bacteria, our collaborators in Russia optimized the fermentative component by examining factors such as exclusion of ammonium; addition of Fe ions, peptone and zinc; and increased phosphate buffering capacity. They reported final yields of 1.6 moles H₂/glucose. Finally, they demonstrated sequential H₂ production from the integrated system with maximum yields at this point of 5.6 moles H₂/glucose if the fermentation effluent is feed to the non-sulfur bacteria.

Conclusions and Future Directions

Task 1: (a) Continue to characterize positive algal transformants expressing the bacterial Ca1 gene; (b) measure the in vivo O₂ tolerance of those transformants; (c) devise a different mutagenesis approach to generate O₂-tolerant [FeFe]-hydrogenase mutants; and (d) complete in vitro studies of Fd/hydrogenase fusions in collaboration with MIT and attempt in vivo expression of the fused promoters.

Task 2: (a) Test the effect of the volume of the photobioreactor’s headspace on the H₂-production properties of algal cultures; (b) adapt and improve on the methods previously used to induce photoautotrophic cultures to produce H₂ in the absence of added acetate; (c) test more advanced truncated antenna mutants from the University of California, Berkeley; and (d) construct and test the performance of an ATP synthase gene expressed in C. reinhardtii behind an inducible promoter.

Task 3: (a) Scale up and further optimize fermentation of suspended and immobilized algal biomass by the fermentative consortium using new fermentors; (b) optimize the integration of the fermentative/photobiological H₂-production system using potato waste as the feedstock.

Special Recognitions & Awards/Patents Issued

1. Seibert was elected the new Operating Agent for the IEA/HIA Task 21 (Biohydrogen). Ghirardi was elected a Fellow of the Renewable and Sustainable Energy Institute (RASEI).

FY 2010 Publications/Presentations

Publications


Presentations

Invited presentations at the CSIC Spanish National laboratory in Zaragoza, Spain, Apr 09 (Seibert); to the group of Dr. X. Zhang at MIT, Apr 2009 (King); plenary talk at the Great Lakes Bioenergy Research Center (GLBRC) Hydrogenase Forum, May 09 (Seibert); at the
American Society for Plant Biology meeting in Hawaii, Jul 09 (Ghirardi); update on EERE BioHydrogen research at the U.S. Air Force Office of Scientific Research Annual Review Meeting, Aug 09 (Seibert); the USA country report at the IEA Annex 21 Biohydrogen Experts Meeting in Jyväskylä, Finland, Sep 09 (Seibert); invited presentation at the University of Washington, St. Louis, Sep 09 (Ghirardi); invited presentation at the Rocky Mountain American Vacuum Society meeting, Denver, Sept 09 (Ghirardi); invited presentation at the Center for Revolutionary Solar Photoconversion meeting in Denver, Oct 09 (Ghirardi); invited presentation at the Fall Rocky Mountain Branch of the American Society for Microbiology in Denver, Nov 09 (Ghirardi); presentation to the Solar Fuels 2009 Meeting, Sigtuna, Sweden, Oct 2009 (King); invited presentation to the Microbiology Department, Colorado State University, Nov. 09 (Seibert); at NREL’s Energy Bioscience Center monthly seminar, Jan 10 (Ghirardi); USA country report at the IEA Annex 21 Biohydrogen Experts Meeting in Florence, Italy, March, 2010 (Seibert); invited talk at the DiBA-UNIFI & ISE-CNR Workshop on BioHydrogen in Florence, Italy, March, 2010 (Seibert); visit J. Zhang’s group at MIT, april 28–30th (King); departmental seminar presentation at the North Carolina State University, Raleigh, NC, May 2–4 (Seibert); invited talk at the Christian-Albrechts-University in Kiel, Germany, May 16–18 (Seibert); the Kendric C. Smith Lecture on Innovations in Photobiology, June 12–14 (Seibert); oral presentation at the Gordon Conference on Iron-sulfur Enzymes, Colby-Sawer College, NH, June 6–11 (King).
II.H.3 Fermentation and Electrohydrogenic Approaches to Hydrogen Production

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Subcontractor:
Bruce Logan, Pennsylvania State University (PSU), State College, PA

Start Date: October 1, 2004
Projected End Date: September 30, 2012

Objectives

- Perform hydrogen fermentation using cellulolytic 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 Targets

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2013 Target</th>
<th>2009 Status</th>
<th>2010 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield of H₂ from glucose</td>
<td>Mole H₂/mole glucose</td>
<td>4</td>
<td>9.95 (Fermentation-MEC Integrated System)</td>
<td>3.2 (Fermentation alone)</td>
</tr>
<tr>
<td>Feedstock cost</td>
<td>Cents/lb glucose</td>
<td>10</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

MEC = microbial electrolysis cell

- 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 (FY) 2010 we achieved a molar yield of 3.2, accomplished by Clostridium thermocellum fermenting avicel (commercial cellulose) via fermentation only.
- 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 cellulolytic microbes to ferment cellulose and hemicellulose directly, which will result in lower feedstock costs.

Accomplishments

- Determined effects of substrate loadings on both rates and yields of H₂ production in scale-up bioreactor experiments using the cellulose-degrading bacterium C. thermocellum fermenting various amounts of avicel cellulose and lignocellulose, the latter prepared from the acid-hydrolysis of corn stover biomass.
- Tested genetic transformation protocols with a custom-designed plasmid in collaboration with University of Manitoba (Canada). Initial finding is promising which warrants further improvement.
- Designed, constructed and tested a bench-scale prototype microbial electrolysis cell of 2.5 L in volume that contained eight pairs of electrodes. The reactor produced H₂ gas at a rate of up to 1,250 mL/d, and produced a steady current of 155 to 180 mA demonstrating the usefulness of this design.

◊ ◊ ◊ ◊ ◊
Introduction

Biomass-derived glucose feedstock is a major operating cost driver for economic H₂ production via fermentation. The DOE Fuel Cell Technologies 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 hydrogen 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 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 moles of H₂ per mole glucose when coupled to a dark fermentation process. Indeed in FY 2009, the team reported a combined molar yield of 9.95 when fermentation was coupled to MEC in an integrated system. Combining fermentation with MEC could therefore address technical barriers AR and AS (waste acid accumulation) and improve the techno-economic feasibility of H₂ 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 developing a genetic method to accomplish this goal. 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 tested effects of substrate loadings on rates and yields of H₂ production in C. thermocellum. Two types of substrates were tested: avicel cellulose and the dilute-acid pretreated corn stover lignocellulose, the latter with a composition of 59.1% cellulose, 25.3% lignin, 6.4% residual hemi cellulose-derived sugars, and 3.7% ash. We performed fermentation in scale-up bioreactors with automated temperature (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. Clostridium thermocellum, previously cultured in crystalline avicel cellulose, was inoculated into a 1.5 L (working volume) bioreactor fed with various amounts of the individual substrates described above. Table 2 summarizes rates, molar yields of H₂, production, and carbon mass balance during a period of 80 hours. Calculation of the carbon mass balance did not account for those carbon substrates assimilated into bacterial cell mass. These experiments conclude that higher carbon loading leads to faster rate of H₂ production whereas lower carbon loading results in higher H₂ molar yield. The molar yield of 3.2 obtained with 1 g/L avicel was the average of two experiments. Overall, these experiments provide the parameters (hydraulic and solid retention time) to conduct fermentation in fed-batch mode in the more realistic scale-up process. Typical compounds found in the fermentation waste are: acetic, formic, lactic, and ethanol, which are ideal substrates for the MEC reaction.

Table 2. Effect of Substrate Loadings on Rates, Yields of H₂ Production in Clostridium Thermocellum

<table>
<thead>
<tr>
<th>Substrate</th>
<th>g/L</th>
<th>Rate (mmol H₂/L/h)</th>
<th>H₂ Molar Yield</th>
<th>Carbon Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel 1.0</td>
<td>0.58</td>
<td>3.2</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Avicel 2.5</td>
<td>0.89</td>
<td>2.1</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Avicel 5.0</td>
<td>0.98</td>
<td>1.6</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Corn Stover 1.0</td>
<td>0.51</td>
<td>2.8</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Corn Stover 2.5</td>
<td>1.06</td>
<td>2.0</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Corn Stover 5.0</td>
<td>1.21</td>
<td>1.2</td>
<td>51</td>
<td></td>
</tr>
</tbody>
</table>

Metabolic Engineering

The ultimate goal of this approach is to develop tools to inactivate genes encoding competing metabolic pathways, thus redirecting more cellular flux to improve...
H₂ molar yield. Transformation in this organism has been unsuccessful thus far in the literature likely due to either an inefficiency of the plasmids used or an active restriction system in the host that is destroying the incoming plasmid. To ascertain any restriction endonuclease activity in *C. thermocellum*, crude cell extracts were prepared from a 20-mL culture grown to late-exponential phase, and adjusted to contain 50% (v/v) glycerol. For restriction assays pIKM1 plasmid deoxyribonucleic acid (DNA, isolated from TOP10 cells) were incubated with a buffer (10 mM Tris/HCl, pH 7.5, 50 mM NaCl, 10 mM MgCl₂, 1 mM dithiothreitol, and 0.01% bovine serum albumin) at 55°C for 2-3 hr. The products were analyzed on 1% agarose gel (Figure 1). Gel electrophoresis analysis indicated that cellular extract indeed digested the pIKM1 DNA in the cellular extract confirming our previous speculation about the *C. thermocellum* endonuclease activity on the plasmid DNA (Figure 1, lane 2). Plasmid DNA incubated without the cellular extract remained undigested (data not shown). To test the endonuclease activity of *C. thermocellum* crude extract on methylated DNA, plasmid PIKM1 was treated with GpC methyltransferase (M.CviPI) that selectively methylate all cytosine residues at the 5° carbon position within the double stranded DNA sequence. Our results indicated that the methylated PIKM1 DNA was protected from the endonuclease activity of *C. thermocellum* (Figure 1, lane 1). Methylated *C. thermocellum* DNA without cell extract or methylated PIKM1 DNA both serve as the controls (Figure 1, lanes 3 and 5, respectively). The outcomes warrant the importance of plasmid DNA methylation to improve overall transformation efficiency.

**Microbial Electrolysis Cell**

Previously examined MECS contained a single set of electrodes and were relatively small (0.03 L) in volume. In order to examine the scalability of the existing single-chamber MEC designs, a multiple-electrode system was designed, constructed and tested for hydrogen production and current density achievable using acetate as a feedstock. The bench-scale MEC was 2.5 L in volume when empty, and contained eight separate electrode pairs made of graphite fiber brush anodes (pre-acclimated for current generation), and 304 stainless steel mesh cathodes (64 m²/m³) (Figure 2). Under continuous flow feeding conditions, and a one-day hydraulic retention time, a maximum current of 181 mA was produced within three days of operation. This is 1.18 A/m² of cathode surface area, and equivalent to 74 A/m³. The maximum hydrogen production (day 3) was 0.53 L/L-d, reaching an energy efficiency relative to electrical energy input of $\eta_E = 144\%$. Current production remained relatively steady (days 3 to 18), but the gas composition dramatically shifted over time from hydrogen to methane. After 16 days of operation, only small amounts of H₂ gas were recovered, and methane production had increased to 0.118 L/L-d. When considering the energy value of both hydrogen and methane, efficiency relative to electrical input remained above 100% until near the end of the experiment (day 17) when only methane gas was being produced. These results showed that MECS could be scaled up primarily based on cathode surface area, but that hydrogen produced in the single-chamber MEC can be completely consumed in a continuous flow system unless methanogens can be completely eliminated from the system.

**Conclusions and Future Direction**

- Using both avicel cellulose and corn stover lignocellulose as the substrate and a sequenced strain of *C. thermocellum*, we found that low substrate loading gives rise to higher H₂ molar yield while high substrate loading yields faster rate of H₂ production.
- We determined that plasmid DNA methylation is necessary for successful transformation in *C. thermocellum*. 
Hydrogen production was successful in a larger-scale (2.5 L) continuous flow MEC, but eventually all hydrogen production was converted to methane. In the future, we will conduct fed-batch fermentation to optimize solid and hydraulic retention time for more realistic scale-up application. We will continue to develop tools for molecular engineering in \textit{C. thermocellum}. In the MEC area, a new reactor design is now in progress to better capture hydrogen gas produced in these systems to avoid its loss to methanogens.

**FY 2010 Publications/Presentations**


**References**

II.H.4 Hydrogen from Water in a Novel Recombinant Oxygen-Tolerant Cyanobacterial System

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

(AH) Rate of Hydrogen Production

(AI) Continuity of Photoproduction

Technical Targets

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Current Status</th>
<th>2011 Target</th>
<th>2018 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of continuous H₂ photoproduction in air</td>
<td>Zero to 30 seconds in air</td>
<td>Produce a cyanobacterial recombinant evolving H₂ through an O₂-tolerant hydrogenase</td>
<td>H₂ production in air for 30 min</td>
</tr>
</tbody>
</table>

Accomplishments

JCVI

- Transferred the genes of the *Thiocapsa roseopersicina* stable hydrogenase to *Synechococcus elongatus* PCC 7942 and detected activity from the heterologously-expressed hydrogenase.
- Cloned a novel NiFe-hydrogenase from Sargasso Sea environmental deoxyribonucleic acid (DNA), expressed it in *T. roseopersicina*, and detected activity from the purified protein in 1% oxygen.
- Transferred the genes of this novel environmental hydrogenase into *S. elongatus*, and detected activity from the heterologous hydrogenase.

NREL

- Cloned the O₂-tolerant *Rubrivivax gelatinosus* hydrogenase genes in two plasmids suitable for expression in *Synechocystis* sp. PCC 6803. 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 the plasmid. Expression from both plasmids is driven by a native promoter in *Synechocystis*.
- Protein western blots revealed the expression of three *Rubrivivax* hydrogenase subunits using the above two expression systems.

Introduction

Photobiological processes are attractive routes to renewable H₂ 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 H₂. However, one major difficulty is that most hydrogen-evolving hydrogenases are inhibited by O₂, which is an inherent byproduct of oxygenic photosynthesis. The rate of H₂ production is thus limited. Certain photosynthetic bacteria are reported to have an O₂-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 O₂-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 roseopersicina* and *Rubrivivax gelatinosus* to cyanobacteria. Since only a very limited number of O$_2$-tolerant hydrogenases are available, our second approach is to identify novel O$_2$-tolerant hydrogenases from environmental microbial communities and transfer them into cyanobacteria.

**Results**

**JCIV: Expression of HynSL hydrogenase from *Thiocapsa roseopersicina* in Cyanobacteria**

We have introduced the O$_2$-tolerant hydrogenase from *T. roseopersicina* into cyanobacteria along with various combinations of accessory genes. These constructs were introduced into a mutant strain of *Synechococcus elongatus* PCC 7942 (Hoxmut) which lacks the HoxYH hydrogenase and has no native hydrogenase activity. The *T. roseopersicina* hydrogenase structural genes, *hynSL*, were introduced into Hoxmut along with the known *T. roseopersicina* accessory genes in plasmids pHyn4, pHyn5, and pHup (Figure 1). Proteins encoded by the accessory genes are necessary to assemble a functional active site for NiFe hydrogenases. While not all accessory genes are known for *T. roseopersicina* because the genome has not been sequenced, the available 16 genes were co-expressed in cyanobacteria to determine whether a hydrogenase with a functional active site could be assembled.

The *T. roseopersicina* hydrogenase was expressed upon isopropyl β-D-1-thiogalactopyranoside (IPTG) induction in the cyanobacterial strains (Figure 2), but no active hydrogenase was produced (Figure 3). However, when the accessory genes from a novel environmental hydrogenase (construct Wav10 described in the following) were co-expressed with the *T. roseopersicina* genes in Hyn4 or Hyn5, a *T. roseopersicina* hydrogenase with a fully assembled active site was produced and possessed activity upon *in vitro* assay (Figure 3).

**Identifying Novel O$_2$-Tolerant Hydrogenases from Marine Microbes and Expression in Cyanobacteria**

We have previously identified sequences of large and small NiFe hydrogenase subunits from the Global Ocean Sampling expedition. One of these environmentally-derived NiFe hydrogenase sequences was expressed in *T. roseopersicina* and found to encode a functional hydrogenase. When the genes encoding the small and large subunits of the hydrogenase and the adjacent accessory genes were transferred to the Hoxmut strain of the cyanobacterium *S. elongatus* (strain RC41, Figure 2), an active hydrogenase expressed (Figure 3). The heterologously-expressed hydrogenase possessed roughly

![FIGURE 1. Constructs used to express *T. roseopersicina* (T. r.) and environmental (Envi) hydrogenases in cyanobacteria.](image-url)
II.H Hydrogen Production / Biological

With the T. roseopersicina HynSL hydrogenase described above, this is the first report describing heterologous expression of active NiFe hydrogenases in cyanobacteria.

Purifying Hydrogenases Expressed in T. roseopersicina and Testing O2-Tolerance

We have previously described purification of the T. roseopersicina HynSL hydrogenase described above, this is the first report describing heterologous expression of active NiFe hydrogenases in cyanobacteria.

FIGURE 2. Expression of T. roseopersicina hydrogenase in cyanobacteria. Proteins from wild-type and HynSL-expressing strains were separated by sodium dodecyl sulfate polyacrylamide gel electrophoresis and Western blots were performed using antiserum raised against HynL.

FIGURE 3. In vitro H₂ evolution assays were performed on crude cell extracts from cyanobacterial strains containing T. roseopersicina constructs (Hyn4, Hyn5, Hyn5/Hup) or constructs Hyn4 and Hyn5 in combination with the environmental hydrogenase accessory gene construct (Wav10). Cells were induced with isopropyl β-D-1-thiogalactopyranoside, lysed, and assays were performed under Ar atmosphere using the synthetic electron donor methyl viologen.

one-tenth the activity of the native cyanobacterial hydrogenase (Figure 3). With the T. roseopersicina HynSL hydrogenase described above, this is the first report describing heterologous expression of active NiFe hydrogenases in cyanobacteria.

the hydrogen-deuterium exchange assay. The environmentally-derived hydrogenase maintained 20% activity in 1% O₂, 5% activity in 5% O₂, and did not possess activity at 5% O₂. This indicates that the novel, environmental hydrogenase is active in the presence of O₂.

NREL: The goal for this part of the work is to construct a cyanobacterial recombinant harboring the O₂-tolerant hydrogenase from Rubrivivax gelatinosus, using Synechocystis sp. PCC 6803 as the model host. We used two plasmids to accomplish this goal. Plasmid pPETE SigD was provided by Prof. Robert Burnap (Oklahoma State University) which enables light-regulated gene expression and homologous recombination. We cloned four structural genes cooLXUH encoding the Rubrivivax O₂-tolerant hydrogenase into the pPETE_SigD plasmid followed by its transformation into a Synechocystis mutant host lacking background hydrogenase activity (Hox⁺ provided by Prof. Teruo Ogawa). Protein western blot confirmed the expression of Rubrivivax hydrogenase subunits CooH (catalytic subunit), CooL (small subunit), and CooU (unknown function) in one of the three LXUH transgenic lines tested (Figure 4A). Expression of CooX is likely but not yet confirmed due to poor quality of its antibody. 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 and transformed the Synechocystis Hox⁻ strain the plasmid carrying codon-optimized Rubrivivax cooL gene alone (pRL1342_L), or cooL as well as the hypA (hydrogenase maturation; pRL1342_LA) genes. As shown in Figure 4B, CooL protein is detected in both transgenic lines, demonstrating the utility of this broad host range plasmid in expressing foreign genes in Synechocystis. It is likely that the HypA protein was also expressed in the +LA line, which will be confirmed once we have the HypA-specific antibody.

Conclusions

JCVI: We have heterologously expressed two NiFe hydrogenases in cyanobacteria, one from T. roseopersicina and the other cloned from environmental DNA, and demonstrated that they are expressed with fully assembled and functional active sites. We have also purified these hydrogenases and verified that the environmentally-derived hydrogenase...
maintains activity in the simultaneous presence of up to 3% O₂. This work demonstrates that novel hydrogenases with potentially useful properties can be isolated from environmental DNA.

**NREL:** The NREL research confirmed the expression in *Synechocystis* of three genes, via homologous recombination, encoding subunits of the O₂-tolerant hydrogenase from *Rubrivivax*. Moreover, we also detected the expression of a *Rubrivivax* hydrogenase subunit via a plasmid-based approach in *Synechocystis* which could be used to express additional genes for building the recombinant.

**Future Directions**

- Re-engineer plasmid constructs and demonstrate increased expression of hydrogenase in vitro (JCVI).
- Test electron mediator requirement of hydrogenase expressed in cyanobacteria strains with increased hydrogenase expression (JCVI).
- Optimize conditions and transfer additional hydrogenase structural and maturation genes of *Rubrivivax* to express a functional O₂-tolerant hydrogenase in *Synechocystis* (NREL).

**FY 2010 Publications/Presentations**


II.I.1 Photoelectrochemical System for Hydrogen Generation

Objectives

- Optimize and refine selection of A2B6 semiconductor photoelectrode materials.
- Synthesize and characterize the A2B6 semiconductor photoelectrode materials.
- Develop large-area photoelectrode panels.
- Develop a scaled-up prototype of a photoelectrochemical (PEC) reactor cell.
- Integrate the scaled-up prototype reactor cell with photoelectrodes and evaluate its performance.

Technical Barriers

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

(Y) Materials Efficiency
(AC) Device Configuration Designs
(AD) Systems Design and Evaluation

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for PEC Hydrogen Production

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2013 Target</th>
<th>2010 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Usable Band gap</td>
<td>eV</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Chemical Efficiency</td>
<td>%</td>
<td>10</td>
<td>TBD</td>
</tr>
<tr>
<td>Solar-to-Hydrogen Efficiency</td>
<td>%</td>
<td>8</td>
<td>TBD</td>
</tr>
<tr>
<td>Durability</td>
<td>hours</td>
<td>1,000</td>
<td>TBD</td>
</tr>
</tbody>
</table>

TBD = to be determined

Accomplishments

- Fabricated A2B6 photoelectrodes using low-cost electrodeposition to produce two distinct architectures: a CdS/ZnS bilayer (n-type) and a ZnTe (p-type).
- Demonstrated CdS/ZnS absorption band edge at 2.2 eV and performed photoelectrochemical testing of samples.
- Designed, fabricated, and tested two generations of photoelectrochemical (PEC) reactor cells.
- Conducted preliminary economic analysis for PEC reactor system.

Introduction

Sunlight is an abundant, renewable and domestically available energy source that can provide a significant proportion of carbon-free energy in the future, particularly if sunlight can be harnessed to generate hydrogen fuel for transportation. PEC hydrogen generation is an approach to generate hydrogen fuel directly from water by using sunlight to drive a water-splitting reaction on the surface of novel semiconductor materials. The primary technical barriers to the development of these semiconductor materials are that they absorb a sufficient amount of the incoming solar energy, efficiently transfer that energy to drive the water-splitting reaction, and remain durable and efficient for long operational times while remaining cost-competitive with other hydrogen generation approaches. In this project, Physical Optics Corporation (POC) is developing an approach for the low-cost fabrication of A2B6 semiconductor photoelectrode architectures and building a prototype PEC reactor cell for testing and demonstration.

Approach

The approach of this project is to increase the solar-to-hydrogen efficiency by using lower band gap A2B6 semiconductor materials (addressing the Materials Efficiency technical barrier). Using a lower band gap enables increased solar absorption due to capturing the abundant lower energy photons inaccessible to traditional high band gap PEC materials. Through a review of potential A2B6 material combinations we selected CdS and ZnTe absorbing materials with band gaps in the 2.2-2.4 eV range. Both materials can be deposited using the low cost, solution process of electrochemical deposition, which is also highly scalable for manufacturing. To address the well-known lack of
durability of CdS we designed a Type-II heterojunction architecture which uses wide band gap ZnS as a capping or window layer to provide photocorrosion protection (addressing the Device Configuration Designs technical barrier). A process for co-depositing CdS with the ZnS capping layer from a single solution was adopted and refined for photoelectrode fabrication.

In addition to fabricating photoelectrode materials, a series of generations of prototype systems to house the photoelectrodes, the PEC reactor cell, were designed, assembled, and tested as part of an iterative design process. Ultimately the photoelectrodes and PEC reactor housing will be assembled as a final prototype for testing and demonstration purposes. Technoeconomic evaluations of the hydrogen production cost will be made based on the prototype fabrication costs, the material costs, and the projected photoelectrode efficiency and lifetime of the mature system. This work directly addresses the Systems Design and Evaluation technical barrier.

Results

Our efforts on this project have focused on the development of the two major cell components: the semiconductor photoelectrode structure and the photoelectrochemical reactor cell housing.

Electrodeposited A2B6 Photoelectrode Development

We developed and refined the process for co-deposition of an n-n CdS/ZnS bilayer film using electrochemical deposition. The bilayer film shown in Figure 1, consists of an approximately 2 micron thick layer of CdS capped with roughly 100 nm of ZnS. After a base layer of CdS is deposited, the incorporation of ZnS is gradual starting around the third hour of the deposition process. Due to the large band gap of ZnS (E_g = 3.5 eV) the CdS/ZnS bilayer films are visibly and spectroscopically (for absorption spectroscopy) indistinguishable from CdS single layer films. Figure 2 shows the Tauc plot for an electrodeposited CdS/ZnS film showing a direct band edge around 2.2 eV, which achieves the DOE target. The reduction in band gap compared to bulk CdS (E_g = 2.4 eV) is attributed to a reduced amount of strain present in the solution deposited film. The influence of different substrate materials on the growth of CdS/ZnS was investigated, which revealed that due to the process by which CdS deposits (i.e., mediated by proton reduction on the cathode) more uniform CdS films were deposited using substrate materials that had slow proton reduction kinetics (e.g., Ti and ITO).

Zinc telluride films were also fabricated using electrochemical deposition which showed a strong dependence on the substrate and growth potential due to the large difference in reduction potential between Zn and Te. Films with an excess of one material or another were typical, as confirmed by energy dispersive X-ray (EDX) and X-ray diffraction (XRD) measurement.

The electrodeposited CdS/ZnS were characterized following standard PEC procedures. The open circuit potential measurement confirmed the n-type doping with an estimated flatband potential of -0.50 V vs. Ag/AgCl in 0.1 M H_2SO_4. Results of PEC testing are shown in Figure 3, which shows the 3-electrode current density-voltage (IV) and unbiased photocurrent characteristics for electrodeposited CdS/ZnS. Air annealing (at 200-300°C) has been investigated as a means of improving crystallinity. Initial results showed similar PEC properties with a decrease in durability attributed to the formation of cracks in the film during
annealing due to the mismatch in thermal expansion between the substrate and film. PEC characterization of ZnTe films are in progress and are expected to offer increased photocorrosion stability due to being p-type and generating hydrogen during the water-splitting reaction (i.e., due to being the photocathode).

PEC Reactor Cell Development

We have designed and fabricated a second generation prototype for the PEC reactor cell which will house the photoelectrode, counterelectrode, water and evolved H₂ and O₂ gases. The second generation design shown in Figure 4 was developed based on the testing of the first generation design performed by using electrolysis on metal electrodes installed in the unit in the locations where the photoelectrode and counterelectrode would sit. Through this testing we observed H₂/O₂ gas evolution and identified potential bottlenecks, weak seals, and other drawbacks. The resulting second generation design improved on the first by including a drastically reduced number of seals, eliminating bottlenecks, and improving the layout of the photoelectrode and counterelectrode configuration to better utilize space. The new design is both scalable (by increasing the size of the basic unit cell) and modular (by allowing multiple cells to be combined together) while providing easy maintenance. While awaiting system level tests with photoelectrodes, the second generation design is being further refined through studies of the durability of the materials (plastics, metals, etc.) to extended exposure to harsh electrolytes and ultraviolet light. This study includes both a literature review and laboratory lifetime testing of various reactor materials in electrolyte solutions.

Conclusions and Future Directions

POC has applied a novel CdS/ZnS bilayer electrodeposition approach to fabricate a semiconductor architecture for photoelectrochemical hydrogen generation. The resulting films exhibit broad absorption of the solar spectrum with a band gap of 2.2 eV. The characterization of the bilayer film using PEC methods demonstrated a photocurrent of 27 µA at 0 V vs. Ag/AgCl under AM1.5 illumination. Future work aims at improving the photocurrent through investigation and optimization of the carrier transport properties of the electrodeposited films to be achieved by optimizing the deposition process. Verification of PEC test results through collaboration with other members of the PEC workgroup are planned. In addition to developing...
photoelectrode materials, we constructed a small-scale prototype PEC reactor, based on the testing of the first generation prototype. The second generation prototype improved on the collection and partitioning of gases, an improvement of the counterelectrode-photoelectrode arrangement, the durability of the materials used in the system, and the modularity and scalability of the design. The future development of the PEC reactor system will include integration with photoelectrodes for full system testing and evaluation. Based on the final prototype system, an evaluation of the commercial potential for the system will be performed including the calculation of the cost of hydrogen production through technoeconomic analysis. The results of the system development and economic analysis will provide a strong basis for further commercial development of photoelectrochemical hydrogen production components or systems in the future while working to overcome DOE technical barriers.

**FY 2010 Presentations**


II.I.2 Nanotube Array Photoelectrochemical Hydrogen Production

Objectives

- Determination of optimal template geometry for photoelectrochemical (PEC) water splitting using TiO₂ as a test bed material.
- Development of additional absorber materials with required composition and architecture to achieve 5,000+ hour lifetime, 2.0 eV bandgap, and >10% conversion efficiency in the prototypes.
- Evaluation of approaches for integration of developed materials into a self-contained system.
- Formation of partnerships for bringing the technology to the market.

Technical Barriers

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

(AA) PEC Device and System Auxiliary Material
(AC) Device Configuration Designs

Technical Targets

This project is conducting studies of PEC hydrogen production by creating a hybrid design that combines multiple layers of materials to simultaneously address issues of durability and efficiency. As part of this effort, techniques are being developed that can manufacture devices at commercial scales. The overall goal of this project is to create a PEC device that meets or exceeds the following DOE 2018 PEC hydrogen production targets:

- Usable bandgap: 2.0 eV
- Chemical conversion efficiency: 12%
- Solar to hydrogen efficiency: 10%
- Plant durability: 5,000 hours

Accomplishments

- Produced conformal transparent conductive oxide (TCO) and TiO₂ nanotubes in a layered manner inside pores of anodic aluminum oxide (AAO).
- Demonstrated photocurrent on PEC devices without applying an external potential.
- Demonstrated ability to reduce bandgap of TiO₂ to 2.5% without affecting conductivity.
- Demonstrated conformal deposition of GaN inside AAO as a separate light absorbing material.

Introduction

The cleanest method of hydrogen production is the use of sunlight to electrochemically split water into hydrogen and oxygen. Advances in photoelectrode materials are required to make PEC hydrogen production practical. Current materials representing the state-of-the-art in this area suffer from significant lifetime limitation, bandgaps poorly matched with the solar spectrum, and low conversion-efficiency. The project aim is to develop and commercialize next-generation PEC materials that incorporate an innovative three-dimensional nanostructured architecture and a tailored bandgap.

Approach

The material architecture includes high-density, high-surface-area arrays of nanotubes formed inside the pores of the honeycomb-like, self-organized matrix of nanoporous AAO. The approach utilizes a synergistic combination of two technologies developed by the project team: (1) synthesis and integration of AAO with the required porous structure; and (2) conformal atomic layer deposition (ALD) of materials inside the high-aspect-ratio pores to produce nanotubes with atomically controlled thickness of coaxial layers. The approach
results in up to a 1,000-fold increase of the cross-section available for light absorption and the surface area available for electrochemical reactions, thus significantly increasing the hydrogen yield per area of the electrode.

The PEC materials developed in this project include a catalytic layer, surrounded by a layer of light absorbing material, surrounded by an outer shell of TCO (Figure 1). In addition, the light absorbing material can also have a vertically graded composition to allow for a vertically graded bandgap for maximum light absorption. The architecture provides a long vertical path length for light absorption with a short lateral path length for efficient charge separation.

Results

During this project we have produced AAO membranes with a variety of pore dimensions and pore densities. Pore diameters ranged from 13 to 300 nm, with corresponding pore periods from 20 to 500 nm. Subsequently, TCO and TiO$_2$ were deposited conformally inside the pores to form hollow PEC tubes and the materials were tested for PEC efficiency. These studies showed that the larger pore periods were more effective as PEC scaffolds and all subsequent tests were performed on these larger period samples.

In order to meet the cost targets for hydrogen from PEC, we also performed a scale-up effort to increase the size of our AAO membranes. Figure 2 shows an anodization cell of sufficient capacity to support large membranes (up to 10”x17”) as well as large batches of smaller membranes. Further membrane production of larger format membranes will be completed in this cell.

In addition to our efforts to scale up the anodization cell, we also expanded our ALD reactor to accommodate up to seven different precursors. Two of these precursors are on a separate dosing line specifically designed to handle the low vapor pressure precursors used for TiO$_2$ deposition. The efficacy of this new reactor design has been demonstrated by depositing highly conformal, pinhole-free layers inside the pores of AAO.

Figure 3 shows the photocurrent in chopped light as a function of the applied potential for our nanostructured PEC samples as well as flat samples with...
materials deposited in identical conditions. Peaks in the current are due to the light incident on the sample and the valleys between are due to no illumination on the sample. A Ag/AgCl reference electrode was used which has a potential of ~0.22 V vs standard hydrogen electrode. Therefore, the far left axis in Figure 3 represents zero applied bias. For the flat sample, there is no current when the applied bias is low, however, for the nanostructured sample there is an appreciable current even without an applied bias. This is a very promising result for this architecture.

In earlier efforts we explored nitrogen and carbon doping of TiO₂ to reduce the bandgap of the material. We were able to reduce the bandgap from 3.1 eV to 2.5 eV using nitrogen doping (Figure 4). These samples were prepared before the ALD reactor was modified and this was the best that could be achieved at the time. In more recent efforts we have developed a chemistry for the deposition of TiN. By combining this chemistry with the TiO₂ chemistry, we anticipate that we will be able to achieve larger doping densities and lower the bandgap to the required 2.0 eV.

In addition to modifying the TiO₂ bandgap, we have also explored the use of a separate absorber material, as shown in Figure 1. We used the expanded ALD reactor to manufacture PEC samples consisting of an outer conductor, a GaN absorber, and a TiO₂ catalytic layer. These samples were extensively tested by our collaborators at the National Renewable Energy Laboratory.

The open-circuit potential (OCP) (measured vs. the reference electrode) shifted negative with the application of broadband illumination from a 250-Watt tungsten lamp. The negative shift in OCP indicates these material configurations behave n-type, making them photoanodes.

Photocurrent spectroscopy was performed and indicated an indirect bandgap transition for these materials. GaN (bulk) is known to have a direct electronic transition at an energy of 3.4 eV, so the absorption of visible light is an encouraging result. That the transition is indirect is less encouraging. One possible explanation for the low-energy indirect transition observed could be mid-gap defect states in the GaN. These defect states limit the utility of the as-deposited GaN as an absorber material.

The reason the GaN/TiO₂ electrodes didn’t generate significant photocurrent is likely due to non-ideal band alignment at the GaN/TiO₂ heterojunction. If the valence band (VB) of the GaN is above the VB of TiO₂, holes from the GaN have an energy barrier that would prevent them from injecting into the VB of TiO₂, where they would be available for oxidation on the electrode surface. A similar argument could be made for electrons in the conduction band (CB) if the CB of GaN is above the CB of TiO₂. X-ray photoelectron spectroscopy measurements by Hansen [1] of a GaN/TiO₂ heterojunction suggest the latter.

The visible light absorption in GaN is intriguing. It is likely that the GaN has defects or impurities that lead to the visible absorption. There are reports that solid solutions of ZnO/GaN can absorb into the visible region, but not as far into the visible as we see with these electrodes. From the two data points we have (5 nm, 10 nm) the thicker the GaN, the better the photoresponse. Though these GaN samples can absorb visible light and generate reasonable photocurrent densities, the band edges appear to preclude these electrodes as unbiased water splitting electrodes.

Currently the lifetime of the materials is low, less than 100 hours. Techniques to increase the lifetime are currently being explored.

Conclusions and Future Directions

Conclusions

We have developed a nanostructured PEC material that is manufactured using scalable techniques. The material shows a significant enhancement in photocurrent over flat anodes, and is active without the need for an applied bias. We have shown that we can lower the bandgap of TiO₂ while increasing the efficiency of PEC. We have also produced samples with GaN as the absorber, and shown that it absorbs visible light; unfortunately, the band edges are misaligned for water splitting.

Future Directions

- Investigate WO₃ as a PEC material.
- Revisit N-doping of TiO₂ as a means to push bandgap down to 2 eV.
- Measure long-term stability of nanostructured films.
• Investigate other absorber materials.
• Explore techniques for increasing robustness of films and their lifetimes.

Special Recognitions & Awards/Patents Issued

1. On May 1st 2009 we submitted a U.S. Provisional Patent Application No. 61/174,577 entitled “ENERGY CONVERSION DEVICES AND METHODS FOR MAKING SAME.” This patent covers the architecture described in this project as well as related architectures for photovoltaics and other applications.

References

II.I.3 Aqueous Phase Base-Facilitated Reforming (BFR) of Renewable Fuels

Technical Targets

This project is conducting pilot-scale system design, construction, and experimental testing for distributed hydrogen production from municipal solid waste. Insight gained from this effort will be applied toward a full-scale hydrogen production system that meets the DOE 2012 distributed hydrogen production targets listed in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2012 Target</th>
<th>BFR Projection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Unit Energy Efficiency</td>
<td>%</td>
<td>72.0</td>
<td>79.0*</td>
</tr>
<tr>
<td>Production Unit Capital Cost (Un-installed)</td>
<td>$</td>
<td>1.0M</td>
<td>$0.664 M – 1.59 M b</td>
</tr>
<tr>
<td>Total Hydrogen Cost $/gasoline gallon equivalent (gge)</td>
<td></td>
<td>3.80</td>
<td>$2.27 - $3.26 c</td>
</tr>
</tbody>
</table>

* Preliminary.
b Linearly scaled down from a 2 tons per day modular production system.
c In 2005USD, includes only H2 production costs, using H2A standard economic assumptions.

Accomplishments

- Developed continuous reactor concept with a fixed-bed catalyst design thereby eliminating the need for complicated particle separation subsystem.
- Achieved similar hydrogen yields on pre-dissolved feedstock thereby allowing a continuous reactor system design to be based on a liquid medium rather than a slurry.
- Experimentally validated that similar hydrogen yields are possible at higher reaction temperatures and lower NaOH concentration which will assist in the precipitation process.

Introduction

Approximately 100-150 million tons per year of municipal solid waste (MSW) are potentially available for hydrogen production [1]. This equates to ~14-22 million tons of hydrogen per year from a source that is normally considered a nuisance or, in some cases, even a hazard. The main advantages of using MSW as a feedstock are its low (or even negative) cost, its already established collection system, and its proximity to population centers which are also hydrogen demand

Objectives

- Experimentally demonstrate a continuous BFR reactor with similar performance to the Phase 1 batch system.
- Experimentally determine the appropriate operating parameters specific to our reactor design.
- Develop a system which allows for reuse of catalysts.
- Determine, through experiments, the appropriate operating parameters specific to our precipitator design.
- Validate process feasibility by correlating experimental results with economic analysis.

Technical Barriers

This project addresses the following technical barriers from Section 3.1 – Hydrogen Production of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reformer Capital Costs
(B) Reformer Manufacturing
(D) Feedstock Issues
(E) Greenhouse Gas Emissions

Accomplishments

- Developed continuous reactor concept with a fixed-bed catalyst design thereby eliminating the need for complicated particle separation subsystem.
- Achieved similar hydrogen yields on pre-dissolved feedstock thereby allowing a continuous reactor system design to be based on a liquid medium rather than a slurry.
- Experimentally validated that similar hydrogen yields are possible at higher reaction temperatures and lower NaOH concentration which will assist in the precipitation process.

Introduction

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Introduction

Approximately 100-150 million tons per year of municipal solid waste (MSW) are potentially available for hydrogen production [1]. This equates to ~14-22 million tons of hydrogen per year from a source that is normally considered a nuisance or, in some cases, even a hazard. The main advantages of using MSW as a feedstock are its low (or even negative) cost, its already established collection system, and its proximity to population centers which are also hydrogen demand
centers. Disadvantages include separation of the heating value constituents of MSW (paper, wood, grass, food) from the non-heating value constituents (rocks, plastic, metal, etc.).

One solution is to use a process not limited by feedstock type such as BFR. The chemical reaction within BFR has been found to produce hydrogen from most MSW materials. BFR allows one to produce highly pure hydrogen gas (>98% purity) in a simple one-step process with no need for water-gas shift systems and minimal, if any, additional gas purification. In Phase 1 of this Small Business Innovation Research project, we investigated process parameters, evaluated case studies of various commercial system scenarios, and performed system analysis using laboratory data to confirm economic feasibility. In Phase 2 we are addressing the hurdles associated with a continuous prototype system to better understand the operation and viability of a commercial product.

Approach

The continuous BFR system is being developed using an iterative test and design approach. As different operating conditions are tested, the results from those experiments influence the design of the feedstock preparation, BFR reactor, and causticizing reactor. Major subsystems are being designed and experimentally tested individually and will not be linked in a complete system as part of this project. Thus current work focuses on developing a system design and defining operating conditions that will optimally work together when all subsystems are linked. This is particularly challenging as the reactor and precipitation subsystems optimum performance are at contradictory conditions.

Results

The main activity conducted to date has been exploration of the integrated BFR system configuration and operating conditions. The complete BFR system consists of four main subsystems (Figure 1). The first subsystem is feedstock preparation which modifies the form of the feedstock so it is more easily handled and reacts best with the catalyst. The second subsystem is the hydrogen generation which takes place in the BFR reactor. The aqueous Na₂CO₃ waste stream from the BFR reactor is transferred to the third subsystem, the causticizing reactor, in order to reconstitute NaOH from the Na₂CO₃. The NaOH is recycled to the feedstock preparation and the CaCO₃ precipitate is transferred to the final subsystem, the calcium carbonate recycle. Here, CaO is reconstituted from the CaCO₃ precipitate and recycled to the causticizing reactor for the slaking reaction. While hydrogen production takes place in the second subsystem, economic studies indicate that the recycling of the reaction components is necessary to lower the cost of hydrogen.

Major subsystems are being designed and individually tested. The optimum feedstock preparation
procedures are being refined. The hydrogen generation subsystem is being fabricated (Figure 2). The major components are a feedstock holding tank, a heating section to bring the fluid up to the reaction temperature, the BFR reactor which contains the catalyst, a hydrogen gas cooling and collection section, and a waste stream cooling and collection section. Using a pump and having sufficient storage at each end point makes this subsystem continuous over a period of time. Once assembled, test will be performed replicating batch BFR reactor conditions to validate hydrogen production capabilities on this subsystem. The reactor hardware will not be linked to the other subsystems previously identified as part of this project. This work’s key results, rather, are the design of a continuous BFR reactor, its fabrication, and validation testing. Additionally, subsystem designs will be developed and tested at the component level. Upon project completion, the team will deliver a future system design, including all four subsystems, and the process parameters necessary for the optimal operation of the system.

In Phase 1 of the project all tests were performed in batch mode on solid feedstock using powder catalysts. While these conditions provided favorable results, a continuous flow system is desirable to allow convenient system scale-up and to achieve high thermal and pressure efficiency. However, the movement of solid feedstock through a continuous system creates complexity and fouling concerns. Consequently, a portion of Phase 2 testing has focused on investigating if the feedstock can be completely liquefied prior to entering the BFR reactor.

Over 40 different tests were completed to determine the extent to which feedstock could be liquefied under various heating profiles. Testing reveals that ~97% (wt) of the wood feedstock dissolves to a liquid1 at 220°C within 10 minutes when combined with NaOH and water (but no catalyst) in a pre-reactor (Figure 3). Pre-dissolving the feedstock in a pre-reactor enables multiple simplifying design elements. First, the liquid feedstock permits use of fixed-bed monolithic catalysts since the absence of solid particles ensures that the catalyst will not foul. This permits repeated use of the catalyst without costly separation equipment. Second, a liquid feedstock allows use of inexpensive, conventional liquid pumps as opposed to costly slurry pumps. Third, pre-liquefying the feedstock allows operating conditions to be easily varied between the pre-reactor and main BFR reactor. Last, hydrogen production can be located independently of the feedstock source and its processing.

Another portion of our experimental work has been focused on lowering the vapor pressure of the BFR solution so that we can operate at lower pressures for a given temperature. Batch testing in Phase 1 confirmed that hydrogen yield2 is proportional

\[ \text{Hydrogen yield} = \frac{\text{Volume of } H_2 \text{ gas obtained}}{\text{Theoretical maximum gas available}} \]

1Dissolves into liquid or liquid-like slurry strainable with a glass-fiber filter having 2.7 micron pore size.

2Hydrogen yield (%) = Volume of H₂ gas obtained / Theoretical maximum gas available
to reaction temperature. In general, higher BFR reaction temperature leads to higher hydrogen yield. Consequently, a high temperature (~340°C) is desired. However, the necessary pressure to raise the boiling point and keep the water in liquid phase at elevated temperature can easily exceed 1,500 psi, a level undesirable for safe, low-cost industrial operation. In Phase 1 equipment was pressure-limited so high NaOH concentrations were used to keep reaction pressures low. However, the causticizer subsystem operates best at low NaOH concentrations which typically result in high operating pressures. Experiments have been conducted in Phase 2 to determine if additional solution constituents are able to suppress pressure while not increasing NaOH concentration. Testing reveals that these additives have a similar effect on vapor pressure as increasing the NaOH concentration. Most importantly though in our experimentation thus far it appears that these additives have no negative impact on the hydrogen production capabilities of the BFR process (Figure 4). These tests were performed in a batch reactor and thus heating and reaction time could not be decoupled. In the case of the Phase 2 continuous BFR reactor the heating section is separated from the catalyst bed and thus we expect lower catalyst residence time and the ability to computed reaction time with respect to hydrogen yield.

Conclusions and Future Directions

- In collaboration with our project team we are building a continuous reactor in which to test various operating conditions and validate batch-mode results.

FY 2010 Publications/Presentations


References

II.I.4 Advanced PEM-Based Hydrogen Home Refueling Appliance

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Monterey Gardiner
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E-mail: Monterey.Gardiner@ee.doe.gov

Contract Number: DE-SC0001179
Project Start Date: July 2009
Project End Date: January 2010

Objectives

The main objective was to examine the real-world technical, operational and market factors that are associated with implementing the hydrogen home refueler (HHR). The detailed effort was comprised of:

• a feasibility study,
• an analysis identifying the technical, operational, and safety requirements of the appliance,
• a preliminary design,
• estimates of energy use and environmental emissions,
• a detailed analysis of the process economics for the proposed technology, and
• a technology development plan.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.14.3) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(G) Capital Cost
(H) System Efficiency

Technical Targets

This project addressed the issue by providing an analysis of the feasibility of an alternative, HHR, where consumers can refuel their cars at home for a competitive price of gasoline.

• HHR production capacity sufficient to support 500,000 vehicles would reduce hydrogen costs to between $3.55 and $4.25 per kg
• Cost of HHR installation to support 500,000 vehicles is between $2,425 at present and $1,336 for future.

Accomplishments

• Preliminary Design – developed specific system designs that meets the system requirements for product operation and commercial acceptance.
• Design Analysis – three different designs were evaluated based on technical, operational, safety and cost.
• Process Analysis – made an economic analysis detailing the process economics.
• Technology Development Plan – defined technical plans to address specific technical factors important to the successful development of the HHR.

Introduction

ElectroChem examined in detail the potential for a novel HHR to provide the daily hydrogen needs for fuel cell passenger vehicles. The HHR appliance uses ElectroChem’s innovative integrated flow field (IFF) stack design in a highly reliable proton exchange membrane (PEM) based electrolyzer system [1]. The appliance is clean, safe, and cost-effective, and provides a significant infrastructure cost savings during the growth phase of the fuel cell vehicle market.

A system design proposed in the report was examined in detail for safety, cost, performance, and market acceptance. Manufacturing costs were examined under the assumptions of a highly automated mass production capacity of 500,000 units annually, commensurate with vehicle manufacturing. The H2A model was used to examine total operating costs and the effective price of fuel to the consumer.

Approach

The key design elements of the proposed HHR appliance are:

• The HHR provides 1 kg of H₂ directly to the vehicle storage tank, using lower cost, off-peak electricity, over an 8-hour period. (Sufficient for a 65-mile driving range.) This effectively “tops-off” the vehicle every night.
• No high-pressure $H_2$ is stored in the appliance and the inherent system design is simplified for maximum safety and minimum cost.
• Appliance installation costs are modest and typical homes already have sufficient electrical capacity to support the unit.
• HHR operation is simple and computer controlled for maximum safety, efficient operation, and can be as easy to use as recharging a cell phone.

Results

The HHR appliance creates a paradigm shift. Hydrogen is generated at night using off-peak electricity and fed directly to the vehicle tank at 5,000 psi for daily commuting. Forecourt hydrogen refueling stations are then only needed to facilitate long distance travel greater than 300 miles. The cost advantage of hydrogen production of ElectroChem’s HHR over forecourt hydrogen station states in the fact that:

a) no manpower is required for operation,
b) no real estate is required for installation,
c) the simple design has few components, and
d) no additional infrastructure is required (electrical power lines, delivery trucks, or natural gas lines).

A system design analysis has found that the safety is readily assured by the adaptation of existing design rules applied to home refueling systems for compressed natural gas, and electric vehicle rechargers [2]. In addition, the HHR is based on ElectroChem’s IFF Electrolyzer (as shown in Figure 1) which passively manages the water content of each cell, guaranteeing reliable performance (enhanced efficiency and superior operational stability) and greatly reducing the number of moving parts. The significant system simplifications also reduce manufactured cost.

Manufacturing costs were examined under the assumptions of a highly automated mass production capacity of 500,000 units annually, commensurate with vehicle manufacturing. The cost estimates partially leveraged the benefits of using materials that are also produced for fuel cell vehicles. Several approaches to cost estimation were used, with each providing similar results, concluding that the HHR can be manufactured for between $1,000 and $2,000.

<table>
<thead>
<tr>
<th></th>
<th>Forecourt</th>
<th>HHR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity kg/day</td>
<td>1,500</td>
<td>3</td>
</tr>
<tr>
<td>number of systems per year</td>
<td>500</td>
<td>1,275,000</td>
</tr>
<tr>
<td>Cost/station (Present)</td>
<td>$6,727,303</td>
<td>$2,425</td>
</tr>
<tr>
<td>Cost/station (Future)</td>
<td>$5,169,290</td>
<td>$1,336</td>
</tr>
<tr>
<td>Total Installed Cost (Present)</td>
<td>$3.36 Billion</td>
<td>$3.09 Billion</td>
</tr>
<tr>
<td>Total Installed Cost (Future)</td>
<td>$2.58 Billion</td>
<td>$1.70 Billion</td>
</tr>
</tbody>
</table>

Because the number of HHR units manufactured is very large (one per vehicle) the manufactured costs are quite low. (The HHR unit is nearly as low a cost on a per kg hydrogen basis as the much larger forecourt station.) This is because, the HHR unit makes up its cost disadvantage by not requiring the excess station costs. It is seen that the total installed cost of the two approaches are nearly the same.

Our primary finding is that HHR production capacity sufficient to support 500,000 vehicles would reduce hydrogen costs to between $3.55 and $4.25 per kg, a cost and energy equivalent that is competitive with gasoline. One gallon of gasoline has nearly the energy equivalent of 1 kg of hydrogen. However, it is also noted that hydrogen vehicles are expected to be twice as efficient on a cost per mile basis. Therefore, it costs half as much to drive a mile with hydrogen.

The forecourt approach to hydrogen refueling was critiqued in detail, particularly during the period of fuel cell vehicle market growth. The problem in the forecourt approach is that large quantities of high-pressure hydrogen must be stored on-site to enable fast vehicle refueling [3]. It is concluded that the serious underutilization of capacity during market growth makes the use of forecourt based fuel very expensive, no matter what technology is used to produce the hydrogen. It is estimated that the perceived need for subsidies to
support infrastructure development can be reduced by a factor of four, if the HHR system is successfully deployed.

The environmental impact of the PEM-based HHR system is minimal because of its inherent use of safe materials, few moving parts, and no toxic emissions. The mass deployment of the HHR refueling system will also reduce carbon emissions. The material components are highly recyclable and the owner will be financially incentivized to recycle by the modest content of precious metal (approx. $100 per unit).

Conclusions and Future Directions

The HHR appliance is a key enabler of fuel cell vehicles. The HHR is seen as a means to rapidly expand the fuel cell vehicle market to all locations simultaneously, without geographic limitations, and with minimal infrastructure cost. Two specific technology development recommendations are made to enable the HHR to achieve its potential of low system cost and high reliability. 1) IFF electrolyzer development to achieve its system cost and reliability potential, and 2) electrolyzer membrane development to reduce hydrogen gas crossover to enable 5,000 psi IFF electrolyzer operation. Additional effort should be placed on low-cost, reliable hydrogen compressor designs, as a fallback to the chance that reduced crossover membrane development only partially meets its goals.

FY 2010 Publications/Presentations


References


II.I.5 Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5,000 psi

Objectives

Develop conceptual design for a unitized electrolyzer system for residential refueling at 5,000 psi to meet DOE targets for a home refueling apparatus:

• Complete preliminary system and stack design of a unitized proton exchange membrane (PEM) electrolyzer.
• Evaluate PEM membrane up to 2,500 psi.
• Complete economic feasibility studies.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(G) Capital Cost
(H) System Efficiency

Technical Targets

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2012/2017 Targets</th>
<th>GES Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Cost</td>
<td>$/kg H₂</td>
<td>3.70/&lt;3.00</td>
<td>2.99*</td>
</tr>
<tr>
<td>Electrolyzer Capital Cost</td>
<td>$/kg H₂</td>
<td>0.70/0.30</td>
<td>0.99</td>
</tr>
<tr>
<td>Electrolyzer Energy Efficiency</td>
<td>% (LHV)</td>
<td>69/74</td>
<td>73.6**</td>
</tr>
</tbody>
</table>

*Using H2A model rev 2.1.1
**5,000 psi operation
LHV - lower heating value

Accomplishments

• Preliminary Electrolyzer Stack and System Design
  - Completed preliminary design of a 5,000 psi “unitized” stack.
    - Designed, fabricated, and tested electrolyzer stack hardware to 2,500 psi.
  - Completed preliminary design for unitized PEM electrolyzer system for home refueling applications.
  - Completed economic feasibility studies.
  - Completed survey of applicable domestic and international hydrogen generation/refueling safety codes and standards.

• Membrane Evaluation
  - Six-cell short stack built with advanced dimensionally stable membrane (DSM™).
  - Conducted testing of DSM™ at pressures of 100, 600, and 2,500 psi.

Introduction

U.S. automakers have invested significant resources in the research and development of hydrogen fuel cell vehicles. However, to enable their widespread use, an additional major investment will be required to construct an infrastructure for hydrogen production and delivery to fueling stations. In order to facilitate this transition, the DOE has recommended that high-pressure hydrogen generation for home refueling of fuel cell vehicles be implemented as an intermediary approach.

GES has developed PEM-based electrolyzer technology for producing hydrogen at moderate to high pressure directly in the electrolyzer stack, while oxygen is evolved at near-atmospheric pressure. In this system, liquid water, which is a reactant as well as coolant, is introduced into the oxygen side at near atmospheric pressure. A low-cost process for producing high-pressure hydrogen from water by electrolysis will significantly advance the development of the hydrogen economy, providing hydrogen for fuel cell vehicles at a price competitive with that of gasoline on a per-mile basis. The ability to produce hydrogen economically, the relatively low capital cost of the electrolyzer unit, and the low maintenance cost of the unit will allow widespread distribution of hydrogen home fueling appliances deemed necessary for the introduction of fuel cell vehicles.
Approach

GES is currently conducting a multi-year, development project for DOE (Contract DE-FC36-08GO18065) that aims to reduce non-military electrolyzer costs while simultaneously raising the efficiencies of the PEM-based water electrolyzer units operating in the range of 400 psi. Future extension of this technology to pressures of 5,000 psig is feasible with modifications to the electrolyzer stack, providing the ability to safely operate in a balance hydrogen/oxygen pressure mode. Based on an innovative electrolyzer stack concept and recent developments in high-strength membrane, GES has designed a PEM-based water electrolyzer system for home refueling applications that can deliver hydrogen at pressures of 5,000 psi. The design concept demonstrates a method for the generation of high-pressure hydrogen by means of “unitizing” the electrolyzer stack and a high-pressure hydrogen/water phase-separator. The combination of components eliminates the need for bulky and costly stack parts and facilitates a method for fabricating an electrolyzer system that can safely operate at a balanced hydrogen pressure of 5,000 psi. In addition, a reduction of major system components and system cost is realized.

Results

**Electrolyzer Stack Design:** The Home Refueling Appliance (HRA) has been designed for on-demand operation. The system is designed with a small six-cell 2 kWe electrolyzer stack, providing a vehicle tank fill of 0.5 kg of hydrogen over a 12-hour period. This will provide 50 miles of driving range based on current fuel cell vehicle fuel economy estimates of 60 miles/kg-H₂. The electrolyzer stack is totally enclosed in a pressure containment dome; the pressure in the pressure dome is matched to that of the electrolyzer’s hydrogen and oxygen production streams. This pressure dome-based design markedly simplifies many of the stack design requirements. Operating in the dome at pressures up to 5,000 psig, the 6-cell stack has a design pressure of 100 psid, and a proof pressure of 150 psid, meeting the requirements of the Draft International Organization for Standardization (ISO) Standard ISO_DIS_22734-2 [2].

**Preliminary Design of a 5,000 psi “Unitized” Electrolyzer System for Home Refueling:** A block diagram outlining the process configuration for the 5,000 psi (34.6 MPa) PEM HRA is shown in Figure 1. The direct production of high-pressure hydrogen in the electrolyzer is shown via combining the water storage tank, electrolyzer stack and hydrogen/water phase-separators inside a pressure-containment dome, eliminating the need for a high-pressure mechanical hydrogen compressor, along with its ancillary equipment. The simplified major subsystems of the high-pressure electrolyzer system include the electrolyzer; the electricity feed sub-system; a user accessible deionized water feed and deionized water handling system. Note that the oxygen/water phase-separator is eliminated in

---

**FIGURE 1.** Cathode Feed Process Flow Diagram
this cathode-fed design; product oxygen that is free of liquid water will be promptly reduced from its high-pressure and vented safely from the system. Figure 2 illustrates a conceptual layout of the HRA pressure dome containing the major items of equipment (electrolyzer stack, water separators, hydrogen cooling coil, and hydrogen dryer).

**Liquid-Gas Phase Separators**: As they will not be subject to any significant differential pressures, the hydrogen/water phase separators located within the dome are designed from low-cost polypropylene material. They do need to be gas-tight; to meet this requirement they will be rotationally molded in a single piece, or injection molded in two pieces, then ultrasonically welded.

**Pressure Dome**: Section VIII of the American Society for Mechanical Engineers (ASME) Boiler and Pressure Vessel Code [3] was used to calculate preliminary material thickness for the HRA pressure dome. Two primary calculations were completed – for the cylindrical shell of the dome, and for the flanged-and-dished heads used to seal both ends of the dome. The cylindrical shell of the dome requires a 2.5″ carbon steel metal thickness to contain the 5,000 psig pressure within the dome.

**Membrane Evaluation at High Pressure Operation**: Polarization scans were obtained in an operating cathode-feed six-cell electrolyzer stack with an active area of 50 cm². The membrane used for this test was DSM™, fabricated by GES personnel. Utilizing a unique structure, DSM™ is a high-performance membrane having excellent dimensional stability over a wide range of temperatures and relative humidities. Compared to conventional ionomer membranes, the supported membrane is stronger, more ionically conductive, and can be optimized for specific applications. The DSM™ used in these tests had a total dry thickness of 2.2 mils, with a polyimide reinforcement layer. Figure 3 illustrates a polarization scan obtained with this electrolyzer, with data taken while operating at 80°C and 100 and 600 psi. The DSM™ demonstrated stable short-term operation and performance superior to that of Nafion® 117 [4]. The voltage ranged from 1.512 V at 100 mA/cm², to 1.688 V at 1,600 mA/cm². At the HRA design current density of 1,200 mA/cm², the operating voltage of 1.655 V translates into a stack voltage efficiency of 75.6% LHV (89.4% higher heating value, HHV). In separate testing using the same hardware, the cell voltage measured during single-cell testing at a balanced operating pressure of 2,500 psi is 1.695 V. Although hardware development is required for 5,000 psi operation, a cell voltage of 1.701 V is achievable (accounting for the Nernst penalty loss at 5,000 psi balanced-pressure-operation) or a cell efficiency of 73.6% LHV (87.0% HHV).

**System Feasibility Studies**: The main challenge to producing commercially viable hydrogen is cost reduction. To determine the feasibility of using a ‘unitized electrolyzer’ as an HRA, it was necessary to examine the individual contributors to the cost of hydrogen production, such as the capital, feedstock
II.1 Hydrogen Production / Production

Norman – Giner Electrochemical Systems, LLC

(electrical costs), and fixed operating and maintenance costs (See Tables 1 and 2).

TABLE 1. System Capital Costs

<table>
<thead>
<tr>
<th>Cumulative Number of Units</th>
<th>1</th>
<th>10</th>
<th>100</th>
<th>1 k</th>
<th>10 k</th>
<th>100 k</th>
<th>1,000 k</th>
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</thead>
<tbody>
<tr>
<td>Electrolyzer Stack</td>
<td>19.14</td>
<td>8.64</td>
<td>4.98</td>
<td>2.90</td>
<td>1.69</td>
<td>0.98</td>
<td>0.57</td>
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<tr>
<td>BOP</td>
<td>17.85</td>
<td>8.06</td>
<td>4.64</td>
<td>3.53</td>
<td>1.57</td>
<td>0.91</td>
<td>0.53</td>
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<tr>
<td>System Assembly Labor</td>
<td>3.70</td>
<td>1.67</td>
<td>0.96</td>
<td>0.56</td>
<td>0.32</td>
<td>0.19</td>
<td>0.11</td>
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<tr>
<td>Total Cost of System ($)</td>
<td>40.69</td>
<td>18.37</td>
<td>10.58</td>
<td>6.99</td>
<td>3.59</td>
<td>2.09</td>
<td>1.22</td>
</tr>
</tbody>
</table>

BOP = balance of plant

TABLE 2. H2A Model Analysis of HRA

<table>
<thead>
<tr>
<th>Cumulative Number of Units</th>
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<th>10</th>
<th>100</th>
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<td>1.22</td>
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A comparison was made between the GES HRA cost estimates and the DOE Hydrogen Program 2015 system cost goal of $30/kWe for light-duty vehicle fuel cells [5]. Using this DOE cost basis, and a scaling factor of 0.60 [6,7], a 2 kWe HRA system would be predicted to cost $234 at a unit production volume of 1,000,000 units. Alternately, a different comparison can be made to the DOE forecourt electrolyzer cost breakdown for 2017 of $125/kWe [8]. Using this alternate DOE cost basis, and a scaling factor of 0.60, a 2 kWe HRA system would be predicted to cost $4,617 at a unit production volume of 1,000. These can be compared to the GES predicted capital costs to verify that the GES costs ($1,220/$6,994) are well above the DOE 2015/2017 scaled costs ($234/$4617). As the modeled GES costs are a factor of 1.5 to 5 above the scaled DOE costs, the magnitude of the GES capital cost predictions appear to be conservative, relative to the DOE 2015/2017 costs.

The total cost of delivered hydrogen ($/kg-H2) via DOE’s H2A analysis model (rev 2.1.1) is shown in Table 2. Our studies indicate that the most significant cost contributions are in two areas: feed stock and capital costs. The feedstock (electricity required to generate H2) contribution of an electrolyzer system operating with a 3-mil DSM™ membrane, average efficiency of 84.1% HHV and a power cost of 4 cents per kWh, is $1.98/kg-H2. Although limited by durability at elevated temperature operation, for comparison the feed stock cost of an electrolyzer system operating with Nafion® 117 (average cell efficiency of 73.7% HHV), is calculated to be >$2.30/kg-H2.

Conclusions and Future Directions

The Phase I project yielded a practical preliminary design for a 5,000-psi “Unitized” design that will be able to provide on-site residential hydrogen refueling at a cost that meets the DOE target of $3.00/kg-H2 in 2017. In addition to unitizing the major components, the design incorporates numerous cost-saving (and reliability enhancing) simplifications, such as eliminating the need for any mechanical pumps, and utilizing passive cooling for low-cost, maintenance-free heat transfer. These design features eliminate the need for bulky and costly stack and system parts, and facilitate a method for producing a low-cost electrolyzer system that can safely operate at a hydrogen pressure of 5,000 psi in a residential setting. Future objectives are:

- Detail design and fabrication of a full-scale electrolyzer stack sized for a hydrogen production rate of 0.5 kg H2 per 12-hour operational period.
- Detail design, component fabrication, and assembly of a “unitized” breadboard HRA electrolyzer system for 5,000 psi delivery pressure.
- Perform in-depth reviews of codes and standards pertinent to hydrogen generation.
- Performance testing of unitized system prototype.
- Develop marketing strategy and partnerships for wide scale adoption of the technology.

FY 2010 Publications/Presentations


References

II.I.6 Design, Optimization and Fabrication of a Home Hydrogen Fueling System

Objectives

- Construct a multivariate system optimization model for a reformer-based home hydrogen fueling appliance that:
  - Provides system selection guidance for optimal system integration.
  - Determines the cost, energy requirement and CO₂ emissions for the selected system integration route.
  - Provides sensitivity analysis for the selected system integration routes with respect to critical cost and energy parameters such as natural gas price, electricity price, hydrogen production rate and bulk production volume.
- Determine the safety issues with the optimal system of choice for a hydrogen production rate of 0.5 kg/day to 3 kg/day. The safety of operation has to be evaluated for the operation of the appliance for a home owner or a person completely unskilled from technical and safety points of view.

Technical Targets

The technical target of the project is to develop an affordable and safe home hydrogen fueling appliance for a daily consumer that speeds up commercialization and general awareness of fuel cell technology. Insights gained from this project will be applied toward the design and fabrication of a home hydrogen fueling appliance in Phase II of the project. The target of the Phase I project was to design a system that meets average home-owners requirements for a fuel cell vehicle application. The specific targets are:

- H₂ production rate: 0.5-5 kg per day
- Fueling time: 2-8 hrs
- H₂ cost: $2.00 to $3.00 per kg H₂ for distributed H₂ production
- Fuel cell grade H₂ quality (SAE J2719 standard)
- H₂ delivery pressure: ≥5,000 psig
- H₂ delivery temperature: 25-40°C

Accomplishments

- Identified safety codes and standards and developed operating guidelines.
- Constructed a user-friendly multivariate model that can perform sensitivity analyses and identified best options for a home fueling station for low H₂ production rates based on cost, CO₂ emissions and electricity consumption.
- Completed preliminary system design calculations for a Phase II prototype system for 0.5 kg/day H₂ production.
- Identified Go/No-Go milestones for Phase II for the optimized system fabrication.

Introduction

Cost, safety and energy requirement are the critical barriers for realizing the concept of home hydrogen fueling for widespread recognition and commercialization of fuel cells in automotive use. Reformation of hydrocarbon fuels such as natural gas and electrolysis of water are the two best options available for hydrogen production. For fuel cell vehicle application, hydrogen at high purity and pressure (>5,000 psig) is required. This presents a system integration problem, where individual processes of hydrogen generation, purification (only for reformation...
route) and compression have to be integrated together efficiently in order to produce an affordable device. Though there have been significant efforts in advancing and optimizing individual systems for centralized and distributed hydrogen generation, there is no effort made on the understanding and optimization of system integration strategies for very low hydrogen production rates (<5 kg/day, 8 hour operation) for a typical home fueling application.

**Approach**

The target of Phase I was to identify, select and integrate the individual subsystems (desulfurizer, reformer, hydrogen purifier and compressor) for a reformer-based home hydrogen generation unit, utilizing natural gas as the fuel feed. The selection criteria were to be based on optimization of critical parameters identified for successful commercial home fueling appliance through a multivariate analysis of the system. The chosen parameters for evaluation of the system were cost, safety and in particular, the electrical energy requirement of the appliance. Lynntech approached the system optimization problem in the following steps:

- Identify and qualify the subsystem or component options and weigh them qualitatively from cost, safety and operability standpoints. This is done by creating weighting factors for each criteria (cost, safety, etc.) and determining the overall system or component score.
- Select appropriate systems for integration from the weighting parameter analysis.
- Construct a quantitative multivariate model to estimate the cost, energy requirement and CO₂ emissions for selected system integration routes.
- Conduct the sensitivity analysis with the model for cost with respect to the variation in natural gas cost, electricity cost and bulk production volume.
- Design the most optimum system from the model results for fabrication of a Phase II prototype for 0.5 kg/day H₂ production.

**Results**

In accordance with the objectives of Phase I, Lynntech developed a multivariate system optimization tool to determine the cost, CO₂ emissions and energy requirement for different system integration strategies for natural gas reformation as well as the water electrolyzer route. The significant findings for a H₂ production rate of 0.5 kg/day to 5 kg/day from the project was that a combination of natural gas reformation for H₂ production with electrochemical purification and compression offers the most economical system design. The competitive system analyzed was a low-pressure electrolyzer with a compressor. The cost of H₂ per kg, electricity requirements and CO₂ emissions are found to be less than the electrolyzer route. The results for H₂ production rate of 0.5 kg/day with 8 hours of operation per day are summarized in Figure 1.

The target of the system optimization was to develop a user-friendly system analysis tool, which allows user inputs for hydrogen production rate, selection of individual system components and their key operating or cost parameters and creates output of cost of hydrogen, CO₂ emission and electricity requirements. A weighting factor analysis procedure was formulated for comparing individual system components for initial screening of the system components for integration. The system components are scored for cost, safety, technology maturity, ease of operation, ease of integration and maintenance. A typical output from the program for comparing different system components is shown in Figure 2.

The selected system components were then linked with each other to create complete system integration strategies. The assumptions for electricity and natural gas cost are taken from H₂A analysis. Capital cost is the primary cost driver in the hydrogen production range under consideration. Figure 3 compares the capital costs of only the reactor-purifier systems under consideration, e.g. the two combinations for the reformer systems, steam methane reformer with electrochemical purifier (SMR-ECM) and steam methane reformer with pressure

![Figure 1](image-url)  
**Figure 1.** Comparison of system optimization results for 0.5 kg/day H₂ (8 hour per day operation) production for Lynntech’s proposed reformer system and a low-pressure water electrolyzer.
Hydrogen production Options

Purification Options

Compression Options

Lynntech’s Reformer System of Choice

FIGURE 2. Scoring comparison for different systems and Lynntech’s reformer system of choice.
CPOX - catalytic partial oxidation; PD - palladium; LP - low pressure

After deducing the capital and operating costs for the systems under consideration, the cost of hydrogen was determined by amortizing the capital cost over a period of 10 years. The rate of return on investment for this period was assumed to be 10%. Figure 4 shows a comparison of hydrogen cost for different production rates for the four system integration options considered under the project. System 1, a SMR-ECM was found to be the best choice among the systems analyzed. It was inferred from the bar plots that for purification and compression, the mechanical systems, PSA and mechanical compression become competitive with electrochemical systems at hydrogen production rates of 5 kg/day, but below that electrochemical systems are the preferred choice. Sensitivity analysis was then
conducted to determine the dependence of $H_2$ cost on the cost of electricity and natural gas feedstock.

Based on the optimal system integration strategy, preliminary plant design for the complete hydrogen production plant was developed for 5,000 psig $H_2$ output as per SAE J2719 quality standard. Safety analysis was then conducted as per ISO 16110, to identify critical failure modes and control strategies or equipment needed. A cheap and effective control strategy was developed to reduce the complexity and cost of the sensor and control equipments used.

Conclusions and Future Directions

- A multivariate model was developed for system optimization and sensitivity analyses of home hydrogen fueling systems.
- Model results for 0.5 to 5 kg/day hydrogen production rate:
  - Reformation of natural gas is the cost-effective way to produce hydrogen gas as compared to water electrolyzers.
  - Capital cost of purification and compression are the critical cost drivers for the reformer-based hydrogen production systems.
  - Electrochemical purification and compression technologies offer the most cost-effective route as compared to conventional PSA and mechanical compression technologies.
  - Combination of reformation for $H_2$ production with electrochemical purification and compression offers the most economical system design.

- The commercial benefits are multiple and include:
  - Small-scale hydrogen refueling stations offering significant cost and process advantages over existing designs.
  - Modeling and simulation tools for implementation of future hydrogen economy equipment items and infrastructure.

- The future task will be to refine the model and convert it into a user-friendly program that can be used as a tool for selection of subsystems for a home hydrogen fueling system.
- Lynntech plans to use the model results to develop and demonstrate a cheap (low capital cost) home hydrogen fueling appliance for 0.5 kg/day $H_2$ production in Phase II.
II.I.7 Hydrogen by Wire — Home Fueling System

Objectives
- Define critical requirements for proton exchange membrane (PEM) electrolysis home fueling system.
- Define hydrogen production capacity for a recharge time relevant to the end-user.
- Estimate the electrical service requirements and physical size.
- Estimate the capital and operating costs.
- Describe the relevant codes and standards and their impact on cost.
- Describe key elements of product safety related to energy content and electrical hazard.
- Describe the types of operation and maintenance required, and estimate costs.

Technical Barriers
This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(G) Capital Cost
(H) System Efficiency

Technical Targets

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2012 Target</th>
<th>2010 Status</th>
</tr>
</thead>
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<td>$/gge</td>
<td>3.70</td>
<td>5.99*</td>
</tr>
<tr>
<td>Electrolyzer Capital Cost</td>
<td>$/gge</td>
<td>0.70</td>
<td>2.62*</td>
</tr>
<tr>
<td>Electrolyzer Energy Efficiency</td>
<td>% (LHV)</td>
<td>69</td>
<td>55**</td>
</tr>
</tbody>
</table>

*Based on H2A model modified for residential (non-commercial) application
**Includes generation and compression to 350 bar
gge = gasoline gallon equivalent; LHV = lower heating value

Accomplishments
- Estimated required hydrogen production capacity for a range of vehicle fuel efficiency values and vehicle usage profiles.
- Estimated physical size and electricity usage.
- Developed home fueling system bill-of-materials.
- Calculated $/kg cost for a range of fuel efficiency and vehicle usage profiles using the H2A model. Demonstrated significant progress toward DOE hydrogen cost targets established for much larger scale hydrogen production systems.
- Tabulated list of relevant codes and standards.
- Estimated cost impact of municipality specific codes and standards environment.
- Defined maintenance strategy.

Introduction
The goal of this study was to develop requirements for a home-based hydrogen fueling system, design conceptual systems, compare the impacts of changing key parameters, and evaluate the feasibility of those concepts in meeting the requirements of the home fueling application. Factors considered in developing requirements included driving scenarios, electrical service requirements, recharge times, compression and storage, and codes and standards. Concepts were evaluated on the basis of capital cost, efficiency, safety, and installation and maintenance.

Approach
The approach was to gather primary data, develop a handful of scenarios representative of typical driving habits, and derive the requirements for the home fueling
system based on the fundamental information. The driving scenarios were based on primary survey data of commuting distances of average Americans including the National Household Travel Survey [1] produced by the U.S. Department of Transportation Federal Highway Administration and the Omnibus Household Survey [2] from the Bureau of Transportation Statistics. The electrical service requirements were evaluated within the context of power available in a typical residence, and compared to other devices currently found in homes. The recharge times were based on the amount of time a vehicle would be parked at home. Proton Energy Systems’ industrial electrolyzer equipment and high-pressure systems were used as sources of information to form the base bill-of-materials for the packaging studies and cost estimates. In addition, Proton’s experience servicing its fleet of fielded commercial electrolyzer products was used to inform the maintenance and service plans. In each of the areas investigated, an approach based on available data and manufacturing experience with commercial electrolyzers was used to ensure the analysis and projections were strongly grounded in practical end-use and the realities of manufacturing.

Results

The hydrogen production capacity was estimated for a range of vehicle fuel efficiency values and driving habits, including serving one, two, or three vehicles within one household. With a single 90 mile per kilogram (mi/kg) vehicle, as little as 0.4 kg of hydrogen are required on average each day (Figure 1). With three 55 mi/kg vehicles and higher driving mileage, as much as 1.8 kg of hydrogen might be required on a given day.

The effects of using an electrolyzer that generates hydrogen and directly fills the vehicles only when the vehicles are home was compared with the option of including a small amount of stationary ground storage. While the inclusion of stationary ground storage does allow the hydrogen production equipment to be smaller, as it can be operating continuously, the cost of the ground storage system outweighs the cost reduction of the electrolysis equipment. Therefore, the electrolysis direct fill configuration has the advantage over a system that includes stationary hydrogen storage.

The compression efficiency of mechanical compressors and the electrochemical compression capability of a PEM electrolysis cell were compared. Electrochemical compression from ambient to 5,000 psi and higher is more efficient than mechanical compression from the same starting pressure. A further optimization showed that there may be a marginal efficiency gain by using a combination of electrochemical compression and mechanical compression where the electrochemical portion ensures that there is only one stage of mechanical compression. The efficiency gains for the combined case may be as much as 10% over pure electrochemical compression. However, including mechanical compression in a home fueling system has several drawbacks. First, the upfront purchase cost is higher with a mechanical compressor. In addition, the life cycle maintenance costs, as well as installation costs, and noise regulations in residential neighborhoods all discourage configurations that include mechanical compression. Electrolysis-only configurations were considered for the balance of the study.

A packaging study was conducted to estimate the physical size of a PEM electrolysis hydrogen home fueling appliance. The result of the detailed packaging exercise yielded a rough sizing of the unit, not including any storage or compression, of approximately 30 to 40 inches wide by 24 to 36 inches deep by 60 to 72 inches tall, smaller than a typical refrigerator (Figure 2).

The cost analysis examined the impact of different driving scenarios, different vehicle fuel economies, the incorporation of either storage or mechanical

![FIGURE 1. Calculated Hydrogen Generation Requirement (average for vehicle driving scenarios and fuel economy)](image1)

![FIGURE 2. A packaging estimate yielded a clean, compact design based on components used in current commercial equipment.](image2)
compression, different cell stack configurations, and long-term cost reductions. Moreover, the sensitivity of the cost of hydrogen to several key factors was studied. Interestingly, for the home fueling application, the usage (as it impacts capacity factor) and the capital cost have a much greater impact on the cost of hydrogen compared to larger hydrogen production plants (Figure 3). The cost of hydrogen for a medium volume, cost reduced product is estimated to be about $5.99/kg. The relative cost reduction from an initial prototype to volume production is estimated to be greater than 50% (Figure 4).

There is a cost impact associated with the current municipality specific codes and standards environment. Based on Proton’s experience with fueling stations as either the prime equipment installer, or the electrolysis supplier, the costs of coordinating with the authority having jurisdiction can be measured from 4 to 50 hours per installation. This type of installation cost would be severely restricting in expanding the reach of a home fueling product to the residential market. The solution is to coordinate national and international standards (such as International Organization for Standardization 22734-2), to assist states and municipalities in adopting the most up-to-date standards, and to educate the local authorities on what key features they should be looking for in a typical installation of this new type of equipment.

For equipment properly designed and properly installed to the latest standards, a PEM electrolysis-based home fueling station exhibits uniquely appropriate characteristics. For example, the maximum on-board hydrogen inventory at full-pressure production is less than 0.05 kg. The amount of energy contained in that amount of hydrogen is less than 1% of what is contained in a couple of lawn mower gasoline filler tanks and less than 0.1% of that contained in two typical gasoline power vehicles. Thus, a PEM electrolysis-based fueling system minimizes the local presence of fuel by converting water directly to fuel only as it is needed.

Conclusions and Future Directions

The case for including the hydrogen home fueling concept in the overall mix of fueling infrastructure is strong. The home fueler can grow in production volume and geographic distribution with individual vehicles as they are placed in the market with more flexibility than centralized fueling stations. Existing utility infrastructure (water, electricity) can be utilized within their existing capacities to cover the distribution aspect of the fueling infrastructure.

- The hydrogen production capacity required for the practical range of home fueling needs is within the capability of existing PEM electrolysis devices.
- The ability to generate hydrogen at 5,000 psi differential pressure—that is, with oxygen at near-ambient pressure—is another significant advantage of PEM electrolysis technology, eliminating the capital cost, footprint constraints, noise, and long-term maintenance costs associated with mechanical compression equipment.
- The footprint of a PEM electrolysis-based home fueling system can fit comfortably within a typical residential garage.
- Cost reduction efforts in line with Proton’s current roadmap can help to bring the hydrogen cost from home fueling down to levels competitive with the targets for neighborhood stations.
- PEM electrolysis-based home fueling equipment has intrinsic characteristics that enhance the opportunities for safe home use, in particular by maintaining a low on-board hydrogen inventory even while operating at full production and pressure.
Proton recommends that the U.S. Department of Energy support near-term prototype fabrication and test of integrated, residential-scale, home fueling equipment based on PEM electrolysis technology.

Proton recommends the support of technology development to extend the differential pressure capability of PEM electrolysis equipment and the support of cost reduction efforts to speed the transition of this technology to initial product release.

**FY 2010 Publications/Presentations**


**References**

II.I.8  Development of a Hydrogen Home Fueling System

Objectives

- Define the requirements for hydrogen home fueling system needs.
- Design and optimize process flows for the hydrogen home fueling system.
- Implement DOE's H2A model to analyze the tri-generation economics and identify barriers to be overcome.
- Setup a technology development plan to advance home application of the technologies.

Technical Barriers

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

(G) Capital Cost
(H) System Efficiency

Technical Targets

Verify feasibility of achieving $3.70/gasoline gallon equivalent (gge) (delivered) from distributed electrolysis (4Q, 2012).

Accomplishments

- Completed analysis of fuel-assisted electrolysis home fueling station process design.
- Showed that using current technology, with current production methods and supply costs, a gge cost of $8.75 can be achieved, with feedstock costs of $1.65/gge.
- Constructed a solid-oxide fuel-assisted electrolyzer and power production hybrid module and used the resulting performance data as input to the home fueling station process design.
- Identified safety codes to be modified for hydrogen home fueling station applications.

Introduction

A critical factor inhibiting the rollout of hydrogen vehicles is the lack of supporting hydrogen distribution and generation networks. Significant use of hydrogen vehicles is not feasible until convenient fueling is accessible to the driving public; a possible solution to this problem is the simultaneous rollout of both hydrogen vehicles and home-based (distributed) hydrogen generation. For such a system to be economical, and avoid the problems associated with on-site hydrogen production via reformation, a fuel-assisted electrolysis method can be used—pairing the purity of electrolysis generated hydrogen with the reduced cost of natural gas feedstock (replacing high cost of the electricity requirement).

Approach

In this project, several system process designs were completed for a hydrogen home fueling system using solid-oxide fuel-assisted electrolyzer cell (SOFEC) technology. Small hybrid SOFEC/solid-oxide fuel cell (SOFC) power generation modules were fabricated and tested, and the performance data were fed into the system process designs to ensure accuracy in the performance component of the cost modeling. The most cost-effective and efficient process was chosen and analyzed for major contributors to the calculated distributed hydrogen production cost.

Results

In conjunction with NREL, MSRI completed a system process design which calls for the use of distributed natural gas as a depolarizing agent to reduce the electrical cost of high-temperature steam electrolysis.
Important considerations in the completion of this design were: (a) projected demand for a fuel cell vehicle operating as a daily commuter, (b) performance of the hybrid SOFEC-SOFC modules, (c) the expected “charge time” allowable (a longer term hydrogen generation cycle allows for reduce system size and correspondingly reduced operational and capital costs), (d) planned operational lifespan of the hydrogen fueling appliance, (e) amount and cost of feedstocks, (f) operational behavior, including system shutdown/startup behavior, expected turndown, required user interaction, etc., and (g) expected subsidiary roles (power and/or heat generation).

Hybrid SOFEC-SOFC (hydrogen and power cogeneration) stacks were built and run using distributed natural gas (directly from the Questar Gas residential/commercial network) and a performance profile was established for the technology at its present state. The data (including performance at a variety of fuel and air utilizations and amperage levels) were compiled and fed into the process design to allow performance analysis according to the H2A model. Figure 1 shows a selection of the performance profiles obtained through the module testing at various utilizations, and Figure 2 shows a steady-state performance profile with set utilizations.

The completed process design included all the requisite components for a hydrogen generation system, including an autothermal reformer, a steam generator, heat recovery devices, hybrid SOFEC/SOFC (hydrogen/power generation) modules, condensers, and a hydrogen compressor. Analysis of the design allowed a current state of technology cost per gge estimate to be made (see Figure 3); it is clear that to meet DOE targets, capital costs (adding $4.51/gge to the production cost) must be reduced significantly.

Conclusions and Future Directions

Hydrogen production via SOFEC has shown to be a viable means of significantly reducing the operational costs of hydrogen generation via electrolysis. It is also clear, that in order to meet the cost goals established by the DOE it will be necessary to reduce the unit capital cost. In addition, a review of existing residential and commercial codes has shown that the regulatory structure necessary for the widespread implementation of residential hydrogen fueling stations is not yet in place.

Future work will include:

- The completion of a complete proof-of-concept hydrogen production unit (including balance-of-plant components).
- Characterization of the complete unit, including the development of practical and optimized startup, shutdown and steady-state operation.
- Recommendations on how the hydrogen home fueling unit can fit into regulatory code development efforts.
- A design for manufacture analysis targeting significantly reduced unit production cost.
FIGURE 2. Steady-State Hybrid Module Performance

FIGURE 3. Solid-Oxide Fuel-Assisted Home Hydrogen Fueling Cost Breakdown

**FY 2010 Publications/Presentations**

II.J.1 Developing Improved Materials to Support the Hydrogen Economy*

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Contract Number: DE-FC36-04GO14215
Start Date: March 1, 2004
End Date: December 31, 2010
*Congressionally directed project

Objectives

- Foster the investigation and advancement of cross-cutting, breakthrough materials technologies to yield an award-winning project 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 addressed a wide range of barriers from the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan.

Technical Targets

The EMTEC solicited and funded hydrogen infrastructure related projects that have a near-term potential for 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, “Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan.” Preference was given to cross cutting materials development projects that lead to the establishment of manufacturing capability and job creation.

Approach

The EMTEC has used the U.S. Department of Energy hydrogen economy goals as outlined in the multi-year plan titled, “Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan” to find and fund projects with near-term commercialization potential. Our request for proposal 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 develops 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. All capstone projects are now complete.
- EMTEC attended and presented a poster at the DOE Hydrogen Program Merit Review, June 7–11, 2010, which featured the most promising technologies.

Conclusions and Future Directions

EMTEC has leveraged DOE initiative funded 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:

Individual Projects: (all complete - see previous reports)
Future Directions

- Technical governance with projects and technology outcomes.
- Seek new opportunities to continue technology development and commercialization activities as appropriate for the most promising technologies.

Conclusions

EMTEC continues to energetically pursue the near-term commercialization of the hydrogen infrastructure technologies that in many cases has been developed with previous DOE support. The EMTEC programmatic collaborative approach is well suited to accelerate technology to market. EMTEC selected high quality projects in appropriate subject areas that have cross cutting materials technology with near-term manufacturing opportunities.

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.

2010 Publications/Presentations

1. EMTEC made a presentation at the 2010 Ohio Fuel Cell Coalition annual Symposium, giving a historical perspective of fuel cell involvement with some of the developmental programs and projects throughout many years.
Objectives

- Investigate and evaluate initial processes for the production of hydrogen from various waste streams using anaerobic microbial fermentation.
- Investigate paths for implementation of the research as a modular energy source initially for application in remote locations.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (Revision 2007) (see page 3.1-30 of Section 3.1.4):

- (AR) H\textsubscript{2} Molar Yield
- (AT) Feedstock Cost
- (AU) Systems Engineering

Accomplishments

- Testing of various combinations of microbial consortia was conducted with organic waste materials to determine parameters that maximize production. It was determined that pH, temperature and waste material concentration had the greatest influence on hydrogen production for the test conditions considered. A central composite design is being used to determine operating values that maximize hydrogen production.
- The automated testing system previously designed and constructed was used to determine optimal operating parameters. Fourth generation tests are now being completed.
- Tests of continuous production are ongoing for Purdue food waste and distiller's grain and inoculum samples.
- The initial design of a modular energy system for local energy production and waste treatment has been completed and is being used to optimize value.
- A 3 L batch/continuous fermentor is being implemented to enhance testing and consider scale up issues.
- The vacuum tube solar collector system is used for pre- and post-waste processing and consideration of other ancillary uses such as building heating and production of potable water.
- Steam generator tests demonstrated ability to distill water with maximum solar energy conversion efficiency of ~70%.
- Initial designs are being investigated for development of a prototype system with reduced substrate water concentration.
- Decreasing water concentration significantly increases the value for the modular energy system design. Water concentration has been decreased from 95% to 75% with little loss in hydrogen production rates.
- Significant hydrogen production was demonstrated using distiller's grain from ethanol production as substrate. Maximized operating procedure has shown significant increase in hydrogen production levels for second generation tests of distiller's grain.
Two advisory board meetings were held in the last year to continue to gain input from industry. Advisory board members include: Cargill, INEOS Technologies, BP, Advanced Power Technologies, and Ajinomoto Food Ingredients, LLC.

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 Fuel Cell Technologies Program. Hydrogen production research of this project is reported in Purdue Hydrogen Systems Laboratory: Hydrogen Production.

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. This effort is investigating ways to develop a modular anaerobic biological hydrogen production and energy system for applications initially in remote locations (Figure 1). It is realized that hydrogen production levels from conventional anaerobic processes are not as great as is desired in the long term perspective for bulk production systems.

This research is focusing on a process that has multiple products and associated values. Value streams include hydrogen, waste disposal function, heat for buildings, drinking water, and possibly a marketable chemical product produced from process carbon dioxide. After it is proven, it is anticipated that the technology will be leveraged to larger applications in continuing research efforts. We have performed preliminary cost analysis studies, but factors such as the water content greatly influence the design and consequently the cost. It is also necessary to consider aspects such as the value of waste disposal, sanitized fertilizer, and ancillary energy. These aspects depend on the details of the process currently being developed. Preliminary estimates indicate that when all costs and benefits are considered, the technology has advantages over other alternatives for this application. The carbon dioxide capture portion of the process is intended principally for gas conditioning. Carbon dioxide is a co-product and hydrogen purification is usually necessary. The potential for utilization of the captured carbon dioxide in the production of chemical products is under investigation as a part of maximizing the utility of the proposed self-contained system.
**Approach**

We are considering methods to optimize hydrogen production from waste through the use of a fermentation process (Figure 2). The optimization procedure is being used to form the foundation for the subsequent development of a modular device that will use various waste streams, including garbage, animal or human waste, and distiller’s grain for the production of hydrogen. This hydrogen will be separated from the biogas stream by use of nanocatalyst 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. The steam generator of the solar system is currently producing 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 75% 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**

Additional inocula have been tested and the concentration of hydrogen in the produced gas has been correlated with the experimental variables: pH, temperature, and substrate concentration. We have preliminary indications that a new procedure for producing hydrogen with distiller’s grain may show considerable higher hydrogen production levels than any observed to date. We are currently investigating this approach. If verified, this may provide a new alternative for increasing hydrogen production levels with distiller’s grain and provide a potential enhancement to the energy balance for ethanol production. Considerable interest in these results has been shown by the Industrial Advisory Board for the project since it could be of value for multiple industrial processes.

Test samples and data are being exchanged between Purdue Calumet and Lafayette and trials to test repeatability continue. A micro gas chromatograph is used to determine gas composition. The testing is based upon a central composite experimental design. We are currently completing the third iteration for the optimization of the hydrogen production levels. This process identifies combinations of operating variables that maximizes hydrogen production. Figure 3 depicts the third generation optimization of hydrogen concentration using the Simplex methodology with an optimum point at 36.9°C, starting pH 5.9 and 1.2 g/25ml concentration. The multiple testing devices are fully operational and is being used to generate data (Figure 4). 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 and initiated at Purdue Calumet with the addition of a batch fermentor (New Brunswick). Initial approaches to a dry substrate design are being investigated at Purdue Calumet and Lafayette. The computer simulation model for the modular energy system was updated based upon new experimental values. Efforts using a catalyst process for capture of carbon dioxide have been initiated.

**Conclusions and Future Directions**

The biological hydrogen production work to develop optimal hydrogen production cultures for different substrates, reduce the water content in the substrate, and integrate results from the vacuum tube solar collector pre and post processing tests into an enhanced energy system model and modular energy system design will continue this year. The automated testing device developed will continue to be used to consider optimal hydrogen production conditions using statistical testing procedures. Testing with the
continuous fermentor will be expanded to consider issues associated with continuous feed of substrate and scale up of the process. A mass flow meter will continuously measure hydrogen production levels from the fermentor. We will also explore existing catalytic methods including nanocatalysts for capture of carbon dioxide from the fermentation process. The next phase of the research will involve the construction a bench top reactor based on these designs that will operate with dryer waste material and use solid material handling techniques. Funding is currently not available for the actual construction of the dry bench top test unit. This research considers hydrogen production, but also considers the leveraging of other value streams to overcome design issues that have arisen in the past. We consider this process to have significant value for waste processing and heat production as well as hydrogen production. The use of catalysis to condition the biogas stream also adds value to the process that has not been considered in the past for this application.

**FY 2010 Publications/Presentations**


III. HYDROGEN DELIVERY
Introduction

Hydrogen must be transported from the production site to the end user (e.g., a fueling station or stationary power site) or produced on-site. It also must be compressed, stored, and dispensed at refueling stations or at stationary power generation sites. Due to hydrogen's relatively low volumetric energy density, the transportation, storage, and final delivery of hydrogen as an energy carrier currently entail significant costs and inefficiencies. The Hydrogen Delivery sub-program activity focuses on developing technologies to reduce the cost and increase the energy efficiency of hydrogen delivery, to enable the widespread use of hydrogen as an 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 de-hydrogenated and re-hydrogenated with a round-trip efficiency greater than 60%. In addition, research and development (R&D) activities include work on compression and off-board hydrogen storage development.

Goal

The goal of the Program’s hydrogen delivery portfolio is to develop hydrogen delivery technologies that enable the introduction and viability of hydrogen as an energy carrier for transportation and stationary power generation.

Objectives

The objective of the Program’s hydrogen delivery portfolio is to reduce the costs involved in delivering hydrogen from the point of production to the end-user and to enable hydrogen to be sold competitively (on a cents-per-mile basis) with gasoline. This overall goal applies to all delivery and dispensing technologies, including those used in centralized hydrogen production pathways and those used in both centralized production and distributed, on-site hydrogen production (e.g., on-site compression, storage, and dispensing). Interim targets and pathway-specific targets are currently being identified. Significant technological advances are needed to lower the cost of hydrogen delivery and to enable a transition to the widespread use of hydrogen. R&D objectives and priorities for hydrogen delivery 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, lower cost, higher efficiency hydrogen compression technology for pipeline transmission and for stationary and refueling station applications.
- **Storage:** Develop lower capital cost off-board storage technology; confirm the technical feasibility and adequate availability of geologic storage for hydrogen.
- **Liquefaction:** Reduce the capital cost and increase the energy efficiency of hydrogen liquefiers and bulk storage (reduce boil-off).
- **Carriers:** Work toward a Go/No-Go decision and leverage research 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. This technology is feasible only if the carrier is used on-board the vehicle.
• **Analysis:** Conduct comprehensive analysis of the options and trade-offs of hydrogen delivery approaches for the near-term and long-term, including: 350-bar, 500-bar, 700-bar, and cryocompressed station and upstream delivery costs.

**Fiscal Year (FY) 2010 Technology Status**

Current costs for the transport of hydrogen range from $2 to $8/gasoline gallon equivalent (gge) and are dependent on the quantity of hydrogen and the distance that the hydrogen is transported. Pipeline transport costs are at the lower end of the cost range and are also dependent on transport distance and quantities. These transport costs do not include compression, storage, and dispensing at fueling sites, which can add $2–3/gge of hydrogen. Progress toward current goals and targets is summarized below.

<table>
<thead>
<tr>
<th>Project Category</th>
<th>Goal (Targets to be met by 2020)*</th>
<th>Status**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube Trailers</td>
<td>Reach H₂ delivery cost target of $1/gge. Reduce capital cost to &lt; $200,000. Increase capacity to 1,100 kg through the use of carbon fiber or low-cost glass fiber.</td>
<td>$2.85–$3.15/gge (high volume demand projection. Completed system design for 1,100 kg capacity with glass fibers and small-scale prototype development. Completed testing of carbon fiber tank with a capacity of 600 kg.</td>
</tr>
<tr>
<td>Pipelines</td>
<td>Reach H₂ delivery cost target of $1/gge. Decrease cost/mile to &lt; $490,000.</td>
<td>$2.20–$2.35/gge (high volume demand projection. Cost/mile (steel): $1M/mile; cost/mile (fiber reinforced plastic): $600,000/mile.</td>
</tr>
<tr>
<td>Liquefaction</td>
<td>Reach H₂ delivery cost target of $1/gge. Decrease installed capital cost to $100M. Increase energy efficiency to 87%.</td>
<td>$2.70–$2.90 (high volume demand projection. Installed capital cost: $170M. Energy efficiency: 40%.</td>
</tr>
<tr>
<td>Compression</td>
<td>Reduce capital cost to $6.2M (transmission compression). Increase energy efficiency to &gt; 98%. Cost contribution: $0.25/kg H₂.</td>
<td>Centrifugal pipeline package cost: $4.5M (projected). Energy efficiency: 98% (projected). Cost contribution: $0.60/kg H₂.</td>
</tr>
<tr>
<td>Bulk Storage</td>
<td>Reduce cost of storage tank to $300/kg H₂ stored. Increase volumetric capacity to &gt; 0.035 kg H₂/liter of storage volume.</td>
<td>Storage tank cost: $820/kg H₂ stored. Volumetric capacity: 0.025 kg H₂/liter of storage volume.</td>
</tr>
<tr>
<td>Carriers</td>
<td>Show a viable carrier material (liquid, non-toxic). Decrease delivery cost contribution to &lt; $1/gge. Increase carrier H₂ content to 13.2% by weight.</td>
<td>N-ethylcarbazole delivery cost: $4.75. N-ethylcarbazole H₂ content by weight: 5.8%.</td>
</tr>
</tbody>
</table>

* Targets shown are currently under review and will be updated in FY 2010 and FY 2011.
** DOE projections—not publicly vetted. Target and Status costs are projected high-volume costs.

**FY 2010 Accomplishments**

**Pipelines**

• Savannah River National Laboratory completed a life management plan for fiber reinforced composite (FRC) pipelines, completed a review of existing FRC design specifications/standards, and initiated environmental and flaw tolerance testing of FRC.
• Sandia National Laboratories examined the fracture properties of X52 pipeline steel in high-pressure H₂ gas and established a relationship between hydrogen-assisted fatigue crack growth rate and load-cycle frequency at frequencies prototypic of a pipeline application.

**Tube Trailers and Bulk Storage**

• Lincoln Composites completed an assembly that includes an International Organization for Standardization (ISO) frame, four pressure vessels, and relevant plumbing. The American Bureau of Shipping approved the entire ISO assembly for manufacture.
• Lawrence Livermore National Laboratory designed a pressure vessel that, when incorporated into a trailer, could deliver hydrogen at a cost below $1/gge (not including forecourt expenses).
Compression and Liquefaction

- Concepts ETI Inc. completed a preliminary design of a six-stage hydrogen pipeline compressor capable of delivering 240,000 kg H₂/day at 1,250 psig.
- Five subsystems of a 290 K to 120 K active magnetic regenerative liquefier prototype were designed, fully assembled, and successfully tested by Prometheus Energy.

Analysis

- Argonne National Laboratory upgraded the Hydrogen Delivery Scenario Analysis Model to evaluate three new delivery pathways, two different station configurations for 700-bar dispensing, and an option permitting user selection of station configuration.
- The National Renewable Energy Laboratory upgraded the Hydrogen Rail Components Model with 700-bar and cryo-compressed dispensing and higher tube-trailer delivery pressure, of up to 480 atm.

Budget

The FY 2010 budget provided $5.4 million for continued hydrogen delivery research. The President’s FY 2011 budget request includes $40 million for hydrogen fuel R&D, out of which $7.2 million is planned for hydrogen delivery, with an emphasis on lower-cost, higher-efficiency compression technology and lower-capital-cost off-board storage technology.

<table>
<thead>
<tr>
<th>Delivery</th>
<th>FY 2010 Funding ($M)</th>
<th>FY 2011 Request</th>
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<tbody>
<tr>
<td>Compression</td>
<td>1.7</td>
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<tr>
<td>Storage</td>
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<td>2</td>
</tr>
<tr>
<td>Liquefaction</td>
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</tr>
<tr>
<td>Carriers</td>
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<td>0.5</td>
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<tr>
<td>Analysis</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Pipelines</td>
<td>0.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

FY 2011 Plans

Annual reports and final reports documenting progress will be issued in late FY 2010 and FY 2011, respectively. H₂A cost projections for delivery pathways, the Hydrogen Delivery Chapter of the Energy Efficiency and Renewable Energy (EERE) Fuel Cell Technologies Multi-Year Program Plan, and the Delivery Roadmap will be reviewed and updated as needed in FY 2011. The applied R&D program in EERE will coordinate with the Office of Science, which plans to include up to $50 million 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 projects funded by the American Recovery and Reinvestment Act of 2009, lessons-learned and best practices related to hydrogen delivery technologies will be developed.
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III.1 Hydrogen Delivery Infrastructure Analysis

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Partners:
• National Renewable Energy Laboratory
• Pacific Northwest National Laboratory

Project Start Date: October 2007
Project End Date: Project continuation and
direction determined annually by DOE

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, C, D, F, H and J) in the Delivery Technical Plan, as well as Barriers B, C and E in the Systems Analysis Plan of the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan. These are:
(A) Lack of H2/Carrier Infrastructure Options Analysis
(B) Stove-Piped/Siloed Analytical Capability
(C) Inconsistent Data, Assumptions and Guidelines
(E) Unplanned Studies and Analysis

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 elements of an optimized delivery system which could meet DOE’s long-term delivery cost target.

Accomplishments
• Completed Version 2.2 of HDSAM which is now available at http://www.hydrogen.energy.gov/h2a_delivery.html. As described in the 2009 Annual Progress Report for the DOE Hydrogen Program, additions include:
  – Three new delivery pathways:
    - High-pressure gaseous tube trailers
    - Cryo-compressed (CcH2) hydrogen dispensing
    - 700-bar gaseous hydrogen dispensing
  – Two different station configurations for 700-bar dispensing:
    - High-pressure cascade system
    - Lower pressure cascade system (with dedicated boost compressors for each hose)
  – Option permitting user selection of station configuration.
• Added a “cold gas” tube-trailer pathway to the development version of HDSAM.
• Analyzed HDSAM fuel station footprint assumptions (including setbacks, separation distances, and other safety constraints) as compared with proposed new standards from the National Fire Protection Association (NFPA). Developed revised station footprints to better reflect minimum separation distances between different components.
• Analyzed cost, energy use and greenhouse gas (GHG) emissions to bring renewable hydrogen to Los Angeles. Estimates include hydrogen production from New Mexican wind power, transmission to the Los Angeles city gate, geologic storage, local distribution, and dispensing.
Introduction

Initiated as part of the H2A project, 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, energy use and GHGs. 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 the full, levelized cost (i.e., summed across all components) of hydrogen delivery, accounting for losses and tradeoffs among the various component costs. A graphical user interface permits users to specify a scenario of interest. A detailed User’s Guide and access to the Energy Efficiency and Renewable Energy (EERE) help desk also assist users in running HDSAM.

Results

Work continued on updating and expanding HDSAM. Release 2.2 includes several high-pressure/low-temperature options discussed in last year’s report. These were further refined, tested and reviewed prior to their inclusion in the new release. Results from work on HDSAM 2.21, to be released in late 2010, are described in the following.

“Cold Gas” Tube-Trailer

This high-pressure/low-temperature pathway might be particularly well suited to early markets. Characterized in Fiscal Year (FY) 2010, this pathway assumes composite tube trailers (characterized by Lawrence Livermore National Laboratory) are loaded with gaseous hydrogen (GH2) at 350-bar (90 K) in order to deliver approximately 1,500 kg of hydrogen to a station where it is compressed to 600-bar (130 K) in a cascade charging unit and dispensed at 500-bar (190 K). Figure 1 shows the major stages in this pathway as compared with three other “early market” pathways contained in HDSAM 2.2. Figures 2 and 3 show preliminary results – installed capital costs of stations and the station portion of levelized hydrogen cost.1 By eliminating the cascade system and reducing site storage and refrigeration, compression costs are much lower for CcH2 delivery (Figure 2) than for the other options. Cold gas delivery appears to get part way to the station savings of CcH2 because of reduced storage costs. Thus, station costs

1 Note that 700-bar GH2 with high pressure cascade is less expensive than the booster-compressed option (not shown). for cold gas delivery may be comparable to those for 350-bar GH2 delivery but with improved energy use and vehicle driving range. Note that some of the CcH2 “savings” is shifted upstream to terminals and tube trailers, thereby reducing the difference among delivery

FIGURE 1. HDSAM Contains Several Early Market Delivery Options Including Cold Gas Tube-Trailer Delivery with 500-Bar Dispensing, Liquid Truck Delivery with Cryo-Compressed Dispensing, and 180-Bar Delivery with 700-Bar Cascade or Booster Compressed Dispensing

FIGURE 2. Station Costs May Be Comparable for 500-Bar Cold Gas and 350-Bar Pathways, Greater for 700-Bar and Less for Cryo-Compressed Pathways
options. As shown in Figure 3, total levelized delivery cost differs by less than $0.40 among CcH2, cold gas and 350-bar delivery pathways.

Station Footprint Analyses

Default footprints in HDSAM 2.2 are approximately 110 x 130 ft for GH2 stations and 150 x 170 ft for liquefied hydrogen (LH2) stations. In response to industry concern that land areas are insufficient to accommodate required setbacks, separation distances and delivery truck maneuvers, layouts were reviewed and compared with proposed NFPA rules for setback and separation distances. Results suggest that GH2 total station land area should be increased from 3,950 to 16,500 ft² (about two-thirds of which is due to land requirements for an additional hydrogen tube-trailer bay, a cascade storage system, truck maneuvering and associated separation distances). Note that HDSAM does not allocate the cost of land occupied by convenience stores, parking, car washes or other amenities to hydrogen storage and dispensing. The impact of fully NFPA-compliant station size on levelized hydrogen cost may be seen in Figure 4. For GH2 stations, full NFPA compliance adds $1.35/kg for stations dispensing 50 kg/day but only $0.17/kg to stations dispensing 1,000 kg/day. For LH2 stations (not shown) the effect is less – full NFPA compliance adds $0.57/kg for stations dispensing 50 kg/day and only $0.07/kg for stations dispensing 1,000 kg/day.

Wind-to-LH2 Analysis

In response to the California mandate that 30% of the state’s hydrogen use must be produced from renewable sources, a study was initiated to evaluate the cost, energy use and GHG emissions of potential renewable hydrogen production/delivery options. As a first step, a “generic” site with Class 3 wind potential and relatively good access to Los Angeles (LA) was selected for analysis. Located near Albuquerque, NM, the site was assumed to include a 252-MW wind farm (i.e., 84 3-MW turbines), a 160-MW electrolyzer, a 40-tpd liquefier and 4,000 t of geologic storage. All output was dedicated to liquid hydrogen production (i.e., no electricity was exported to the grid) for 80,000 fuel cell vehicles approximately 800 miles to the west. Initially, five potential pathways, both renewable and nonrenewable were compared: Albuquerque-to-LA via wind-to-LH2, Albuquerque-to-LA via steam methane reforming (SMR)-to-LH2, Albuquerque-to-LA via electrolysis-to-LH2; centralized production in LA via SMR, and centralized production in LA via electrolysis. Preliminary results (Figure 5) show that hydrogen production tends to be the major contributor to levelized
III. Hydrogen Delivery

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 options on those costs. 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, the National Renewable Energy Laboratory and Pacific Northwest National Laboratory with the advice and assistance of several industrial partners. Regular interaction has also occurred with the Fuel Pathways and Delivery Tech Teams.

Through FY 2010, results affirm that hydrogen delivery could add $4 or more to the levelized cost of hydrogen “at the pump.” The most promising options for reducing delivery cost tend to smooth demand (thereby reducing the need for hydrogen storage) or increase the energy density of delivered fuel (by maintaining low temperature or high pressure in the delivery pathway). Tasks completed through June 2010 have been discussed above. The following tasks will be completed by the end of FY 2011:

- Further analyses of hydrogen delivery cost targets.
- Completion of the wind-to-liquid hydrogen analysis and publication of results.
- Further expansion of HDSAM’s capabilities to include a cold gas tube-trailer pathway, advanced compression technologies, and revised approaches to modeling fuel station land requirements, cryo-compressed dispensing and geologic storage (the latter in conjunction with Sandia National Laboratories).
- Completion and posting of HDSAM 2.21 on the EERE Web site.
- Continued interaction and collaboration among the project partners and with the Fuel Pathways Integration Tech Team, the Delivery Tech Team, industry, and the broader hydrogen modeling community.

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 options on those costs. 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, the National Renewable Energy Laboratory and Pacific Northwest National Laboratory with the advice and assistance of several industrial partners. Regular interaction has also occurred with the Fuel Pathways and Delivery Tech Teams.

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- Completion of the wind-to-liquid hydrogen analysis and publication of results.
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- Completion and posting of HDSAM 2.21 on the EERE Web site.
- Continued interaction and collaboration among the project partners and with the Fuel Pathways Integration Tech Team, the Delivery Tech Team, industry, and the broader hydrogen modeling community.

Publications/Presentations

III.2 H2A Delivery Analysis and H2A Delivery Components Model

Accomplishments

- Upgraded H2A Delivery Components Model with 700 bar and cryo-compressed dispensing and increased tube-trailer delivery pressure to 480 atm.
- Designed seven new delivery components accommodating gaseous hydrogen delivery in composite tubes.
- Updated rail delivery components with new cost and technical input data.
- Performed comparative cost analysis of various delivery pathways for long-distance delivery.
- Completed the first stage of developing multi-node delivery scenarios.

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 Components Model is part of a larger set of H2A or “Hydrogen Analysis” models, including the H2A Production Model, and the H2A Delivery Scenario Analysis Model (HDSAM). The H2A Production Model calculates the cost of producing hydrogen from a variety of feedstock types. The HDSAM, developed at Argonne National Laboratory, allows the user to choose between multiple production and delivery pathways to calculate total scenario costs. The H2A Delivery Components Model also calculates delivery costs but provides the 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 Scenario Evaluation and Regionalization Analysis (SERA), Hydrogen Demand and Resource Analysis (HyDRA), and the H2A Fuel Cell Power Model.

Approach

Since its start in 2004, the project has followed the general H2A approach and guidelines: closely collaborating with industry to update cost data and technical specifications, keeping consistency of the cost inputs across all H2A models, employing H2A standard assumptions, and maintaining publicly available models.
Results

Pursuing the project objectives, we upgraded the H2A Delivery Components Model with new dispensing options and an additional delivery pressure. We added a second dispensing pressure of 700 bar to the gaseous refueling station. At the 700 bar station, hydrogen can be dispensed via a cascade system or booster compressor. We also added a new dispensing option at the liquid refueling station: hydrogen can be dispensed not only as gas, but also as liquid or cryo-compressed fluid. Figure 1 shows the impact of the refueling station upgrade on the station share of hydrogen cost, as well as station capital cost. The gaseous truck-trailer component was upgraded with the second tube pressure of 480 atm. As Figure 2 reveals, pressure boost from 180 atm to 480 atm enables an increase in tube-trailer capacity by 140% and a decrease in the truck-trailer share of hydrogen cost by 37%.

Addressing the barrier (A) - Lack of Hydrogen/Carrer and Infrastructure Option Analysis, we are developing new rail delivery components. Six new rail delivery components 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 daily demand. At the city gate terminal hydrogen is reloaded from the rail cars to trucks, which deliver hydrogen

![FIGURE 1](image1.png)

**FIGURE 1.** Hydrogen refueling station costs: a) station share of hydrogen levelized cost; b) station capital cost. Station capacity is 100 kg/day. (GH2 – gaseous hydrogen, LH2 – liquid hydrogen)

![FIGURE 2](image2.png)

**FIGURE 2.** Gaseous truck-trailer: a) capacity (kg of hydrogen); b) truck share of hydrogen levelized cost ($/kg). The cost analysis is made for delivery to the refueling station with an average capacity of 100 kg/day.
to the refueling station. Whenever possible, the H2A default sizes have been preserved in designing both types of terminals. This year our update of the rail components concerned freight data, rail car leasing data, and intermodal facility crane technical specifications and cost. The updated rail components were used to perform comparative delivery cost analysis. Figure 3 demonstrates the hydrogen delivery cost sensitivity to the distance. For the distances longer than 1,500 km, liquid hydrogen rail and truck delivery outperform all other options, becoming serious candidates for delivery of hydrogen produced from renewable sources.

Addressing the barrier (F) - Gaseous Hydrogen Storage and Tube Trailer Delivery Costs, we analyzed the possibility for delivering gaseous hydrogen in composite tubes instead of metal tubes. Using composite tubes with a pressure of 250 bar decreases the cost of delivery via gaseous truck-trailer by 20-30% (see Figure 3). Also, preliminary analysis has shown that with a pressure increase to 550 bar, delivery costs drop by 33% for gaseous rail delivery and up to 50% for gaseous truck-trailer delivery.

Barrier (F) also was addressed through developing a novel method of hydrogen delivery: when a hydrogen plant not necessarily serves only one city, but can accommodate demand from multiple cities. By introducing these multi-node delivery scenarios, we can model pipeline and hydrogen storage systems shared between multiple cities, which potentially can decrease the cost of storage designed for plant outage and demand surge. For designing multi-node delivery networks, we have used the SERA Model. This model is a geographical information system-based dynamic optimization tool that determines optimal production and delivery infrastructure build-outs and their evolution. The first stage of SERA scenario development was completed this year. We coded four delivery components directly into the SERA model in order to gain extensive flexibility of placing delivery components at different geographical locations. Also, we added transmission pipeline branching to allow sharing a production plant between multiple cities. Figure 4 displays an optimized pipeline network, demonstrating mature multi-node delivery at the Midwestern region.

Conclusions and Future Direction

- In Fiscal Year 2010, by introducing new dispensing and delivery options, we reached the following conclusions:
  - Gaseous hydrogen tube-trailer capacity can be increased by 140%, and its share of the total cost of hydrogen delivery can be decreased by 37%.
  - The cost of gaseous hydrogen delivery via truck can be decreased by 50% by the introduction of composite tubes.
  - Liquid rail and truck delivery are the least cost long-distance options for delivering hydrogen produced from remote renewable sources.
  - Multi-node delivery configurations have the potential to reduce the cost of storage by sharing systems between two or more production plants.
In the upcoming year, the major effort for the H2A Delivery Analysis and H2A Delivery Components Model will focus on:

- Developing go/no-go decision on delivering hydrogen via existing natural gas pipeline network.
- Refining rail delivery components.
- Continuing multi-node delivery scenarios design.
- Developing scenarios for delivering hydrogen that has been produced from wind.
- Maintaining and updating the H2A Delivery Components Model.

**FY 2010 Publications/Presentations**

III.3 Oil-Free Centrifugal Hydrogen Compression Technology Demonstration

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 Fuel Cell 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 the 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 following DOE technical targets from the Hydrogen Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (see Table 1).

<table>
<thead>
<tr>
<th>TABLE 1. Technical Targets for Hydrogen Compression</th>
</tr>
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<tbody>
<tr>
<td>Category</td>
</tr>
<tr>
<td>Reliability</td>
</tr>
<tr>
<td>Energy Efficiency</td>
</tr>
<tr>
<td>Capital Investment ($M) (based on 200,000 kg of H₂/day)</td>
</tr>
<tr>
<td>Maintenance (% of Total Capital Investment)</td>
</tr>
<tr>
<td>Contamination</td>
</tr>
</tbody>
</table>

Accomplishments

- Completed compressor design with nine compression stages and established the impeller diameter, blade design and desired rotational speed.
- Conducted stress analysis to determine the range of stresses developed in the rotor for several selected materials and established the safety margin for each material.
- Conducted rotor dynamic analysis to ensure dynamic stability of the rotor at the operating speed.
- Prepared preliminary drawings of the compressor frame and the overall system layout, including the drive system and transmission.

Introduction

One of the key elements in realizing 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, the 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, and 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 conduct 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) Program management and reporting.

**Results**

The goal of the compressor design analysis was to determine the number of stages necessary to reach a discharge pressure of 1,200 psig and 500,000 Kg/day mass flow. The investigation began by using the maximum allowable tip speed (1,600 ft/s), as determined by earlier finite element analysis (FEA) stress analysis. This condition is labeled “Full Speed” in Figure 1. While higher tip speeds are possible in a non-hydrogen environment, the potential reduction in material strength under hydrogen embrittlement dictates that lower stress conditions be used. Two under-speed conditions were also investigated, denoted as “95% of Full” and “90% of Full”. The results show that the Full Speed condition would require seven stages to achieve the desired discharge pressure, while the under-speed conditions would require eight and nine stages, respectively. Previous preliminary analysis had indicated that a maximum of three frames (i.e., nine stages) should be used. Therefore, using a lower speed and nine stages would be convenient because it allows a system to be designed with three identical compressor frames. The use of lower speed also provides increased stress and fatigue safety margins.

Further analysis was performed to evaluate if other designs could achieve the desired discharge pressure in two identical frames (i.e., six stages) without exceeding the selected maximum allowable tip speed. The two most common approaches used in compressor design to increase discharge pressure are employing forward-swept blade angle and vaned diffusers. A single compression stage was analyzed to determine the performance gain of forward-sweep and vaned diffusing. As expected, the discharge pressure increased in both cases. The costs of these approaches, however, are increased power requirement, increased manufacturing costs and decreased surge-choke margin. In the multi-stage analysis, both a vaned diffuser and a forward-swept blade resulted in about 8% differential pressure improvements. The power penalty was much greater with the forward-swept blade (15%) compared to only 2% from the vaned diffuser. However, the vaned diffuser and forward-swept blade approaches greatly increase the likelihood of system instability. Since the operating conditions could vary greatly, the most versatile, stable and cost-effective design is a three-frame design (i.e., nine stages) with vaneless diffuser and back-swept impeller blades.

Rather than using three identical stages, frames 2 and 3 were modified with alternate shroud contours through a technique known as reprofiling, which dramatically improves stability and surge margin without the added cost of designing and manufacturing unique compressor stages. The additional pressure margin achieved in the reprofiled design is due, primarily, to the addition of the vaned diffuser. The use of a vaned diffuser in the identical stage design was not practical because it would only add instability to the compressor system.

A detailed blade design was conducted using a quasi-three dimensional inviscid internal flow analysis with well-known, commercially available compressor design software. The flow field was analyzed for areas of excessive diffusion, sudden velocity gradients and flow separation. The design was optimized through minor changes in impeller blade geometry. Once a design was found to have satisfactory flow field characteristics,
structural and rotordynamic evaluation was performed. Four key design iterations were conducted between aerodynamics, structural and rotordynamics in order to arrive at the final compressor concept. This was followed by computational fluid dynamics (CFD) analysis of a single stage to validate the aerodynamic performance predictions.

Compressor designs created from aerodynamic analysis were verified for structural integrity using FEA. Structural analysis was focused on the rotor, impeller hub and impeller blades. Three high strength materials were evaluated: an aluminum alloy; a titanium alloy and a high-strength steel. The results confirmed low stresses in the impeller blades. Peak stress in the impeller was on the backface of the hub; however, stress magnitudes were well below the yield strength of the material. The results indicated significant safety margin with respect to strength for all three selected materials. However, the low fatigue limit of the aluminum alloy is of major concern. In fact, the blade stress is three times larger than the fatigue limit of this material. Since the steel and titanium alloy provide sufficient safety margins based on strength and low cycle fatigue, and aluminum does not, aluminum was dropped from further consideration.

The MiTi® 9-stage hydrogen compressor design consists of three double entry systems, each with three back-to-back compression stages (Figure 2). Two MiTi® foil journal bearings are located towards either end of the shaft. Two foil thrust bearings are located at the center of the shaft. Coupled finite difference and finite element methods were used to analyze the foil thrust bearing. The pressure profile was predicted through elastohydrodynamic analysis using the finite difference method and applied to the structural finite element model of the foil thrust bearing. Four MiTi® compliant radial foil seals, which are being characterized under a parallel effort, are used for inter-stage sealing. The predicted elastohydrodynamic plus hydrostatic pressure was applied to the finite element model of the radial foil seal.

Whirl speed and stability analysis were conducted using dynamic FEA. The speed-dependent stiffness coefficients were calculated and damping properties were estimated for the foil bearings and seals. Rotor dynamic analysis was conducted for one frame. Based on preliminary aerodynamic analysis, an optimized shaft diameter between the compressor wheels was selected. Rotordynamic analysis was performed with the three selected materials. It was determined that the material type had little impact on the rotordynamic behavior. The whirl speed map in Figure 3 shows the first four damped natural frequencies, including the cylindrical and conical rigid body modes, as well as the 1st and 2nd bending modes as a function of rotational speed. The logarithmic decrement values for these four modes indicated excellent stability for all four modes.

The configuration of the 9-stage hydrogen compressor has been finalized. The system consists of three frames operating at 56,000 rpm. Each frame is a double entry design consisting of three back-to-back compression stages. The design includes vaned diffusers and a return channel. The final stage of each frame discharges to a volute. A complete system layout was drawn (Figure 4).
15,128 hp for a specific energy metric of 0.439 kW-hr/kg of compressed H₂, which is less than the DOE’s target of 0.6 kW-hr/kg. The system contains three frames coupled to a single rotating shaft. The overall system footprint is estimated to be 160 ft², which includes intercoolers located beneath each compressor frame, the drive system and the transmission.

Conclusions and Future Directions

During this reporting period, the design of a 9-stage centrifugal hydrogen compressor was completed. The design process included detailed analysis of a single stage as well as overall system layout, bearing analysis, rotordynamics, and system costs and economics. Analysis methods employed included FEA modeling of stress and deflection of the impeller hub and blades, multi-stage system stability, rotordynamic analysis of the compressor rotor, CFD analysis, and full system layout, including drive components. The results of this analysis indicate that an oil-free centrifugal hydrogen compressor is capable of achieving the performance goals requested by the DOE.

In addition to further analysis of the design concept presented in this report, several other design concepts will be evaluated during the next reporting period. A high-performance and high-speed concept is being analyzed in which the maximum allowable impeller tip speed has been increased to 2,000 fps. While this design will allow for a reduction in the total number of stages, reduced input power and overall system size, such high tip speeds present several technical challenges that are being addressed. A trade-off study will be performed in which the costs and benefits of increased tip speed on system performance is assessed. The following tasks are planned for the remainder of Fiscal Years 2010 and 2011:

- System cost analysis
- Increased speed designs and trade-offs
- Development of a single stage simulation test rig
- Fabrication of components for testing
- Single stage performance testing

FY 2010 Publications/Presentations

III.4 Development of a Centrifugal Hydrogen Pipeline Gas Compressor

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DOE Project Officer: Paul Bakke
Phone: (303) 275-4916
E-mail: Paul.Bakke@go.doe.gov

Contract Number: DE-FG36-08GO18059

Subcontractors:
- Praxair Corporation, Tonawanda, NY
- Texas A&M University, College Station, Texas
- 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 (compressor package of $5.4M) for 240,000 kg/day system by FY 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 capital investment by Fiscal Year (FY) 2017.
- Increase system reliability to avoid purchasing 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 3) of the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan [1]:

(B) Reliability and Costs of Hydrogen Compression

Technical Targets

The project has met the following DOE Targets as presented in DOE’s 2007 Technical Plan for Hydrogen Delivery Projects[1] (Table 1 and Figure 1).

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE Target</th>
<th>Project Accomplishment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Efficiency (f)</td>
<td>[btu/btu]</td>
<td>98%</td>
<td>99%</td>
</tr>
<tr>
<td>Hyd. Capacity (g)</td>
<td>kg/day</td>
<td>100,000 to 1,000,000</td>
<td>240,000</td>
</tr>
<tr>
<td>Hyd. Leakage (d)</td>
<td>%</td>
<td>&lt;.5</td>
<td>0.2 (per Flowserve Shaft Seal Spec.)</td>
</tr>
<tr>
<td>Hyd. Purity (h)</td>
<td>%</td>
<td>99.99</td>
<td>99.99 (per Flowserve Shaft Seal Spec.)</td>
</tr>
<tr>
<td>Discharge Pressure (g)</td>
<td>psig</td>
<td>&gt;1000</td>
<td>1285</td>
</tr>
<tr>
<td>Comp. Package Cost (g)</td>
<td>$M</td>
<td>6.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Main. Cost (Table 3.2.2)</td>
<td>$/kWh</td>
<td>0.007</td>
<td>0.005 (per CN Analysis Model)</td>
</tr>
<tr>
<td>Package Size (g)</td>
<td>sq. ft</td>
<td>300 to 350 (per HyGen Study)</td>
<td>175 to 200 (per CN Design)</td>
</tr>
<tr>
<td>Reliability (e)</td>
<td># sys req’d</td>
<td>Eliminate redundant system</td>
<td>Modular systems with 240K kg/day with no redundancy req’d</td>
</tr>
</tbody>
</table>

TABLE 1. Progress towards Meeting Technical Targets for Delivery of Hydrogen via Centrifugal Pipeline Compression

(Note: Letters correspond to DOE’s 2007 Technical Plan-Delivery Sec. 3.2 - page 16)
Accomplishments for Phase I (Completed) and Phase II (in Progress)

Developed computer models to aid in analysis of hydrogen compressor:

- **System Cost and Performance Model**
  - Suitable as a macro for DOE “HDSAM v2.0” economics model.
  - Identifies hydrogen compressor package performance and component cost with respect to a variety compressor–gearbox configurations.

- **System Reliability and Maintenance Cost Model**
  - Estimates comparative reliabilities for piston and centrifugal compressors for pipeline compressors developed.
  - Failure Mode and Effects Analysis (FMEA) for component risk and reliability assessment.
  - Estimates operation and maintenance costs for compressor system.
  - Uses Federal Energy Regulatory Commission operation and maintenance database as the basis for determining the maintenance costs for a centrifugal compressor.

- **Anti-surge algorithm developed to assist in controls analysis and component selection preliminary design (completed) and detailed design of pipeline compressor module (in progress) including:**
  - Compressor design conditions confirmed by project collaborators.
    - $P_{inlet} = 350$ psig, $P_{outlet} = 1,250$ psig; flow rate $= 240,000$ kg/day.

- A six-stage, 60,000 revolutions per minute (rpm), 3.6 (max) pressure ratio compressor with a mechanical assembly of integrally-geared, overhung compressor impellers.
- Stress analysis completed.
- Volute (compressor housing) design in progress for two-stage prototype.
- Rotordynamics completed to verify shaft-seal-bearing integrity at operating speeds.

- Design of compressor’s major mechanical elements completed and satisfied by two manufacturers per component:
  - Titling-pad radial and thrust bearings designs validated for use.
  - Two commercially available gas face seals have been validated for use.

- Interconnect pipe diameters selected to minimize pressure drop.
  - Including volute with low solidity airfoil as the flow guide vanes and diffusing and Bellmouth at the inlet of the volute.

- 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).

- Piping and instrumentation diagram for module.
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 BTU energy content per kg, equivalent to the BTU 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. This technology development is the responsibility of the Production and Delivery sub-programs within the DOE. 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 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). To meet these goals, the DOE has commissioned Concepts NREC with the project entitled: The Development of a Centrifugal Hydrogen Pipeline Gas Compressor.

Approach

A three-phase approach has been programmed to implement the technical solutions required to complete a viable hydrogen compressor for pipeline delivery of hydrogen. This approach is summarized in Figure 2.

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 \((\text{rpm}^2)\) and the square of the radius \((\text{radius}^2)\). 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 \(\text{rpm}^2\) and \(\text{radius}^2\), 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. The selection of a rotor material that can enable the high tip speeds to be achieved while avoiding damage from hydrogen embrittlement was selected as the major technical challenge for the project.

To eliminate other more conventional challenges when developing a new compressor, the engineering directive was also to select only 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. Principal among these components is the choice of the bearings, shaft seals, gearing, and hydrogen controls and safety instrumentation.

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**

Concepts NREC has developed several computer design models that have helped to optimize the design choice for the pipeline compressor module that complies with DOE requirements. These models include:

1. Compressor Package Performance Model,
2. Cost Model using algorithms to determine the relative component cost and operational risks,
3. Engineering Reliability and Maintenance Cost Model [2,3],
4. Anti-surge Algorithm for providing anti-surge component specifications; and
5. Failure Mode and Effects Analysis (FMEA).

The engineering analysis, conducted in Phase I and continuing in Phase II, resulted in the design of the pipeline compressor package shown in Figure 3. The complete modular compressor package 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

![FIGURE 3. Engineering Analysis and Design Results: Pipeline Hydrogen Centrifugal Compressor 240,000 kg/day; 350 to 1,285 psig; 6,300 kWe](image)
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.

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 4, 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%. Each compressor impeller 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 does not disturb the shaft seal and bearings. 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 \( \frac{S_{\text{yield}}}{\rho} \) which can be shown to be a characteristic of the material’s ability to withstand centrifugal forces. Several grades of aluminum have a strength-to-density ratio that is similar to titanium and high-strength steels at the 140°F (max) operating temperatures that will be experienced by the hydrogen compressor. However, unlike titanium and most steels, aluminum is recognized by the industry as being very compatible with hydrogen.

Aluminum also helps to reduce the weight of the rotor, which leads to an improved rotodynamic 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, led by 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 \( \text{H}_2 \); Dr. Andrew Duncan).
3. Argonne National Laboratory (Dr. George Fenske).

The team determined that a small punch test (Figure 5) is appropriate for properly assessing the relative effects that hydrogen has on the strength of the material. A protocol for hydrogen charging of the 3 mm diameter x 0.5 mm thick specimens included prolonged exposure (4 months) in an atmosphere of hydrogen at 10,000 psig and 200°F.

The results of a preliminary test, also shown in Figure 5, indicate that the 2618-T61 and 3003-H14 aluminum alloys appeared to be minimally (if at all) affected by hydrogen, whereas the titanium Ti-6Al-4V was affected by the presence of hydrogen.

**Conclusions and Future Directions**

The preliminary engineering and design of an advanced pipeline compressor system has been completed and 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 75% of DOE’s target, and a maintenance cost that is less than the $0.01/kWh. The detailed analysis of this pipeline compressor system is in progress in Phase II of the project. The advanced centrifugal compressor-based system can provide 240,000 kg/day of hydrogen from

![FIGURE 4. Mechanical Detailed Assembly of One of Six Stages of Pipeline Compressor](image-url)
Detailed integrated systems analysis.

Critical components design, testing, and development.

Phase III.

- System Validation Testing (November 2010 to June 2011)
  - Component procurement.
  - Two-stage centrifugal compressor system assembly.

Special Recognitions and Awards/Patents Issued


FY 2010 Publications/Presentations


References

1. DOE Multi-Year Research, Development, and Demonstration Plan.

III.5 Advanced Hydrogen Liquefaction Process

### Objectives

Develop low-cost hydrogen liquefaction systems to produce 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 Delivery section (3.2.4) of the Fuel Cell 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**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2012 Target</th>
<th>2017 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small Scale Liquefaction (30,000 kg/day)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Installed Capital Cost</td>
<td>$</td>
<td>40M</td>
<td>30M</td>
</tr>
<tr>
<td>Energy Efficiency</td>
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<td>85</td>
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<tr>
<td>Large Scale Liquefaction (300,000 kg/day)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Installed Capital Cost</td>
<td>$</td>
<td>130M</td>
<td>100M</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>%</td>
<td>&gt;80</td>
<td>87</td>
</tr>
</tbody>
</table>

We are addressing the capital cost and energy efficiency targets.

- 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 solve 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.
- Developed process models for existing and proposed liquefier designs.
- Showed that overall power consumption can be reduced by about 2.5% if catalyst is used in the high-temperature heat exchanger.
- Identified a process where the performance of the improved ortho-para conversion process is sufficient to reduce total power consumption.
• Identified a process where the performance of the improved ortho-para conversion process, even when accounting for future improvement, is unlikely to be sufficient to reduce total power consumption.

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 is attempting 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. Project the impact of further improvements in process equipment, including novel devices currently being developed.

• 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 did not allow for testing over a temperature range. The previous system 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 was built and testing has begun (Figure 2). This new 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 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.

FIGURE 1. Material Screening Test System
This new test system has been used to determine performance characteristics of the ortho-para conversion system. These results have been used in the process model to determine the overall performance of a system using the improved ortho-para conversion process. These results are shown in Figures 3 and 4.

Modeling

Process simulations were developed for hydrogen liquefaction processes that used the improved ortho-para conversion process to compare those to processes that did not. Of the processes that did not use the improved ortho-para conversion process, it was found that adding ortho-para conversion catalyst to the high-temperature heat exchanger reduced overall energy consumption by about 2.5%.

Several different processes have been conceived that use the improved ortho-para conversion process. The modeling portion of the project will compare these processes to hydrogen liquefaction processes with standard ortho-para conversion. Concept α and Concept β have been evaluated to this point. Figures 3 and 4 show the results.

The point in the center is the target based on ortho-para performance meeting the base case power target. The y-axis represents the power required for hydrogen liquefaction as a percentage of the base case power target. The x-axis shows ortho-para performance as a percentage of demonstrated performance in the laboratory. The target is based on demonstrated performance (100% of current ortho-para performance) meeting the base case power target. In Figure 3, about 150% of the current demonstrated performance is required to meet the base case power target. Although there has been steady improvement in demonstrated performance throughout the project, marginal gains are lower than they were earlier in the project. It is unlikely that Concept α will meet the target required to be an economically viable process.

In Figure 4, 100% of the current demonstrated performance results in total power consumption below the base case power target. There has been steady improvement in demonstrated performance throughout the project and some future advancement is expected. Concept β has already met the target required to be an economically viable process on an energy basis. The difference in capital cost will be evaluated later this year and compared to the power cost savings possible through Concept β.

Conclusions and Future Directions

- Ortho-para conversion performance has been measured using laboratory and pilot reactors.
- The demonstrated performance is sufficient for at least one identified process concept to show reduced power cost when compared to hydrogen liquefaction processes using conventional ortho-para conversion.

FIGURE 2. Pilot-Scale Test System

FIGURE 3. Ortho-Para Performance for Concept α

FIGURE 4. Ortho-Para Performance for Concept β
The impact of improved ortho-para conversion can be significant, but ortho-para conversion uses only about 20-25% of the total liquefaction power.

Most of the energy used in liquefaction is for gas compression. The focus of the project will now be to evaluate different compressors and compression schemes to find possible efficiency improvements.

**FY 2010 Publications/Presentations**

1. DOE Annual Hydrogen Review Meeting
III.6 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 intended to experimentally demonstrate highly efficient hydrogen liquefiers. These include:

- Develop validated engineering design data for active magnetic regenerative liquefiers (AMRLs) for liquefied hydrogen (LH₂) (or liquefied natural gas) to meet or exceed DOE’s liquefaction targets for both capital and energy efficiency.

- Analyze, design, fabricate, and test one or more liquefier prototypes to experimentally demonstrate this technology and answer numerous questions such as how to design optimized layered magnetic regenerators with bypass flow of the heat transfer fluid.

- Validate the high figure of merit (FOM) predicted by our unique numerical simulation model used to analyze and design AMRL prototypes.

- From June 2009 through May 2010 our focus has been to analyze, design, fabricate, and test our first AMRL prototype with a target of spanning from ~290 K to ~120 K with a high FOM.

Technical Barriers

This project addresses the following Delivery barrier from the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan:

(C) High Cost and Low Energy Efficiency of Hydrogen Liquefaction

Technical Targets

Conventional hydrogen liquefiers at any scale have a maximum FOM of ~0.35 due primarily to the intrinsic difficulty of rapid, efficient compression of either hydrogen or helium working gases (depending on the liquefier design). This novel AMRL project uses regenerative magnetic refrigeration with solid working refrigerants to execute an efficient thermodynamic liquefaction cycle that avoids the use of gas compressors. Detailed modeling of the AMRL technology indicates it has promise to simultaneously lower installed capital costs/unit capacity and to increase thermodynamic efficiency from a FOM of ~0.35 toward ~0.5 to ~0.6. Results from experimental prototypes should support the design and deployment of hydrogen liquefier plants that meet the DOE 2010 hydrogen production and delivery targets:

- Delivery cost of LH₂ at <$1.00/kg;
- $40 MM capital cost for a turn-key plant with a capacity of 30 te/day; and
- Operational efficiency of a complete liquefier plant of 75% as defined by DOE and commensurate with a liquefier FOM of ~0.6.

Accomplishments

- Finished design five subsystems of a 290 K to 120 K AMRL prototype including:
  - The 7-T solenoidal superconducting magnet subsystem;
  - Cold box including the annular access tube subsystem;
  - Gifford McMahon cryocooler subsystem;
  - Cryogenic structural subsystem; and
  - Cryogenic instrumentation and LabVIEW control subsystem.

- Procured all components and completed the assembly of the five subsystems above.

- Successfully tested the five subsystems after diagnosing/fixing several vacuum leaks, sensor electronic noise, and cryocooler performance to obtain ~1.5 W of cooling at 4 K.
• Began the design of remaining three subsystems for our first AMRL prototype:
  – Wrote Mathcad programs for design of efficient active magnetic regenerators by optimizing heat transfer, pressure drop, and longitudinal thermal conduction.
  – Began to design heat transfer fluid subsystem to match requirements of the AMRL prototype and keep pressure drop low for required flow rates.
  – Analyzed force imbalance due to dual magnetic regenerators reciprocating in/out of the 7-T s/c solenoidal magnet to design the mechanical drive subsystem.
  – Used our AMRL performance simulation code to calculate the impact of the thermal mass differences due to temperature and magnetic field dependence of ferromagnetic refrigerants using controllable bypass heat transfer fluid flow rates.

Introduction

AMRL technology promises cost-effective and efficient liquefaction of hydrogen because it eliminates the compressors, the largest source of inefficiency in Claude-cycle liquefiers. However, as with any innovative technique, many questions have to be investigated and understood before commercial applications happen. Since the mid 1970s, magnetic refrigeration technology has been investigated with increasing understanding of magnetic cycles and magnetic refrigeration prototype designs. The seminal patent on the ‘active magnetic regenerator’ was issued in 1982. Only in the last decade or so has there been significant engineering effort on two applications; non-chlorofluorocarbon refrigeration near room temperature using permanent magnets and cryogenic liquefiers for hydrogen and natural gas.

The AMRL project funded under this DOE contract is an extensive engineering effort to analyze, design, fabricate, and test several natural gas and hydrogen liquefer prototypes. Successful demonstration of AMRL prototypes will enable use of advanced liquefiers into various hydrogen infrastructure projects to cost-effectively provide LH₂ energy storage/delivery for gaseous hydrogen produced by electrolysis at renewable energy stations such as wind or solar. The AMRL technology readily scales up or down in capacity so it could be scaled to DOE’s target of 30 te/day to a vehicular refueling station size (~2-3 te/day) where gaseous hydrogen is produced via steam methane reformation, liquefied/stored and supplied as LH₂ and/or as compressed hydrogen produced from liquid hydrogen.

Approach

During the past year our approach was to analyze, design, build, and test our first AMRL prototype that will eventually span from ~290 K to ~120 K. The experimental data will validate our numerical simulation model. It will also guide the design of the second AMRL prototype.

Results

A block process flow diagram of a complete turn-key LH₂ facility was created and is illustrated in Figure 1. The function of various modules is shown. The AMRR is combined within a cold box with a process heat exchanger to produce LH₂ from a gaseous feedstock stream. Also shown are nominal compositions, flow rates, heat/work flows, and other features of a safe operational plant.

The mechanical design of a reciprocating design of a 290 K to 120 K AMRR prototype required numerous calculations of the thermodynamics, heat transfer, fluid dynamics, structural loads, and many related items. One of the more challenging design features was the support of the 4 K superconducting magnet that has to be structurally capable of withstanding large magnetic forces between the magnetic materials in the regenerators and the magnetic field of the magnet. The large magnetic forces impact the design of mechanical drive mechanism; i.e., an AMRR cycle takes ~0.1 seconds to magnetize/demagnetize by moving the dual regenerators ~26 cm along the vertical z axis of the solenoid. The regenerators stop for dwell periods of ~0.4 seconds while the heat transfer fluid flows from hot to cold or cold to hot through the regenerators. Figure 2 illustrates the calculated magnetic forces on a single gadolinium cylindrical regenerator with ~5” outer diameter and ~5” length at 7 Tesla. The same figure includes the force reduction that is possible when two identical magnetic regenerators are balanced as much as possible. This force imbalance is several times larger than the net magnetic force required to provide the work input for the thermodynamic cycle and suggests a future rotary AMRL choice.

Figure 3 shows a two-dimensional mechanical design of the prototype that includes the superconducting magnet, the Gifford McMahon (GM) cryocooler to conduction cool the magnet and thermal shield, the elaborate support structure, and the top plate to mount the prototype in the double-walled Dewar that serves as the cold box. The center access tube through the magnet is insulated from the magnet to enable the dual regenerators to operate between ~290 K and ~120 K.

Figure 4 presents a photograph of the partially assembled AMRR prototype with the bottom heat shield.
III. Hydrogen Delivery

FIGURE 1. Block Process Flow Diagram of AMRL LH2 Facility 04/08/2010

FIGURE 2. Calculation of Magnetic Forces between S/C Magnet and Magnetic Regenerators
III. Hydrogen Delivery

Barclay – Heracles Energy Corporation

ready to be raised and attached to the ~40 K thermal shield. The prototype has been instrumented with numerous sensors and connected to a LabVIEW-based data acquisition system. The cold box was evacuated to ~1 x 10^-7 torr for excellent thermal isolation from the surroundings. The GM cryocooler cooling power on the first and second stage was measured and found to be better than the manufacturer’s specifications. The GM cryocooler successfully cooled the magnet before it was charged with a proper power supply designed for high current, low voltage and operated in persistent mode. The magnetic field profile was measured as was the adiabatic temperature change in a sample of gadolinium. Both of these measurements gave results that agree very well with calculated values.

Conclusions and Future Directions

Heracles/Prometheus is making excellent progress toward completion of its first AMRL prototype spanning a large temperature span from near room temperature to the temperature of liquefied natural gas. Five subsystems of the first lab-scale prototype have been designed, built, and successfully tested. The designs of the remaining three subsystems of the prototype are in progress; when the resultant subsystems are completed and integrated with the first five subsystems, full prototype testing will be done. The results will 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. We expect that ~15% of bypass flow should significantly improve the thermodynamic performance. The measurements will include the temperature span, cold thermal cooling power, hot heat rejection power, and thermodynamic efficiency (as FOM) as a function frequency, heat transfer fluid flow rate, applied magnetic field, hot temperature, bypass flow, layering technique, etc. The experimental results will be analyzed and compared to performance simulations to further validate the numerical performance model. Assuming the progress on this project is sufficient for a “GO” decision for additional funding, we expect to use results from the first AMRL prototype to design a multi-stage, ~290 K to ~20 K AMRL to make ~10-15 kg/day of LH₂. Results from the second prototype will be used to establish an engineering database for larger AMRL designs. Such a prototype will be the world’s first AMRL to make LH₂. The report obligations for this project are completed when due.

FY 2010 Publications/Presentations

III.7 Inexpensive Delivery of Cold Hydrogen in High Performance Glass Fiber Pressure Vessels

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Subcontractor:
Spencer Composites, Sacramento, CA

Project Start Date: April 30, 2005
Project End Date: September 30, 2012

Objectives
- Quantify economic performance advantages of cold glass composites.
- Develop delivery trailer capable of realizing most of those advantages.
- Demonstrate this delivery approach can surpass all significant technical risks.

Technical Barriers
This project addresses the following technical barriers from the Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
(G) Storage Tank Materials and Costs

Technical Targets
This project is expected to meet several of the 2012 DOE technical targets for hydrogen delivery. It addresses all the key targets relevant to a hydrogen infrastructure between centralized production and the filling station. Capacity targets it meets include a delivered hydrogen capacity over 1,000 kilograms, well above the 700 kilogram 2012 target, and delivered hydrogen pressure of 7,000 psi. The end-to-end cost of delivered hydrogen is minimized by a projected trailer capital cost below $140 per kilogram delivered. This detailed estimate for delivery trailer capital cost allows cold, compressed, glass composite pressure vessel delivery trailers to compete with and ultimately to beat the alternatives in minimizing delivery cost from identical hydrogen sources into identical vehicular hydrogen storage.

Table 1 shows that project’s estimated capital costs (on a per-kilogram delivered basis) exceed DOE’s Multi-Year Program Plan technical targets. Detailed capacity modeling shows both 200 K and 140 K designs can even surpass the 1,000 kg capacity target for 2017 while continuing to meet the capital cost target. Table 1 summarizes much more detailed costs from component-level modeling (based on DOE’s H2A Delivery model) of our project’s approach. The same detailed results show our approach’s superiority over other compressed hydrogen delivery alternatives. Colder designs can deliver far more hydrogen in a volume limited trailer envelope. (Our project presumes an International Organization for Standardization standard twenty-foot equivalent unit shipping container.)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2012 Targets</th>
<th>LLNL 2012 (Projected Cost)</th>
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<tbody>
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<td>Delivery Capacity</td>
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<td>1,000</td>
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<td>Operating Pressure</td>
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<tr>
<td>Purchased Capital Cost</td>
<td>$/kg of H₂</td>
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<td>$140</td>
</tr>
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</table>

Accomplishments
- Designed a pressure vessel suitable for affordable development at full-scale which enabled the reduction of all technical risks when incorporated into a trailer capable of delivering hydrogen at a cost below $1.00 per kilogram (not including forecourt expenses). This design is proceeding to prove this delivery concept will work both technically and economically. The effort is on schedule, and makes use of prior Spencer-proprietary materials testing efforts and licenses.
- Subscale S-Glass fiber wound pressure vessels were successfully built and burst at 500 and ~170 K, failing within 2% of design at 20,000 psi.
• The first batch of full-scale S-Glass fiber vessels were built, demonstrating the manufacturability of all high technical risk trailer components and processes.

• Several novel manufacturing problems were found and fixed to achieve these results. Along the way various materials properties were investigated, including tensile strength, toughness, and thermal shock tolerance, and some beneficial changes were made to proprietary formulations.

Introduction

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. Preliminary H2A-based analysis indicated that our system concept has the potential to greatly reduce the cost of hydrogen delivery by taking advantage of increased strength in inexpensive glass fiber proven to be available at cold temperature.

LLNL embodied this concept to minimize the total cost of hydrogen delivery by reducing the cost of tube trailers. Information gained from ongoing experimental research is being applied to a full-scale hydrogen pressure vessel development program.

Approach

• 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 (between ~140 K and 200 K, at 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 achieves higher strength in low-temperature operation, strengthening as much as 80% as it is cooled down from 300 K to 70 K. Our project confirmed this effect on one of the least expensive glass fibers in 2008, and found legacy published data on an even less expensive glass where the effect was even stronger. Cold glass fiber should maximize delivered hydrogen per dollar of delivery cost, maximizing capacity of the truck’s trailer. The combination of higher density reducing trucking labor, fuel, and capital expense with direct reductions in trailer capital cost more than compensates for the increased capital and energy costs of refrigeration and compression (as demonstrated above in Table 1), keeping delivered cost projections well below $1/kg-hydrogen (excluding forecourt expenses).

Results

Experimental Program

LLNL is developing a hydrogen delivery solution that can function at various temperatures and pressures. However, design, manufacturing processes, and capital plus operating costs of this solution depend on currently unknown properties of fibers, plastics, and processed surfaces. 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, the cold glass pressure vessel delivery option minimizes delivery cost per kilogram of hydrogen.

Last year we identified legacy data that shifted our projection of delivery-cost-optimal trailer storage temperature down to ~140 K. (At temperatures somewhat lower than this, the increasing costs of refrigeration would not be repaid.) Since 2006, LLNL has been experimentally pursuing the collection of new cold strength data for all the grades of commercially available glass fiber. In 2008, LLNL data confirmed experimentally that the cold strength effect was sufficient to give our concept the lowest projected hydrogen delivery cost. Since that time, it has become clear that neither proven plastic liners nor metal liners can serve as the vital hydrogen containing layer of a composite pressure vessel that would advantageously operate at cold enough temperatures.

Spencer Composites is collaborating with LLNL in pursuit of a fundamental advance in the manufacturing cost of large composite structures, including pressure vessels. That advance relies on the properties and manufacturing process savings implicit in a new category of plastics. This category will be termed “ROMP” catalyzed, which stands for Ring Opening Metathesis Polymerization. Spencer Composites intends to apply ROMP plastics in numerous aerospace and energy applications. Among the features of this advance are low thermal expansion and full properties retention at temperatures as low as 77 K. These plastics are expected to form both liner and matrix of a new generation of inexpensive pressure vessels. LLNL has sized vessels built with these advanced plastics for low temperature hydrogen delivery trailers.
Experimental research is underway to measure unknown properties of available cold glass composites. Additional experimental research centered on the toughness of high-performance ROMP plastics at low temperature is underway as a direct component of this project’s development effort.

Subscale Vessel Development

Figure 1 shows several of the 3” diameter experimental test articles prototyped to affordably determine unknown properties and improve formulations. Roughly 40 of these articles began prototyping, and roughly 25 survived enough of the ~18 steps in a minimal process sequence to become hydroburst test articles. Another three process steps were added to the most successful prototypes, while three articles received post-prototyping steps intended to improve permeation. All 18 were burst tested to gain feedback for manufacturing process improvement. One of these was burst at ~170 K in acetone cooled by dry ice, a process Spencer had used before, while LLNL is setting up to burst with liquid nitrogen fill.

The decision to proceed with subscale development was obvious given the development cost of full-scale tooling. Several iterations in 3” spin casting tools were conducted in Fiscal Year (FY) 2009. The small size proved convenient for storing and displaying the results of testing. However, the small size implied a factor of roughly 7 scale-up to transfer into a full-scale process. It also made it more difficult to observe defects, and imposed tolerances too tight to prototype Spencer’s full-scale pressure vessel seal design.

Spencer has a proven seal design of the right size to specify the 3” liner tooling for ROMP plastic liner molding. That design was known to seal to 18,000 psi, and relied on a spring-compressed Teflon® C-ring (similar in cross section to a square ‘O-ring’) whose excessive thermal coefficient of expansion and tendency to plastic deformation made it unlikely to survive thermal cycles below 200 K. Such a compromise turned out to be warranted because the full-scale seal design (which was computationally tested to withstand worst case thermal and pressure cycling to 77 K and 25,000 psi without exceeding 20% of the elastic limit of the advanced plastic) could not realistically be scaled down. Ultimately the expedient C-ring seal withstood 22,000 psi before leaking.

Three of the best 3” test articles survived hydroburst to greater than 20,000 psi, with one of these being nearly thermally equilibrated at ~170 K before its seal leaked. The winding design for the ambient test article that failed at slightly over 20,000 psi burst within 2% of its design value. The low temperature result did not fail structurally. Its leaking seal did not re-seat well enough to try a second cycle, but its strength exceeded 23,000 psi, at least 15% higher than the same design and fabrication process at ~300 K. In the course of the subscale test program, both graphite and S-glass fibers were wound with epoxy and ROMP catalyzed plastic matrixes. The two successful articles just mentioned were both made with epoxy matrix S-Glass.

Before achieving these successful subscale results, the development process had to go back to process development for ~4 months after the 2009 Annual Merit Review. An apparently well-formed ROMP liner that passed all visible and thickness inspections failed at unexpectedly low pressures in the earliest subscale burst tests. Cracks that were not apparent in the ROMP liners before they were wound were obvious in the end dome region. Some of these premature
failures occurred at pressures that could not have strained liners in the regions that cracked more than 0.5%. Yet the same ROMP material, processed into flat specimens and cut into “dog bone” tensile test articles was stretching ~18% before failure! Figure 2 shows some of the expedients it took to solve this problem.

Over 60 round plaques of a standardized shape were cast with different formulations of ROMP plastic and broken by dropping an impactor from an ASTM-specified toughness test apparatus built to debug this problem. A large number of hypotheses emerged for what our project called the “anomalous toughness” problem, and a full matrix of seven plaques times seven formulations would not suffice to sort these out. Tensile test “dog bone” specimens were broken at room temperature and roughly dry ice temperature for original and candidate fix formulations. Ultimately our team decided that a slight decrease in strength was a good tradeoff for significant improvement in toughness, and the improved formulation liners sailed through burst testing without cracks. Subsequent employment of the 3” subscale vessel test articles has been restricted to testing with less wound fiber in order to achieve strains anticipated in the full-scale design, since the materials we have developed withstood their worst case design stresses.

Full-Scale Development Program

A first generation of tooling for full-scale liner production was assembled in FY 2009. That tooling realized the liner and boss details that build a calibrated finite element design, which combines with already-measured ROMP plastic strengths to keep all structural components well within their elastic range during independent pressure cycles to 22,500 psi (maximum design burst pressure) and temperature cycles from 77 K to 365 K. LLNL enabled this design in 2007 by performing preliminary pressure optimization in order to size vessel diameter. This design resulted in an economic optimum of 8,000 psi maximum expected operating pressure (MEOP) for the delivery trailer at the time that tooling diameter was specified in May of...
2009. LLNL also made sure this full-scale design is robust enough to fit in our container when wound with sufficient fiber to preserve “Safety Factors” of 2.25 at any MEOP from 1,500 psi to 11,500 psi. This robustness allows the same tooling to minimize cost for stationary hydrogen storage applications (including filling station storage and renewable energy buffering).

The tooling for ROMP catalyzed spin casting is highly affordable compared to tooling for other plastic articles as big as our full-scale design. This affordability was put to the test through a series of mechanical redesigns. Conventional rotational molding tooling is very similar in degrees of freedom, but needs to operate inside an oven, which means every potential change must be designed to withstand thermal cycling. Several rounds of drive alignment changes were needed just to achieve sufficient rotational symmetry in molded liners, and those drive mechanism alterations could be bought out of catalogs because they need not run at high temperature. Other unexpected phenomena emerged at full-scale that could not have been noticed at the 3” subscale, and affirmed our strategic assertion that only full-scale development proves that a technology really works.

The most alarming encounter our development effort had on the way to achieving its Go/No-Go milestone of full-scale component production came the first time a full length liner emerged from the tooling. The surprise is shown in Figure 3 – the full length wasn’t full length even though two shorter length vessels had been built from liners made ‘successfully’ in the same tooling. Full diameter turned out not to be full-scale because of the effect of the greater mass of plastic resin that had to be introduced and spun up to mold the same diameter liner at full length. The part that emerged had an incomplete cylindrical section because most of the resin had solidified in a flat-topped lump at the bottom of the mold before it had a chance to spin up. Yet this same formulation had a 20 minute “pot life” in the 3” tooling, and it didn’t take even a minute to spin up the tool. The answer has to do with the rate of catalysis that solidifies the ROMP resin, and the reconfiguration of the tooling (to introduce the resin progressively after the tooling was already spun up) rendered subsequent liners acceptable.

**Trailer Integration Design and Field Test Program**

Figure 4 shows our first batch of full-scale pressure vessels. The first produced was a ‘shortie’ with a 5” cylindrical section of the liner and S-Glass epoxy overwrap. It was designed to burst at 18,000 psi,
Aceves – Lawrence Livermore National Laboratory

III. Hydrogen Delivery

molding was completed on a large lathe. Bubbles in that liner were ‘fixed’ by a subsequent spin in the lathe, but this part was not considered to have full quality, and was intended to be a permeation rig debug article and showpiece. Given these intended roles, it was wrapped with 700 ksi graphite fiber epoxy composite to illustrate the relevance of this technology for vehicular applications. The third article shown was full length, making use of the progressive resin introduction step described above, and was the first to have a full-scale S-glass fiber overwrap (with epoxy) matrix, thereby completing the promised milestone.

Building more of these full-scale test articles is only the beginning of a test program that is intended to remove all significant technical risks from this advanced, inexpensive pressure vessel technology. That test program has been planned to make the best use of the extended development timeline of 4 years, culminating with cycling of pressure and temperature as its final milestone. All of the risk reduction testing we have planned was presented in our FY 2009 progress report. In the last year, a test site has been selected for the dangerous permeation and cycle testing. We are in the process of designing and building a second generation transport case capable of carrying full-scale

and was produced before slight eccentricities in the tooling spin axis drive were corrected. It therefore had asymmetric liner thicknesses, which were not noticed in the customary inspection (with bright internal lamination) before wrapping. This unit was intended to survive as a souvenir small enough to keep after being exercised as a seal test unit through pressure cycling and then subsequent thermal cycling. Its relatively small size makes it less expensive in time and refrigerant to cycle. In hindsight, it was too short to be a fully representative example of the stresses in a wound high-pressure vessel of this diameter because the spreading out of the transition between cylinder and dome that accompanies the fiber trajectories of an 18,000 psi burst design built from S-Glass meant that it has no truly cylindrical section far enough from the domes to obtain the most accurate strain gage readings.

The other short pressure vessel that appears in Figure 4 was almost 48” from boss to boss, and proved that finished liners could be extracted from the mold. Even though drive eccentricity had been fixed, there were still many pounds of liquid resin inside the mold before it spun up, and this eccentric mass was enough to cause one spin axis bearing to seize. In order to prevent this partially solidified liner from slumping, its

FIGURE 4. Full-Scale Test Articles: The photograph at top shows the first completed full-scale, full-length pressure vessel developed by this project, wrapped with S-Glass fiber in an epoxy matrix, over a ROMP catalyzed plastic liner sealed into 316L stainless steel bosses at either end. The photograph at lower left shows that vessel’s liner dome with thickness markings reflecting quality control of its molding, mounted on one end boss and bolted to a removable winding spindle. Middle and right photographs in the lower row show the first (short white) and second (48” long, graphite composite wound) test articles produced on the same tooling.
and full-length test vessels weighing up to 900 pounds. (Our current heaviest design weighs 650 pounds, but it is conceivably that more fiber can be wound on linings from this tooling to burst over 36,000 psi.) This next generation of case will be gas tight to sense hydrogen permeation and ventilate with chilled nitrogen.

Complete plans for addressing the remaining significant technical risks in our vessel technology will be complete by mid-FY 2011 with the exercise of full-scale vessels in the new transportable case. This case raises the issue of shifting vessel mass during transport, which is already undergoing preliminary design to handle atypical mounting requirement of these vessels inside our delivery container design. The cold strength effect enables vessels that use it to stretch perhaps twice as much as conventional plastic lined (Type IV) composite pressure vessels, and as much as 8 times more than metal or Type III pressure vessels. The accommodation of this stretching must be accompanied by the ability with withstand significant vehicle acceleration loads in a design that favors spreading these external loads over several bands around each delivery vessel.

LLNL’s diameter specification and length margin budgets provide sufficient room for this design to expand in routine service without its vessels touching, even assuming the most extreme likely cold strength effect. One other unavailable component is necessary to make these geometric budgets feasible, and its technical risks are moderate. Our team has begun designing and prototyping a hollow tile (made from cast plastic and metal foil) to provide planar vacuum insulation in a thin form inside the delivery container’s walls. A second generation of trailer thermal management design indicates that two layers of such tiles could provide more than seven days of durability for a stranded delivery trailer before hydrogen would need to be vented to avoid any safety decrease due to diminished cold strength. Variants of this design have been modeled for three layers with nearly three weeks durability, and for single cylindrical tank delivery configurations. A development pathway that can affordably prove single tank configurations is also being considered for a follow on development effort that can make best use of the next generation of (larger) full-scale tooling.

**Conclusions and Future Directions**

- Subscale S-Glass fiber wound pressure vessels were successfully built and burst at 500 and ~170 K, bursting within 2% of design at 20,000 psi.
- The first batch of full-scale S-Glass fiber vessels were built, demonstrating the manufacturability of all high technical risk trailer components and processes.
- Several novel manufacturing problems were found and fixed to achieve these results. Along the way various materials properties were investigated, including tensile strength, toughness, and thermal shock tolerance, and some beneficial changes were made to proprietary formulations.
- Designed a thermal management system for containerized and single cylinder delivery trailer that preserves trailered hydrogen for more than a week before needing to vent. This effort included planning an affordable development pathway for single large pressure vessel delivery.
- Future work culminates development of full-scale pressure vessels with a test program that eliminates all unique risks of this technology. Planned proof-of-concept tests include hydrostatic burst of a statistically significant number of full-scale vessels, pressure and temperature cycling of one such article before bursting it, and hydrogen permeation testing. A site has been selected for these dangerous tests, and will be prepared to safely mitigate the explosion risks of testing experimental vessels filled with hydrogen.
- Materials research and further development efforts are planned to extend our improved understanding of toughness to lower temperature, and to improve permeation of hydrogen through ROMP materials with mitigation layers.
- Design and modeling efforts planned for our future trailer integration efforts include the full specification for insulating tiles containing thin vacuum layers, suspension for vessels that isolates them from worst case trailer acceleration loads, and suspension design that also isolates the container and its insulation from the significant length and diameter expansion under pressure expected due to the cold strength effect on glass composites.
- Spencer Composites and other industrial partners will assist LLNL’s formulation of realistic production cost models. In future years we anticipate adding a tube-trailer-integration-capable subcontractor to form a team of industrial partners with the capability and incentive to prototype advanced hydrogen delivery trailers.
- Future work includes initiatives to prepare federal regulators in other agencies to consider cold hydrogen systems pressure safety, funding initiatives with potential Department of Transportation collaboration to demonstrate a full hydrogen delivery container in the field, and initiatives to partner with gas vendors.

**Special Recognitions & Awards/Patents Issued**

2. Four patents in process.
III. Hydrogen Delivery

Invited Presentations


FY 2010 Publications/Presentations

Publications in Books and Technical Journals


III.8 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
Project End Date: June 1, 2011

Objectives

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 Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(G) Storage Tank Materials and Costs

Technical Targets

This project has focused primarily on the design and qualification of a 3,600 psi pressure vessel and International Organization for Standardization (ISO) frame system to yield a storage capacity solution of approximately 8,500 liters of water. Second phase is to perform and qualify same size container at higher pressures.

Accomplishments

- Successful completion of design and qualification of a 3,600 psi pressure vessel.
  - Qualification testing included:
    - Hydrostatic Burst
    - Ambient Pressure Cycle Test
    - Leak Before Burst Test
    - Penetration Test
    - Environmental Test
    - Flaw Tolerance Test
    - High Temperature Creep Test
    - Accelerated Stress Rupture Test
    - Extreme Temperature Cycle Test
    - Natural Gas Cycle Test with Blow-down

- Successful completion of design and qualification of an ISO frame capable of holding four 3,600 psi pressure vessels with a combined capacity of 600 kg of hydrogen. In addition to the structure, a system for loading, unloading, and pressure relief have been designed and implemented.
  - Qualification testing included:
    - Stress Analysis
    - Dimensional Analysis
    - Stacking
    - Lifting – Top and Bottom
    - Inertia Testing

<table>
<thead>
<tr>
<th>TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Storage</th>
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<tr>
<td><strong>Characteristic</strong></td>
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<tr>
<td>Storage Costs</td>
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<tr>
<td>Volumetric Capacity</td>
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<td>Delivery Capacity, Trailer</td>
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Introduction

Hydrogen holds the long-term potential to solve two critical problems related to energy use: energy security and climate control. 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 Phase 1 of this project, Lincoln Composites will design and qualify a large composite pressure vessel and ISO frame that can be used for storage and transport of compressed hydrogen over road, rail or water.

The baseline composite vessel 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% of the tank weight (5.7% 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 (Figure 1). Installing the compressed hydrogen vessels into an ISO frame offers a benefit of having one solution for both transportable and stationary storage. This decreases research and development costs as well as the amount of infrastructure and equipment needed for both applications.

The large size of the vessel also offers benefits. A limited number of large tanks is easier to package into the container and requires fewer valves and fittings. This results in higher system reliability and lower system cost. The larger diameter also means thicker tank walls, which will make the vessel more robust and damage tolerant.

Phase 2 of the project will be to evaluate using the same approximate sized vessel(s) and ISO frame at elevated pressures. The pressures that are targeted for scope are 5,000 psi and 8,300 psi. Basic design of the individual vessels will remain approximately the same size at the 5,000 psi pressure and minor changes may be needed for the higher pressure. Higher pressures are needed to accommodate goals of the project.

Results

Design and Manufacture of a 3,600 psi Pressure Vessel

The design of the 3,600 psi pressure vessel architecture has been completed using finite element analysis to find a composite solution that resolves the internal pressure requirements and expected external loads. This design was translated into a manufacturing process that addresses the feasibility of vessel production. Several development 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 vessels were fabricated and tested to address optimizing manufacturing issues and minimize 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 materials, more leverage is available during procurement and lower production costs can be realized. Another vessel was fabricated to help establish confidence with migrating to a design having a higher margin of safety. Both of these vessels were subjected to a proof cycle and hydraulic burst test. The result of the testing met the expectations predicted by the design.

Qualification of 3,600 psi Vessel

Due to the tanks geometry and construction, there are no published standards that can be used to directly qualify the product. 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)
- ASME Code Case in Work/ASME BPV Project Team on Hydrogen Tanks and Section X

All qualification vessels have successfully been fabricated and completed through the following tests:

- Hydrostatic Burst
- Ambient Pressure Cycle Test
- Leak Before Burst Test
- Penetration Test
- Environmental Test
- Flaw Tolerance Test
- High Temperature Creep Test
- Accelerated Stress Rupture Test
- Extreme Temperature Cycle Test
- Natural Gas Cycle Test with Blow-down

Qualification of the ISO Frame

A complete assembly was constructed including ISO frame, four pressure vessels, and all relevant plumbing including pressure relief system. The following tests were performed on the entire assembly:

- Stress Analysis
- Dimensional Analysis
- Stacking
- Lifting – Top and Bottom
- Inertia Testing
- Impact Testing
- Bonfire Testing

American Bureau of Shipping has successfully approved the entire ISO assembly for production including, pressure vessels, ISO frame and subsequent valves, fittings and pressure relief system.

Conclusions and Future Directions

Proposed objectives for Phase 1 of this project were completed in the fourth quarter of 2009. This includes successful completion of a large 3,600 psi pressure vessel able to contain 8,500 liter water capacity. The successful qualification of an entire assembly into an ISO container was also completed. Lincoln Composites will continue to evaluate cost reductions in design of the vessel as well as in the manufacturing processes. Pursuant of a higher pressure vessel is underway and will continue. Trade studies will be completed followed by fabrication and testing of the higher pressure vessels. Pressure targets are set at 5,000 and 8,300 psi. This will show results more closely to the targets for Hydrogen Storage.

FY 2010 Publications/Presentations

III.9 Fiber Reinforced Composite Pipelines

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DOE Technology Development Manager:  
Monterey Gardiner  
Phone: (202) 586-1758  
E-mail: Monterey.Gardiner@ee.doe.gov

Project Start Date: October 1, 2006  
Project End Date: October 1, 2012

Objectives

Fiber Reinforced Composite (FRC) Pipeline

- Focused evaluation of FRC piping for hydrogen service applications.
- Development of structural integrity life management methodology.
- Evaluation of structural integrity – environmental effects and flaw tolerance.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell 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 FRC piping for hydrogen service applications. Assessment of the structural integrity of the FRC 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:

- Pipeline Transmission and Distribution Cost: $0.6M/mile and $0.27M/mile, respectively.
- Hydrogen Leakage: to be determined, <0.5% by 2017

Accomplishments

- Completed plan for life management methodology of FRC.
- Completed review of existing FRC design specifications/standards.
- Initiated FRC environmental effects testing.
- Initiated FRC flaw tolerance testing.

Introduction

The use of FRC piping 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 FRC from oil and natural gas use to high-pressure hydrogen use. In Fiscal Year (FY) 2010 an FRC life management plan was developed by SRNL and ASME to focus the direction for the research and testing needed to have FRC codified in the ASME B31.12 Hydrogen Piping Code. The plan also provided the tasks needed for the post construction management of FRC to insure structural integrity through end of life. The plan calls for detailed investigation of the following areas:

- System design and applicable codes and standards
- Service degradation of FRC
- Flaw tolerance and flaw detection
- Integrity management plan
- Leak detection and operational controls evaluation
- Repair evaluation

Approach

SRNL has begun investigation into the first three areas of the Life Management Plan. Codes and standards for the high-pressure FRC and process and transport pressure vessels were reviewed. Creep data on glass fiber was also reviewed to evaluate the effect of creep life on the glass fiber. The results indicate that a design margin of at least 3.5 is required to address long-term creep effects.

The effect of flaw tolerance has also been evaluated in the current FY 2010 funding. Samples for FRC design to a recognized national consensus standard were
III. Hydrogen Delivery

Additional test have been performed to evaluate the effect of chemical environment on the FRC. The purpose of the chemical exposure tests are used to determine a measure of soil pH on the FRC materials. The first series of tests measured the chemical resistance of S- and E-type fiberglass strands typical of those which are used to fabricate the load-bearing overwrap used for the composite pipeline segments.

Results

S and E glass fiberglass strands were exposed to aggressive chemical environments in order to determine reasonable bounds on the base mechanical properties of tensile strength and chemical resistance. These bounds were adopted by consultation with technical literature on the subject [1] as representative of the range where reasonable differences might be observed relative to samples which have not seen chemical exposure. These samples were subjected to solutions of pH 2.4, 7 and 10.6 for periods of either 24 hours or 120 hours (5 days). These samples were then subjected to tensile strength testing using an Istron 4507 Electromechanical System with a strain rate of 200 μm/sec per ASTM 1557-03.

Results typical of these tests are shown in Figures 1 and 2. These tests were performed using thread grips and the samples were inspected after testing to ensure that failure occurred in a position not associated with applied stress or pinching at the grip surfaces. As can be seen, mechanical failure typically occurred for the untreated samples below the 3% strain threshold, with the both samples showing impressive reproducibility in the strain point of the initial point of failure.

A series of tests have been performed to evaluate the burst capacity for FRC containing flaws.

Samples were taken from the same lot of fiberglass and were subjected to the chemical environments described above. These results are summarized in Table 1. S-Glass samples are, in most cases, the stronger of the two fiberglass make-ups, which is consistent with technical literature available on the subject. It can be seen that the aggressive chemical environments that the samples are subjected to have a deleterious effect on their mechanical properties, as is expected. These results confirm that preconditioning of the component fiberglass materials in harsh chemical environments can have an effect on the overall mechanical durability of the composite pipeline materials, and thus is an area that warrants continued scrutiny in the development of the

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<th>Time of Exposure</th>
<th>Untreated Samples</th>
<th>Treated Samples</th>
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</tbody>
</table>

TABLE 1. Summary of Tensile Strength Testing for Fiberglass Samples Exposed to Solutions of Varied pH. All Results Given in Units of ksi.
high-density polyethylene pipelines for hydrogen service. It should also be noted, however, that the test conditions to which these glass samples were exposed are very aggressive and do not necessarily represent actual field conditions; these test conditions were selected to demonstrate the potential for an environmental effect and to highlight the need for further work and consideration of this potential effect.

To address third party damage issues the sensitivity of FRP to flaws must be established. The flaw testing was performed over a range of flaw sizes to determine the flaw tolerance of the FRC piping. FRC piping with single-layer reinforcement and multi-layer reinforcement was evaluated. The results of the single-layer tests are shown in Figure 3. A reduction in burst pressure from unflawed condition to a 2 inch long flaw cutting the reinforcing layer of 75% was observed. With the 2 inch long flaw cutting the reinforcing layer the burst pressure drops below the rated pressure for the single-layer product. The single-layer reinforced piping does not provide sufficient redundancy to tolerate third party damage. The results of the multi-layer tests are provided in Figure 4; reduction in burst pressure from the unflawed condition to a 40% through wall flaw of 28% were observed. With the 40% through wall flaw there is still a margin of 3 above the rated pressure of the FRC multi-layered piping product. Larger flaws and creep effects still need to be reviewed for the multi-layered FRC product.

Conclusions and Future Directions

Conclusions

- FRC Pipe Fabricated API 15HR is the most relevant standard reviewed to date for the fabrication of FRC line pipe for hydrogen service. This standard can be tailored to address the need for hydrogen pipelines.
- Scoping tests show that the burst pressure obtained using the ASTM D2992 (Hydrostatic Design Basis) provides additional design margin above what is needed for stress rupture when compared to the Lawrence Livermore National Laboratory long-term tests. This additional margin provides needed excess capacity to address third party damage and environmental effects.
- The initial environmental test indicate that a service factor for will need to be evaluated for all installations. Acceptable performance tests need to be developed to address the field environmental effects and flaw tolerance.

Future Work

- Initiate FRC life management methodology development.
- Initiate flaw tolerance/third party damage testing for FRC piping.
- Evaluation of environmental degradation of FRC piping.

FY 2010 Publications/Presentations

III.10 Hydrogen Embrittlement of Pipeline Steels: Fundamentals, Experiments, Modeling

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Contract Number: GO15045
Start Date: May 1, 2005
Projected End Date: December 31, 2011

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 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 FCT 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 (2015 target).

Accomplishments

• Discovered the nature and characteristics of the hydrogen degradation mechanisms of two promising microalloyed, low-carbon steel microstructures
designated as B\textsuperscript{1} and D\textsuperscript{2} hereafter. The samples were provided by the DGS Metallurgical Solutions, Inc. The mechanisms of fracture were identified by 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.

- Characterized the microstructure of pipelines 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 provided by DGS Metallurgical Solutions, Inc.
- Developed a thermodynamic theory of hydrogen-induced decohesion that was used to model and simulate hydrogen-induced subcritical cracking in high strength steels.
- Augmented our modeling and simulation capabilities of transient hydrogen transport to account for the mechanical deformation and hydrogen-induced grain boundary decohesion in high strength steels. Predictions have been made of threshold stress intensities associated with subcritical crack growth.
- Demonstrated environmental similitude between the single edge notch specimen (SENT) and a pipeline with an axial crack on the inner diameter surface. Hence, the SENT specimen can be used as a laboratory specimen to reliably estimate the fracture resistance of a pipeline steel in the presence of hydrogen.

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.

Last year we focused our attention on identifying and characterizing the mechanisms by which hydrogen induces fracture in microalloy steels B and D. We used FIB machining to lift out sections underneath the fracture surfaces in order to examine whether hydrogen-induced fracture follows a crystallographic 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 inner diameter surface of a pipeline, and determined through constraint fracture mechanics that the SENT specimen is the appropriate laboratory specimen for the study of the fracture resistance of a pipeline.

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.

To understate the hydrogen-induced fracture processes, we use high resolution SEM with three-dimensional (3-D) visualization and TEM studies of samples taken from just below the fracture surface by the lift-out technique using FIB machining. 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 diameter or the outer diameter surface of a pipeline. Using finite element simulations of the hydrogen transport in the neighborhood of the crack tip, we explore the transient and steady-state hydrogen population profiles and how their development influences the 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. We used first-principles calculations of the hydrogen effect on these interfaces, which constitute potential fracture initiation sites, 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 information for the fracture mechanisms from the experiments and the hydrogen concentration profiles from the
III. Hydrogen Delivery

Simulations 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 is assessed through the development of engineering fracture criteria in terms of macroscopic parameters.

Results

Identification and Characterization of the Fracture Mechanisms

The study of the fractured surfaces of our compact tension specimens using optical and SEM analyses revealed that hydrogen-induced fractures are distinctly different from the overload fractures in the absence of hydrogen. Figure 1 shows the SEM images of B and D type steels where the direction of the cracks was from bottom to top. In the fracture of these materials, the ductile fracture features such as microvoid nucleation, growth, and coalescence process expected for low and medium strength pipeline steels are not clearly identifiable.

In order to understand the fracture processes, we use high resolution SEM with 3-D visualization and TEM studies of samples taken from just below the fracture surface by the lift-out technique using FIB machining (see 2009 annual progress report). This technique can identify microstructural features such as grain boundaries and secondary phases such as carbides immediately below the fracture surface.

Examination of the fracture surfaces reveals several distinct morphologies such as precipitate nucleated failure, feathery region, ductile ridges, and flat fracture features. It is concluded that except for the precipitate nucleated failure, these features are not due to any compositional variation. The high-resolution SEM image (Figure 2b) of the feathery morphology (Figure 2a) reveals the presence of “saw-teeth” on top of the ridges and no evidence of precipitates at the ridges. These ridges are reminiscent of “saw-teeth” formed on final separation of thin sections as can be seen in Figure 2c for Cu-3%Co alloy deformed in situ in TEM. The presence of such ridges (Figure 2b) suggests plastic processes [1].

Certainly, our research so far points away from the traditional and vague designation of the fracture processes as quasi-cleavage – this is the designation frequently used when the fracture surface appearance is neither clearly ductile nor clearly cleavage and the underlying fracture mechanism is not understood. In fact, the 3-D visualization of the fracture topography (January-March 2010 trimester report) demonstrates clearly the absence of cleavage characteristics and confirms the ridge formation. Feature height

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**FIGURE 1.** Wide-view SEM of compact tension specimens made from B and D type steel samples and fractured in 3 ksi hydrogen gas.
measurement shows that ridges are protrusions of approximately 400 nm. In particular, TEM analysis of the lift-out section beneath the fracture surface (Figure 3) shows slip bands parallel to ridge edges, suggesting a fracture mechanism completely governed by dislocation slip. In fact, enhanced and confined slip activity is consistent with the hydrogen enhanced local plasticity mechanism [2]. This year’s discovery requires the development and introduction of a new component in our model of the hydrogen-deformation interaction which is the subject of ongoing work.

The identification and characterization of the precise mechanism of hydrogen-induced fracture in pipeline steel materials serves all objectives of the project.

Micro- and Macro-Modeling and Simulation

We used our hydrogen-transport/material-deformation simulation tool (see 2009 annual progress report) to investigate for the first time issues of environmental similitude which is a key requirement for the transferability of fracture toughness results from laboratory specimens to a real-life pipeline.

We solved the initial/boundary-value problem for transient hydrogen diffusion coupled with material elastoplasticity in an SENT specimen embedded in a hydrogen atmosphere with a shallow crack under tension load. The dimensions of the specimen and the applied tension load were chosen such that the cracks in the SENT specimen and pipeline were subjected to the same stress intensity factor $K_I$ and $T$-stress for a given hydrogen pressure which is the hydrogen transport pressure.

The stress and deformation fields close to the crack tip for the SENT specimen and the pipeline structure are shown in Figure 4. In view of the fact that the stress intensity factor and $T$-stress for the SENT specimen and the pipeline are the same, the associated stress and deformation fields near the crack tips are almost identical. This ensures mechanical transferability of the fracture resistance results obtained from the SENT specimen. Superposed on Figure 4 are the normalized normal interstitial lattice sites (NILS) hydrogen concentrations $C_I/C_0$ ahead of the crack tip from the

FIGURE 3. Electron micrograph showing the microstructure immediately beneath the ridges on the fracture surface. Two ridges on the fracture surface are evident. Image shows slip bands parallel to ridge edges, suggesting that quasi-cleavage is not a cleavage like process but is related to dislocation slip.
hydrogen transport solutions for the SENT specimen and pipeline for two different boundary conditions respectively on the remote boundaries and outer diameter surface: zero flux and zero NILS hydrogen concentration. One can clearly see that the hydrogen concentration profiles for the two solutions (SENT specimen and pipeline) are extremely close with a deviation of only about 2% between the two solutions at the location of the peak NILS hydrogen concentration. Hence, one can state that environmental transferability is also warranted [3].

We are continuing on with the modeling and simulation of the rising load fracture toughness tests performed at the Sandia National Laboratories on steel types B and D. In this test, the load on the fracture specimen which is embedded in a hydrogen environment is increased at a constant stress intensity factor rate. The test is used to determine the “initiation threshold”, a very important parameter which denotes the critical stress intensity factor for the onset of crack propagation in hydrogen containing vessel.

The simulations described in this section are meeting all objectives of our project.

Conclusions and Future Directions

- In collaboration with Sandia National Laboratories, we carried out fracture testing of promising microalloyed, low-carbon steel microstructures. Using FIB machining, high-resolution SEM, and TEM studies, we discovered that the hydrogen-induced failure mechanism in these steels is hydrogen induced localized plasticity. In particular, we found that the fracture process is governed by intense slip activity despite the fact that the fracture surfaces have the appearance of what is known to be quasi-cleavage type of fracture. In fact, our research establishes that quasi-cleavage is a mode of fracture fully controlled by ductile processes.

- We will model the discovered mechanism of failure and implement the result in our finite element codes to simulate and predict onset of crack propagation under gaseous hydrogen transport at fixed pressure (static conditions). The predictions will be compared with results from rising load fracture toughness testing. This will lead to the development of a fracture criterion for pipeline safe operation in terms of the hydrogen pressure, geometric, and material characteristics of the pipeline. Next, we will carry out fatigue fracture testing and modeling for damage tolerance assessment under cyclic pressure conditions.

- Carrying out hydrogen transport simulations coupled with material deformation, we demonstrated that the fields in the SENT specimen exhibit mechanical and environmental similitude to those ahead of an axial crack in a pipeline. Therefore the SENT specimen can be used to reliably assess the fracture resistance of pipeline steels.

- We continue our collaboration with the Hydrogen National Institute for Use and Storage (HYDROGENIUS) of Japan. We participate in the annual meetings of automobile Industry of Japan (Toyota, Honda, Nissan) on Hydrogen Technology Standards.

Special Recognitions & Awards/Patents Issued

1. 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.

2. 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, and February 3-4, 2010.

3. Sofronis was elected a fellow of the American Society of Mechanical Engineers (ASME) for his contributions to the field of hydrogen embrittlement.

FY 2010 Publications/Presentations

Publications


References


III.11 Composite Technology for Hydrogen Pipelines

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Start Date: January 2005
Projected End Date: Project continuation and direction determined annually by DOE

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.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4.2) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

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/gasoline gallon equivalent (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 Delivery Tech Team)

Accomplishments

- Completed evaluation of Polyflow braided aramid fiber reinforced pipeline:
  - Hydrogen leakage is below nominal target for pipeline delivery.
  - Co-extruded polyphenylene sulfide-polyamid (PPS-PA) liner has lower permeation than a comparable high-density polyethylene (HDPE) liner.
  - Hydrogen blowdown test produced delamination of layer in co-extruded liner.
- Hydrogen compatibility measurements for glass fiber used as FRP underway with preliminary results showing no deleterious effects of hydrogen on fiber tensile strength.
- New and improved polymer diffusion and permeation measurement apparatus now in operation.

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 a 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 completed hydrogen leak rate measurements in Polyflow Thermoflex® FRP pipeline. These measurements were designed to assess how well this particular pipeline contains high-pressure hydrogen gas. The specimen was a 4.8-cm inside diameter, 6.1 cm outside diameter, 77-cm-long specimen of Thermoflex®, which had a liner of coextruded PPS (inner layer) and nylon PA-6 (outer layer), with each layer ~1.7 mm thick. The fiber reinforcement architecture was aramid fiber rovings helically braided on top of the liner and laid over four longitudinal rovings. The pipeline had an exterior jacket of 2-mm-thick polypropylene with damage indicating colorant. The pipeline ends were terminated with swaged steel couplings and sealed with threaded steel caps. The specimen was pressurized to ~100 bar (1,500 psia), which is the maximum allowable operating pressure, and leak rate measurements were made at 30 and 60°C. The leak rate determinations were based on our typical temperature-corrected pressure-decay measurement technique. The hydrogen decay curves are shown in Figure 1. The leak rates associated with the two temperatures are shown with the curves. These rates are approximately 50% less than those measured in similar lengths of glass fiber reinforced pipeline with a 5-mm-thick HDPE liner. For both pipelines – PPS-PA6 lined, aramid-reinforced and HDPE lined, glass-fiber-reinforced – the leak rates are significantly below the nominal 0.5% leakage target.

Following the completion of the leak rate measurements we performed a hydrogen blowdown test on the Thermoflex® specimen. We used the procedure in Appendix D of American Petroleum Institute (API) standard 15S to perform the test [2]. We pressurized the specimen with hydrogen to its 1,500-psi maximum pressure rating, heated the specimen to its 60°C temperature rating, and held it at these conditions until the pipeline liner was saturated with hydrogen gas. Following this hold period, we depressurized the specimen at -3,800 psi/min, which was almost four times greater than the prescribed rate of 1,000 psi/min. (We used a simple ball valve to

![FIGURE 1. Hydrogen leakage curves dn/dt, where n is the number of moles of hydrogen in the pipeline, for a 77-cm-long Polyflow Thermoflex® pipeline specimen.](image-url)
we observed a small decrease in the tensile strengths of fibers that were aged for eight months in hydrogen compared to those that were aged in air. Although statistically significant, we could not rule out the possibility that the reduction in tensile strength was due to improper post-conditioning handling. Thus we are in the process of repeating the hydrogen conditioning and accelerated aging on a larger number of glass fibers with better controls, 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. Table 1 displays selected measurement results obtained on fibers tested weekly through 11 weeks (2.5 months) of exposure. These fibers have not exhibited any significant degradation in tensile strength. The tests will continue through a minimum of 35 weeks (eight months) of exposure.

TABLE 1. Results of tensile tests performed on glass filaments subjected to accelerated aging in air and high-pressure hydrogen environments.

<table>
<thead>
<tr>
<th>Test Property</th>
<th>Hydrogen 1000 psi 60°C</th>
<th>Control ambient air ~25°C 5 weeks</th>
<th>Hydrogen 1000 psi 60°C</th>
<th>Control ambient air ~25°C 11 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength (ksi)</td>
<td>268.6 (26.6)</td>
<td>320.9 (26.1)</td>
<td>305.1 (23.4)</td>
<td>275.6 (23.8)</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>9.8 (14.3)</td>
<td>11.2 (17.7)</td>
<td>9.3 (18.3)</td>
<td>8.6 (16.3)</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>2.8 (28.8)</td>
<td>2.9 (23.8)</td>
<td>3.0 (19.6)</td>
<td>3.3 (19.6)</td>
</tr>
</tbody>
</table>

Numbers in parentheses are coefficients of variation (in %) for the data set.

**Conclusions and Future Directions**

Conclusions from this year’s work:

- Hydrogen leakage rates in off-the-shelf FRP pipelines with different liner materials, liner constructions and reinforcement architectures are comparable in magnitude, are lower than predicted using a simple analytical model, and a strong argument can be made that they are significantly lower than the leakage target.

- Liners constructed from co-extruded polymers could have reliability and longevity problems in instances where rapid pipeline depressurization occurs.

During the remainder of this project year and the entirety of the next we plan 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.

- Update our economic feasibility analysis to determine if additional pipeline cost reductions can be realized from recent advancements in composite pipeline technology.
- 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 microcracking, 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.

Our out-year plans are to:
- 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 2010 Publications/Presentations**


**References**

1. HFCIT MYRDD Plan, Table 3.2.2, page 3.2-13, and footnote b, page 3.2-16.
Objectives

(1) Demonstrate reliability/integrity of steel hydrogen pipelines under cyclic pressure conditions:
   - Measure fatigue crack growth rates and fracture thresholds of line pipe steels in high-pressure hydrogen gas.
   - Evaluate performance of steel pipelines by applying a code-based structural integrity model coupled with steel properties measured in hydrogen gas.
   - Optimize materials test methods in hydrogen pipeline design codes.

(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 (3.2.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

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 well-established failure mode for steel hydrogen containment structures subjected to pressure cycling. This pressure cycling represents one of the key differences in operating conditions between current hydrogen pipelines and those anticipated in a hydrogen fuel distribution infrastructure. Applying code-based structural integrity models coupled with measurement of relevant material properties allows quantification of the reliability/integrity of steel hydrogen pipelines subjected to pressure cycling. 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 the application and optimization of structural integrity codes for steel hydrogen pipelines. The new ASME B31.12 design code for hydrogen pipelines includes a fracture mechanics-based design option, which requires material property inputs such as the fracture threshold and fatigue crack growth rate under cyclic loading. Thus, one focus of this project is to measure the fracture thresholds and fatigue crack growth rates of technologically relevant 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. These data can be used to evaluate the reliability/integrity of steel hydrogen pipelines and to establish pathways for optimizing materials test methods in the design code.

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**

Efforts during Fiscal Year (FY) 2010 focused on measuring fatigue crack growth rates and fracture thresholds of X52 line pipe steel in hydrogen gas. The fatigue crack growth rate (da/dN) vs. stress-intensity factor range (∆K) relationship and the fracture threshold are necessary material-property inputs into code-based structural models that allow the reliability/integrity of steel hydrogen pipelines to be quantified. One such reliability/integrity methodology was recently published in the ASME B31.12 code.

The X52 line pipe steel was selected for this activity because of its recognized technological relevance for hydrogen pipelines. We decided to test the X52 steel from the round-robin tensile property study (FY 2008) for the following reasons: 1) some characterization of the material was already provided from the round-robin study, 2) ample quantities of material were still available from Concurrent Technologies Corporation, one of the participants in the Pipeline Working Group, and 3) the X52 steel was in the form of finished pipe, which is the most relevant product form and also allows samples to be extracted from the seam weld.

The hydrogen-affected fatigue crack growth law (da/dN vs. ∆K) for the structural steel is the basic element in pipeline reliability/integrity models. Results from the technical literature indicate that the da/dN vs. ∆K trends for steels in hydrogen gas exhibit several transitions, and these transitions can depend on variables such as the R ratio (i.e., ratio of minimum applied load to maximum applied load). Consequently, it is important to measure the da/dN vs. ∆K relationship over a wide enough range in ∆K to capture the transitions. The da/dN vs. ∆K relationships were measured for the X52 steel at two R ratios (0.1 and 0.5) to establish baseline trends. These tests were conducted in 21 MPa (3,000 psi) hydrogen gas and a load-cycle frequency of 1 Hz. The pressure represents the upper limit specified for hydrogen pipelines in the ASME B31.12 code. The load-cycle frequency was selected to balance test effectiveness and test efficiency, since fatigue crack growth rates are enhanced at lower test frequency but the test duration can become prohibitively protracted. The measured da/dN vs. ∆K data are plotted in Figure 1.

The data in Figure 1 illustrate the expected transitions in the da/dN vs. ∆K trend measured in hydrogen gas. In particular, data for the test conducted at R=0.1 show that crack growth rates are similar to those measured in air until a critical K level is reached. At this point, the crack growth rates accelerate and the da/dN vs. ∆K relationship has a characteristic slope in the log-log plot. As ∆K continues to increase, another transition is observed in which the slope of the da/dN vs. ∆K trend abruptly decreases.

The da/dN vs. ∆K relationships in Figure 1 were measured at a load-cycle frequency of 1 Hz. This frequency was selected to enhance the efficiency of measuring the baseline da/dN vs. ∆K relationships. However, fatigue crack growth rates are known to depend on the load-cycle frequency, and it is important to ensure that the da/dN vs. ∆K relationships represent.
conservative data for reliability/integrity calculations. This dependence of crack growth rate on frequency is related to the kinetic steps necessary for hydrogen transport from the gas into the steel. To address the limiting test frequency for producing conservative da/dN vs. ∆K data, the fatigue crack growth rates for X52 steel were measured at a fixed ∆K and R ratio (0.5) over a range of frequencies. The fixed ∆K levels were selected as 10.0 and 17.5 MPa m^{1/2}, since the crack growth rates at these ∆K levels are high (Figure 1). Establishing the limiting test frequency at high fatigue crack growth rates ensures that this test frequency will yield reliable data at lower crack growth rates as well, since the limiting test frequency for conservative crack growth rates increases as the growth rate decreases. The da/dN vs. load-cycle frequency data measured for X52 in 21 MPa hydrogen gas are summarized in Figure 2.

Several features are notable in the da/dN vs. load-cycle frequency plots in Figure 2. First, the fatigue crack growth rates are consistent with the growth rates in the da/dN vs. ∆K plot from Figure 1 at ∆K levels equal to 10.0 and 17.5 MPa m^{1/2}, respectively. Second, the growth rates appear to be essentially constant below a limiting frequency, i.e., 1 Hz and 0.1 Hz for ∆K equal to 10.0 and 17.5 MPa m^{1/2}, respectively. These trends suggest that the da/dN vs. ∆K results in Figure 1 do not represent conservative data in the higher range of crack growth rates. In addition, the limiting test frequency for conservative crack growth rates depends on the absolute crack growth rate. Further testing is planned to determine limiting test frequencies for lower crack growth rates.

It must be noted that the results in both Figures 1 and 2 represent tests that have rather extended durations. For example, the test in Figure 1 at R=0.5 required almost 6 days to complete. In addition, the data point at f=10^{-3} Hz in Figure 2 represents 5 days of testing time. These results demonstrate that reducing test duration by developing more efficient test methods is one pathway for optimizing pipeline structural integrity codes.

Fracture threshold measurements were conducted on the X52 steel under rising-displacement conditions in hydrogen gas. Recent results from the Materials Compatibility task in the Safety, Codes and Standards project at Sandia indicate that fracture threshold measurements under rising-displacement loading may yield more conservative values compared to measurements under static-displacement loading. As such, the fracture thresholds for X52 were measured under rising-displacement loading at rates of approximately 0.0051 and 0.051 mm/min. Similar to the issue with load-cycle frequency in fatigue crack growth rate testing in hydrogen gas, the limiting displacement rate for measuring lower-bound fracture thresholds must be established. The crack growth resistance curves in Figure 3 indicate that the fracture thresholds (indicated by the intersection of the dashed “blunting line” with the resistance curve) for X52 steel are not sensitive to loading rate over the range explored.

**Conclusions and Future Directions**

- Measured fatigue crack growth laws allow evaluation of reliability/integrity of steel hydrogen pipelines under cyclic pressure conditions. Hydrogen embrittlement can be accommodated by measuring fracture properties in hydrogen following ASME B31.12 pipeline design standard.
- Measurements show that fatigue crack growth rates in hydrogen depend on load-cycle frequency. These results can help optimize test methods in pipeline codes, i.e., enhancing test efficiency without compromising data reliability.
III. Hydrogen Delivery

- (future work) Complete measurements of da/dN vs. frequency for X52 steel in hydrogen at lower fatigue crack growth rates.
- (future work) Complete fracture threshold measurements for X52 steel in hydrogen as a function of displacement rate.
- (future work) Measure fatigue crack growth laws for X52 steel seam welds and girth welds in hydrogen.

FY 2010 Publications/Presentations


FIGURE 3. Crack-growth resistance curves measured for X52 steel in 21 MPa hydrogen gas at two rising-displacement rates. The fracture thresholds are indicated by the intersection of the dashed “blunting line” with the crack-growth resistance curves.
III.13 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

Project Start Date: August 1, 2005  
Project End Date: August 1, 2011

Objectives

Reduce the cost and improve the 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 hydrogen liquefaction cycle that are not commercially available.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) High Costs of Hydrogen Liquefaction

Technical Targets

This project is designing an innovative hydrogen liquefaction cycle. The resulting design will meet the DOE Fiscal Year (FY) 2012 technical targets (nearest term target) for small-scale liquefaction (30,000 kg/day) of:

• Installed Capital Cost: $40 million for a 30,000 kg/day system or $1,333/kg of daily output
• Energy Efficiency: 75%

The results of the first year work have shown that the GEECO innovative hydrogen liquefaction cycle design results in both significantly increased efficiency (50% better) and significantly lower capital cost.

Accomplishments

• Designed a practical hydrogen liquefaction cycle that significantly increases efficiencies over existing technologies.
• Identified and designed the key component – the continuous catalytic heat exchanger (CHEX).
• Began fabrication of testing apparatus.
• Designed a 50,000 kg/day plant using low/no risk development components.
• Documented a significant reduction in the total cost of hydrogen liquefaction at the complete 50,000 kg/day production level.

Introduction

The purpose of this project is to produce a pilot-scale liquefaction plant that demonstrates GEECO’s ability to meet or exceed the efficiency targets set by the DOE. 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 a 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.

**Approach**

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 -95ºF. The Joule-Thomson 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 liquify 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 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.

The project as originally proposed was intended to use an optimized combination of the Reverse-Brayton expansion cycle (or a modified Claude cycle) with the Joule-Thomson expansion cycle. At the beginning of the project, the scope was expanded to look at a broader range of alternate cycles. The resulting innovative cycle is shown in Figure 1. 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.

**Results**

The following is a summary of the major work efforts and accomplishments to date.

- Completed development and validated accuracy of CHEX numerical model.
- Through modeling, demonstrated that typical heat exchanger channel dimensions are satisfactory for pressure drop, heat exchange, and catalyst reaction rate criteria.
- Completed design of CHEX article test apparatus.
- Fabricated sensor for measuring para/ortho make-up and verified sensor performance.
- Verified through testing that the selected hydrogen and helium compressor will support the planned testing of the CHEX.
- Designed auxiliary heat exchangers.
- Designed test article “cold box.”

The results of the first year work showed that the innovative liquefier cycle design results in both significantly increased efficiency (30% better) and significantly lower capital cost. During the second year, a numerical model was developed for the catalytic heat exchanger and validated against previous testing performed on simplified catalytic heat exchangers. The continuous catalyst numeric model was created and successfully tested against known data. The model uses MATLAB for controlling inputs, outputs, and referencing thermo-physical properties, and COMSOL Multiphysics for the finite element computations. The model breaks the heat exchanger into alternating lengths of adiabatic catalytic conversion and “normal” heat exchange. 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 inch length). The heat exchanger tube design is similar to the existing adiabatic catalytic heat exchanger test data examining the para to ortho transition (cold to warm). A satisfactory step size was determined so that the model acceptably simulates a continuous and simultaneous catalytic and heat exchange process. The model was then exercised by comparing it to known data and test conditions. The model results were in good agreement with the results from existing data. In addition, several parametric runs using the model confirmed the very weak pressure dependence expected for the process.

During the second year, the basic design of the test facility was completed. This is shown in Figure 1. Figure 1 also indicates the detailed design and fabrication responsibility for the test article system split between GEECO and MIT. Work has been started on the fabrication of the test apparatus to test scaled-down versions of the heat exchangers. The test apparatus para to ortho measurement devices were built and successfully tested, catalytic material acquired, and compressors to run the helium and hydrogen flow loops were identified and tested (Figure 2). In addition, sizing the auxiliary heat exchangers (recuperators for the independent hydrogen and He loops) has been
completed (Figure 3). The CHEX test article cold box has been designed to use an existing cryostat. The cold box has been sized to accept cryogenic recuperators and heat exchangers. The tubing and instrumentation will pass through the cryostat upper lid (Figure 4).
Conclusions and Future Directions

Based on simulations run using the 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 during the first year. GEECO is proceeding with the 2010 work plan outlined as follows:

- Finish design and build of test apparatus
- Build adiabatic catalyst bed
- Test adiabatic catalyst bed
- Build CHEX
- Identify full-scale compressor
- Test CHEX
- Assess and report
Objectives

The primary objective of this project is to design and fabricate optimized dehydrogenation reactor/heat exchange systems to deliver hydrogen using liquid organic hydrogen carriers. Specifically, the project comprises the following tasks:

- Liquid organic hydrogen carrier sourcing and processing (Task 1).
- Dehydrogenation reactor development. Iterative design and fabrication of 0.1 to 1 kW prototypes of dehydrogenation reactor/heat exchange systems to deliver H₂ (Task 2).
- 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 Fuel Cell 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

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<thead>
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<td>Carrier H₂ Content (% by weight)</td>
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<td>Carrier H₂ Content (kg H₂/liter)</td>
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<td>Carrier System Energy Efficiency</td>
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<td>forecourt, $/kg of H₂)</td>
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Discovery of hydrogen carriers that maximize the carrier H₂ content was the subject of a separate project for H₂ storage (“Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen”, DE-FC36-04GO14006) that was completed in FY 2009. The objectives of the current project address the carrier system energy efficiency (through activities in Tasks 1 and 2) and total system cost contribution evaluation (Task 3).

Accomplishments

- A microchannel dehydrogenation reactor prototype developed by PNNL has successfully achieved a 7X improvement over packed-bed reactor performance; the reactor demonstrated 1.5 g H₂/g Pt/minute catalyst productivity in initial proof-of-principle testing.
- BMW has successfully performed dehydrogenation tests at conversion rates above 90% with packed-bed and annular tube reactors, provided by Air Products.
- BMW has established a direct in situ gas analysis of the produced hydrogen during dehydrogenation.
- BMW completed the construction of a (re)hydrogenation unit (5 liter inner volume, 100 bar and 250°C max working pressure and temperature).
specially designed to handle the exothermic hydrogenation reaction. Testing the newly built facility demonstrated complete hydrogenation (up to >99% conversion).

- BMW performed a comparative theoretical parameter study for the two different catalysts, palladium and platinum, during system evaluation.

**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 decreased FY 2010 funding (vs. FY 2009) and delays in receiving obligated funds, work towards FY 2010 objectives was delayed until the third quarter of FY 2010. The decreased funding level has resulted in the performance of no experimental work by Air Products or UTRC. Therefore, the reported results 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 one 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. 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 perhydro-N-ethylcarbazole and perhydrofluorene for reactor testing at PNNL and BMW. A suitable inventory of the two hydrogenated liquid carriers exists to supply all of the carrier needs for reactor testing anticipated during FY 2010. The successful completion and testing of a hydrogenation reactor at BMW adds additional flexibility for sourcing liquid carrier under this task.

**Task 2. Dehydrogenation Reactor Development and Systems Integration Modeling**

**PNNL:** The microchannel reactor concept originally pursued in FY 2009 focused on segregating the liquid carrier from the H₂ being produced to prevent the catalyst from drying out as the 2-phase flow transitioned from exclusively liquid to up to 98% H₂ gas by volume. Catalyst was coated onto thin porous substrates that wetted the liquid carrier and behaved as wicks. When placed in a microchannel with a vapor plenum adjacent to the wick, the H₂ was separated from the liquid as it was generated to keep the catalyst from drying out. Proper balancing of the liquid and vapor pressures keeps the liquid in the wick by capillarity and causes the liquid to flow through the wick. Experimental results from microwick reactors showed significantly lower catalyst productivity in comparison to a packed bed of 210-420 micron particles. The two principal causes were volatilization of the liquid carrier and diffusion limitations.

N-ethylcarbazole has a small but significant vapor pressure at the operating temperatures of 200-230°C that allowed the liquid carrier to volatilize into the vapor plenum and bypass the catalyst, which limited conversion and suppressed catalyst productivity. In addition, an analysis of diffusion limitations in the packed-bed revealed that the reaction kinetics are an
order of magnitude faster than the H\textsubscript{2} diffusion rate within the pores of the liquid-filled catalyst particles and is of the same order of magnitude as the H\textsubscript{2} diffusion rate through the liquid boundary layer surrounding the particles. Furthermore, the wick reactor concept exacerbates the mass transfer resistance by slowing the liquid space velocity and increasing the mass transfer boundary layer thickness. The project team concluded that although the wick reactor effectively accomplished its intended purpose of segregating gas and liquid and keeping the catalyst wetted, mass transfer limitations is the more important technical issue to address.

The effort shifted toward brainstorming ideas that would enhance mass transfer. A reactor concept emerged that enabled using smaller catalyst particles to enhance internal and external mass transfer without introducing untenable pressure drop through the reactor. Proof-of-concept results from this new ‘suspended slurry’ concept are shown in Figure 1 for three different versions. The data showing conversion as a function of catalyst loading divided by liquid feed rate are compared to results from a packed bed of 210-420 micron catalyst particles. Quantitative comparison is facilitated by fitting to first-order reaction rate kinetics. The best results obtained show a 7X increase from packed bed productivity of 0.2 g H\textsubscript{2}/g Pt/minute to 1.5 g H\textsubscript{2}/g Pt/minute at 90% conversion for the suspended slurry reactor.

At the outset of the project, a catalyst productivity target was set at 2 g H\textsubscript{2}/g Pt/min to enable microchannel reactor technology that could be installed on a vehicle to support H\textsubscript{2} production for primary power. The project has now achieved 75% of this initial target at 90% conversion with significant gains remaining as this novel technology matures.

**BMW:** The planned upgrade of the dehydrogenation reactor testing apparatus with additional test equipment (e.g. flow meter, temperature controller and pressure gauges) was successfully completed. With the new equipment, a quantified validation of prototype reactors developed during the project during FY 2010 will be possible. To establish the reactor test protocols, dehydrogenation measurements with a packed-bed reactor using a 5% Pd on alumina catalyst were completed. Following this, the reactor testing progressed to a microchannel annular tube reactor with a platinum catalyst (Figure 2), originally constructed by Air Products. For all experiments, an excellent repeatability of the test results could be demonstrated.

The dehydrogenation reactor testing apparatus capability has been extended by an in situ direct gas analysis of the produced hydrogen. The extension of the test rig is shown on the right hand side (“H\textsubscript{2} quality testing”) of Figure 3. Routine analysis of the hydrogen produced from the dehydrogenation reactor confirmed the high purity of the hydrogen product.

In support of system design activities in Task 2, the necessary reactor residence time for 95% conversion of the fully hydrogenated N-ethylcarbazole have been calculated for reactors containing platinum (Figure 4). Similar modeling clearly shows much faster reaction kinetics of platinum in comparison to palladium at a given temperature. The comparison of platinum-catalyzed dehydrogenation at different temperatures shows an increase of reaction speed by a factor of approximately 10, if temperature is increased by 100 K. Very short residence times can be achieved at temperatures suitable for heat integration with hydrogen internal combustion engines.
III. Hydrogen Delivery

Cooper – Air Products and Chemicals, Inc.

For the (re)hydrogenation of liquid organic hydrogen carrier, an apparatus has been constructed at BMW. The apparatus can process several liters of liquid organic hydrogen carrier during the exothermic hydrogenation reaction. It consists of a commercially available autoclave from Swiss company Buechi (5 liter inner volume, 100 bar and 250°C max working pressure and temperature) with a magnetically coupled turbo stirrer. The autoclave is oil heated by using a Julabo Forte HT60-C.U. system with a max working temperature of 400°C, in combination with a water cooling system (max cooling power 15 kW). Based on designs of similar autoclaves in use for liquid organic hydrogen carrier hydrogenation at Air Products, process diagrams have been drawn and a worst case overtemperature/overpressure scenario analysis has been performed. Based on the derived results, during the risk assessment, we decided to operate the autoclave unit in a separate, remote controlled autoclave room.

The autoclave was tested by performing several test hydrogenations and it was possible to easily handle the exothermic reaction and to finally achieve reaction conversions of up to 99%.

Task 3. Hydrogen Delivery Economics

A detailed economic analysis was completed in FY 2009 and is in preparation 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.

Conclusions and Future Directions

- A viable microchannel dehydrogenation reactor concept has been invented that is capable of achieving catalyst productivity to support H₂ delivery on board vehicles. Further development of this new, novel technology promises additional improvements. Proof-of-concept reactors that are heated with hot gas and scalable to larger reactors will be first demonstrated at 0.1 g H₂/min (nominally equivalent to 100 W e proton exchange membrane fuel cell output) and subsequently scaled to 1 g H₂/min.
- A fully tested and capable dehydrogenation reactor testing apparatus is ready for the testing of the third-generation dehydrogenation reactor prototype (scheduled for the fourth quarter of FY 2010) and the final proof-of-concept reactor (FY 2011, pending funding).
- Extension and modification of existing dehydrogenation testing apparatus from electric heating to gas heating of the reactor.

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III.15 Materials Solutions for Hydrogen Delivery in Pipelines

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:

• The most important aspect of the project is to identify base steel compositions/microstructures 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 Fuel Cell 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 2017 hydrogen delivery pipeline transmission targets:

• Reliability (relative to hydrogen embrittlement concerns and integrity; the first two bullet points are of main importance to the project):
  – Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen. Based on results to date, there appears to be commercially available pipeline microstructures that perform better than others in the presence of gaseous 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 ($M/Mile): $0.49 for 16” outside diameter 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.

- The four commercially-available pipeline steel microstructures and mechanical property data have been characterized.
- Commercial X70 pipeline welds available.
- Two traditional screening tests have been explored.
- In situ Automated Ball Indentation (ABI) 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 on the four pipeline steels
  - Two strain rates - $1 \times 10^{-4}$, $1 \times 10^{-5}$, 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.
- The in situ tensile testing was evaluated and used to screen the four pipeline steels for further fracture and fatigue testing. From this evaluation, two of the pipeline steels were selected for further testing.
- Fracture and fatigue testing have been completed in hydrogen for the two selected pipeline steels. Gaseous hydrogen test pressures for fracture and fatigue testing were bracketed between 800 and 3,000 psi to represent potential transmission pressures. Fatigue testing utilizing two R-ratio values has been explored along with testing in air for comparison purposes.
- 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.

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**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 and Technologies, 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
III. Hydrogen Delivery

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, 2,000 psi testing at ATC, corrosive National Association of Corrosion Engineers (NACE) testing and in situ 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 (grade, base chemistry, microstructural characterization comparisons) [1]. The results were reported in previous reports; however Figure 1 shows results from $10^{-5}$ strain rate for review. 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.

Fracture toughness testing measuring ($K_{IC}$) was completed on Alloys B and D at 800 and 3,000 psi (5.5 and 21 MPa) [2]. Both alloys performed well however, Alloy B with the ferrite/coarse acicular ferrite microstructure performed better at each pressure.

![Figure 1. In Situ High-Pressure Gaseous Hydrogen Tensile Test Results (Reduction in Area) at $10^{-5}$ Strain Rate from ORNL of Alloys A – D](image)

TABLE 1. Alloys and Microstructures Tested in Gaseous Hydrogen

<table>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Nb</th>
<th>Cr</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A API X70</td>
<td>.08</td>
<td>1.53</td>
<td>.28</td>
<td>.01</td>
<td>0</td>
<td>.05</td>
<td>.061</td>
<td>.01</td>
<td>92% Polygonal Ferrite/8% Upper Bainite</td>
</tr>
<tr>
<td>B API X70/</td>
<td>.05</td>
<td>1.52</td>
<td>.12</td>
<td>.23</td>
<td>.14</td>
<td>.001</td>
<td>.092</td>
<td>.25</td>
<td>90% Polygonal Ferrite/10% Coarse Acicular Ferrite</td>
</tr>
<tr>
<td>X80</td>
<td></td>
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<td>1.61</td>
<td>.14</td>
<td>.22</td>
<td>.12</td>
<td>.0</td>
<td>.096</td>
<td>.42</td>
<td>90% Polygonal Ferrite/10% Coarse Acicular Ferrite</td>
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<tr>
<td>X80</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>– Small Amount Upper Bainite</td>
</tr>
<tr>
<td>D API X52/</td>
<td>.03</td>
<td>1.14</td>
<td>.18</td>
<td>.24</td>
<td>.14</td>
<td>.001</td>
<td>.084</td>
<td>.16</td>
<td>100% Polygonal Ferrite</td>
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<td></td>
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<tr>
<td>E 100 KSI</td>
<td>.08</td>
<td>1.71</td>
<td>.22</td>
<td>.06</td>
<td>.67</td>
<td>.002</td>
<td>.044</td>
<td>.01</td>
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<td>1.42</td>
<td>.42</td>
<td>.05</td>
<td>.02</td>
<td>.003</td>
<td>.014</td>
<td>.22</td>
<td>TBD</td>
</tr>
<tr>
<td>Abrasion</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
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</tbody>
</table>

TBD - to be determined
Figure 2. In addition, opposite to what others have reported, increasing strength did not degrade fracture toughness which demonstrates the importance of microstructures in this pressure range, Figure 3.

Fatigue testing utilizing two R-ratio values (0.5 and 0.1, R is the ratio of the minimum to maximum load applied to the specimen) was completed on Alloys B and D at 800 and 3,000 psi (5.5 and 21 MPa). In addition, testing was completed in air for both alloys for comparison. There was no significant difference in fatigue results by R-ratio values or microstructures. However, both microstructures showed tendencies of convergence with those values generated in air at lower stress intensity factor range values (stress state near the tip of the crack caused by remote loading) during fatigue, (ΔK expressed in MPa m1/2), Figures 4 and 5.

Remaining work for Fiscal Year (FY) 2010 and FY 2011 includes:

Steels
- Optical, scanning electron microscope (SEM) and transmission electron microscope (TEM) microstructural characterization of alternative Alloys E and F.
- Fracture and fatigue testing of alternative Alloys E and F at 3,000 psi.
- Publish final report of microstructure vs. mechanical property performance in gaseous hydrogen under pressure for the alloys selected.
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 microstructures, especially those containing pearlite/upper bainite, are susceptible to cracking in the presence of hydrogen. FY 2009 testing at ORNL utilizing high pressure in situ tensile testing confirmed that microstructure does appear to play a role in resistance to the effects of hydrogen, especially with increasing pressure. In FY 2010 testing, fracture toughness testing of the polygonal ferrite microstructure (Alloy D) vs. a polygonal ferrite/10% coarse acicular ferrite microstructure (Alloy B) showed that the acicular ferrite microstructure performed better at both lower and higher hydrogen pressures. There was no significant difference between the Alloy B and Alloy D in fatigue testing, even under two different R-ratio values. There does appear to be a convergence of performance of the two alloys with that tested in air at lower ∆K values. This may be a positive in fatigue performance in relationship to gaseous hydrogen transmission as lower ∆K values may be more realistic in actual operation.

Based on current available funding, the following represents additional work in FY 2010 and FY 2011:

Steels

- Fracture and fatigue testing of Alloys E and F at 3,000 psi gaseous hydrogen.
- Complete microstructural characterization of Alloys E and F by optical microscopy, SEM and TEM evaluation.
- 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 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. This work has generated ASME Codes and Standards interest along with private industry that has resulted in additional fracture and fatigue testing to take place of additional alloys/microstructures in a Phase 2 project.

FY 2010 Publications/Presentations

1. An oral presentation regarding the overall project status was given at the DOE Pipeline Working Group Meeting – NIST Boulder, CO (August 2009).
2. Poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (June 2010).

References

II.16 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 Fuel Cell 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

- Hydrogen Pressure: Reached 6,000 psi hydrogen pressure (single cell).  
- Compression Efficiency: Reduced specific energy consumption by >80% compared to the best Phase I result (Figure 1).  
- EHC Scale Up: Cell technology scaled up from 3-cell to 10-cell stack.  
- Compression Mode Operation: Demonstrated compression ratio of over 500:1 in a single step.  
- Operation Hours: 3,000 hr operating time at up to 3,000 psi in single cell, and >500 hr at 3,000 psi in 3-cell stack.  
- Hydrogen Recovery: Achieved >98% hydrogen recovery rate in single cells, and 95% in a 10-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
III. Hydrogen Delivery

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. The specific energy consumption to compress hydrogen from atmospheric pressure to 2,000 psig is 3.8 kWh/kg, as shown in Figure 1. This is a >80% reduction compared to the best Phase I result. The goal of demonstrating a compression ratio of 300:1 has been met. Moreover, in the past year the EHC has been scaled up from a 3-cell stack to a 10-cell stack. It was designed, fabricated and tested at pressures up to 3,000 psi. Hydrogen recovery rates of >98% and 95% have been demonstrated in single cells and a 10-cell stack, respectively.

Conclusions and Future Directions

This project has successfully demonstrated the feasibility of the EHC technology. All major technical targets of this project have been met. They include:

- Compressed hydrogen from near-atmospheric pressure to up to 6,000 psi in a single step without any moving parts.
- Developed multi-cell stack design and validated in a 10-cell stack.
- Demonstrated compression ratio of 300:1.
- Achieved stack performance stability at 3,000 psi for more than 500 hours.
- Demonstrated hydrogen recovery efficiency of >98% in EHC single cells.

This project is ending in Fiscal Year (FY) 2010. Additional work required to further advance the EHC technology includes:

- Improve stack performance to reach 98% hydrogen recovery efficiency.
- Further scale up EHC to increase its capacity to meet demands of near-term applications.
- Further reduce power consumption to approach Nernst equation.
III. Hydrogen Delivery

Special Recognitions & Awards

1. 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 2010 Publications/Presentations


References

1. HFCIT MYRDD Plan, Table 3.2.2 “Technical Targets for Hydrogen Delivery”, section on Forecourt Compressors, page 3.2-14.
III.17 Hydrogen Permeability and Integrity of Steel Welds

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Project Start Date: May 1, 2004
Project End Date: September 30, 2012

Objectives

- Develop welding/joining technology that greatly reduces the capital cost and eliminates hydrogen embrittlement (HE) concerns in constructing new pipelines and converting existing pipelines for high-pressure hydrogen delivery.
- Quantify the effects of welding and joining on the resistance to HE of high-strength pipeline and other structural steels under high-pressure hydrogen.
- 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 risk assessment-based approach to manage the integrity and safety of hydrogen pipelines including weld joints.
- Determine the hydrogen transport behavior (absorption, diffusion, trapping, etc.) in steels.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Fuel Cell Technologies Program’s 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

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

Accomplishments

- Baseline high-pressure hydrogen permeation measurements established the effects of weld microstructure, surface conditions, temperature and hydrogen pressure on hydrogen permeation, diffusion and trapping of selected pipeline steels.
- Initial studies on friction stir welding of pipeline steels indicated considerable improvement of weld toughness and strength over the conventional arc welds.
- Testing with recently developed spiral notch torsion test (SNTT) and multi-notch tensile testing was able to quantify and rank the sensitivity of different microstructures in the weld region to hydrogen embrittlement.
- A general approach based on the finite element model has been developed to determine the fracture toughness of materials tested by SNTT.

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 hydrogen embrittlement are not limited to steel pipelines; according to a recent DOE Basic Energy Science Office report [3], hydrogen embrittlement 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 hydrogen embrittlement) 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 hydrogen embrittlement 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 H₂ 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 improving existing welding technology to optimize weld microstructure and proactively control the weld residual stress for H₂ 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, a risk assessment-based approach will be developed to manage the integrity and safety of hydrogen pipelines including the weld joints.

**Results**

The Fiscal Year (FY) 2010 activities focused on the development of the SNTT method and associated finite element analysis for measuring the fracture toughness degradation of steel welds and base metals under high-pressure hydrogen.

Current standard methods for testing hydrogen-induced mechanical property degradation of base metal have shown to be inadequate when applied 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 environment. The compact size and self-loading mechanisms employed in the 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 2010, we focused on the further development of the SNTT method to test the fracture toughness of weld metal consisting of highly inhomogeneous microstructure. AISI 4340 high-strength steel samples with different level of microstructure inhomogeneity were studied. One sample was prepared by heat treatment at 850°C for one hour followed by oil quenching. The microstructure distribution was relatively uniform in this quenched sample. The other sample was prepared with simulated weld heating and cooling curves using the Gleeble system, a dynamic thermo-mechanical simulator. Highly non-uniform microstructure distribution was obtained resembling that encountered in the heat-affected zone of a weld.

Optical microscopy images of microstructure for the quenched sample at two transverse cross-sections are shown in Figure 1. The microstructure appears...
to be predominantly martensite. The average prior austenite grain size is estimated to be roughly 250 μm. The average Vickers harness is about 650. The Gleeble sample exhibited very different microstructure than the quenched sample, as shown in Figure 2. Preliminary analysis indicates that the microstructure at the center appears to be a mixture of bainite and martensite, whereas that at 12 mm away from center is mostly bainite. It is noted that the martensite in the quenched sample is different from that in the Gleeble sample in terms of the chemical homogeneity. The rapid heating and cooling in Gleeble sample provides little time for the alloy elements to redistribute themselves in the microstructure. On the other hand, the microstructure in quenched sample is expected to be much more homogenous since the high-temperature holding permits the homogenization of alloying elements.

Fracture Toughness Analysis for SNTT

A full three-dimensional (3-D) finite element analysis (FEA) model was developed to calculate the
stress intensity factor and the fracture toughness of SNTT sample as a function of the fracture load recorded in the SNTT experiment. The model was used to study the effect of microstructure inhomogeneity on fracture toughness. Figure 3 displays the 3-D finite element model mesh of the SNTT specimen. In the analysis, one end of the sample is fully constrained, while the other end is rotated to provide the torsional load to the SNTT specimen.

For the quenched sample, the fracture torque during testing is 1,100 in·lbf. Using the 3-D model, the critical fracture energy ($J_{lc}$) is found to be 33 kJ/m². For simplicity, it is assumed that the plastic component of $J$-integral is much smaller than the elastic component. Therefore, the fracture toughness $K_{lc}$ can be converted from $J_{lc}$ by

$$J_{lc} = \frac{K_{lc}^2}{E(1-\nu^2)},$$

and is found to be 84.1 MPa·√m (76.5 ksi·√in). This value is in good agreement with the reported fracture toughness ranging from 67 to 86 ksi·√in based on the compact tension test of 4340 base steel available in the

![FIGURE 2. Distribution of Microstructure and Hardness in the Gleeble Sample](image)
literature [5]. On the other hand, the Gleeble sample failed at a lower fracture torque of 77 kN·m (680 in·lbf). The post-test examination reveals that the fracture initiates from the central region of the sample where the hardness is highest and the microstructure consists of a mixture of bainite and martensite. The fracture toughness is calculated to be 51.8 MPa·\(\sqrt{\text{m}}\) (471 ksi·\(\sqrt{\text{in}}\)), i.e., 62% of that of quenched sample. The difference in fracture toughness between the Gleeble and quenched samples is largely due to the local microstructure. The microstructure in the quenched sample consists of mostly fine martensite, whereas the microstructure in the fractured region of Gleeble sample consists of a mixture of bainite and martensite. Furthermore, as discussed previously, the microstructure in the quenched sample is expected to be more chemically homogenous than that in the Gleeble sample.

The significance of the above results is the following. Firstly, the SNTT tested fracture toughness of quenched sample is very consistent with that based on the standard ASTM compact tension test. This demonstrates that SNTT is a sound and accurate technique for measuring fracture toughness. Secondly, the miniature specimen design and high constraint in SNTT offers potential advantages over the standard compact tension test when testing mechanical property degradation due to HE in high-pressure hydrogen. As reported in the literature, it is difficult to test weld fracture toughness in hydrogen using the compact tension test due to the irregular crack growth in non-uniform microstructure [4]. As demonstrated in the Gleeble sample, the ability to test fracture toughness in the sample with a highly non-uniformed microstructure provides a solid basis for testing the weld in high-pressure hydrogen using SNTT.

Further Enhancements to SNTT

The SNTT testing technique was further improved in the following two areas. First, an extensometer was installed to accurately measure the local rotational displacement during testing. Figure 4(a) shows the in-house biaxial extensometer with a gage length of 0.5 inch. The relationship between the applied torque and rotation angle measured from the rotary variable differential transformer and the extensometer is shown in Figure 4(b). It can be seen that under the same applied torque, the angle of twist per unit length measured by the extensometer was larger than that from the rotary variable differential transformer. This indicates that the middle section of the SNTT specimen underwent a larger twist deformation than the average of the whole sample. The deformation measured from the extensometer, a more realistic representation of the actual deformation in the notched section, will be used to further validate the 3-D model.

FIGURE 3. Mesh used in the Full 3-D Finite Element Model

FIGURE 4. (a) SNTT testing utilizing a biaxial extensometer; and (b) applied torque versus rotation angle per unit length measured from rotary variable differential transformer and extensometer.
Another improvement to SNTT is that sharp pre-cracks at the groove roots were induced using cyclic fatigue. Two samples were studied: One sample was machined in the as-received annealed condition; while the other was first annealed at 850°C for 1 hour and then oil-quenched to room temperature. Fatigue cycling was performed at room temperature for 10,000 cycles at 1 Hz frequency. The maximum and minimum torques applied during fatigue pre-cracking were 300 and 30 in-lbf, respectively. The pre-fatigued samples were then tested at an applied loading rate of 20 in-lbf/s.

Postmortem surface examination was performed on the fracture surfaces of the two samples using a stereo optical microscope and a scanning electron microscope (SEM). The photographs of the fracture surface of the samples are shown in Figure 5. As shown in the figure, for the as-received material, the fracture surface contains three regions. Region A appears to be smooth from a macroscopic point of view, while region B and region C appears to be rough. For the quenched material, the fracture surface contains only two regions, in which region A appears to be smooth and region B appears to be rough. Region A in both samples were suggested to be precracks introduced by fatigue loading, and region B in both samples were suggested to be the fast growth region of crack during final fracture. A possible cause for the occurrence of region C in the as-received material is that during the torsion test, the as-received sample was loaded and unloaded twice prior to the final fracture. So region C was probably introduced during the first two loading cycles. Region B exhibited a cleavage fracture feature, which is typical for the rapid growth region of cracks. The shape of region A is well-defined, and the crack length is similar measured from different parts of region A. This verifies the strong material constraint at the crack front in SNTT specimen.

Detailed FEA of a model with fatigue precrack is ongoing to calculate the fracture toughness from the fracture load. The above enhancements are expected to further improve the consistence and accuracy of the tested fracture toughness using SNTT. This is especially important for testing fracture toughness in high-pressure hydrogen.

Conclusions and Future Directions

This project focuses on the resistance of HE in the weld region of steels. Such region is regarded as the weakest link for the structural integrity and safety of hydrogen pipeline and hydrogen delivery infrastructure. In FY 2010, we have successfully demonstrated the SNTT method for testing fracture toughness of non-uniform microstructures in the heat-affected zone and weld region.
The project plan for the remaining of FY 2010 includes: (1) completing the development of SNTT method for fracture toughness testing in high-pressure hydrogen, and (2) performing tests on different arc welds and friction stir welds of pipeline grade steels and establishing a database of material performance in high-pressure hydrogen.

**FY 2010 Publications/Presentations**


**References**

III.18 Hydrogen Pipeline Compressors

Objectives

- Develop advanced materials and coatings for hydrogen pipeline compressors.
- Achieve greater reliability, increased 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 Fuel Cell 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 2017:

Technical Targets for Hydrogen Delivery

<table>
<thead>
<tr>
<th>Category</th>
<th>FY 2012 Targets</th>
<th>2009 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reliability</td>
<td>Improved</td>
<td>Low</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>98%</td>
<td>&lt;98%</td>
</tr>
<tr>
<td>Total Capital Investment</td>
<td>$12M</td>
<td>&gt;$15M</td>
</tr>
<tr>
<td>Maintenance</td>
<td>7%</td>
<td>&gt;10%</td>
</tr>
<tr>
<td>Contamination</td>
<td>Varies</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

FY – Fiscal Year

Accomplishments

- Completion of installation and initial acceptance tests of new high-temperature hydrogen tribometer.
- Identification of new coating material (NFC7) that shows no measurable wear in two-hour test.
- Completion of tests that assessed friction and durability of proprietary diamond-like carbon (DLC) coating.

Introduction

Compressors are critical components used in the production and delivery of hydrogen. Current reciprocating compressors 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).

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 Technology, 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. MiTi® and Argonne 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**

The approach that is being undertaken is to evaluate the tribological performance of candidate seal and bearing materials under consideration by compressor manufacturers and provide data required to select the optimum seal and bearing material/coating configuration for a 300-kg/min centrifugal compressor and high-pressure, low-flow positive displacement compressor. This effort will include:

- Evaluating the effects of a hydrogen environment on the mechanical properties of Ni alloys,
- Evaluating the feasibility of coating suitable substrates with Argonne’s near frictionless coating (NFC) and outside vendor coatings,
- Establishing the requirements and testing needs for NFC and a series of foil seal coatings, and
- Evaluating foil seal and bearings under conditions prototypic of the proposed MiTi® hydrogen compressor.

The research uses facilities and expertise at Argonne – notably the ability to deposit advanced high-performance coatings (e.g., 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 – 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. The coating deposition is focused on NFC and commercial coatings based on conventional solid lubricants. The substrates chosen are stainless steels, nickel alloys, and Cr-Mo steels.

**Results**

**New Test Machine**

In the past year, the main focus was the receipt and installation of a new high-temperature test rig, as shown in Figure 1. The machine exhibited deficiencies in performance acceptance tests. The operation requirements (speed of 2,000 rpm, test period of 1 hour, pressure of 0.9 bar, temperature of 800°C) with continuous measurement of friction, wear, temperature, and sliding distance were attained in N₂ gas but not in H₂. Safety interlock switches were installed to limit the maximum pressure to approximately half the specified pressure. The pressure issue is being addressed by using dual redundant differential pressure switches. The specified temperature could not be attained due to excessive convective cooling of the specimen holder as a result of the high heat conductivity of H₂, which is approximately seven times that of air. The convection issue is being addressed by the installation of quartz heat shields. During acceptance tests, the H₂ pressure regulation was lost because a pirani pressure gauge did not operate correctly in H₂ at pressures above 1 mbar. The regulation issue was solved by substituting a capacitance diaphragm gauge, which reads correctly over the complete pressure range, independent of gas species. The reducing nature of H₂ on uncoated nickel alloys was dramatized when the new machine jammed and galled during maintenance – necessitating factory repair.

**FIGURE 1. Photograph of New High-Temperature Hydrogen Test Machine**
Continuing Tests

Additional tribological data were obtained in FY 2010, particularly focusing on extended duration tests (2 hours). Summary results are shown in Table 1. At nominal room temperature, the new Argonne NFC7 carbon performs better than the former best-performing material, NFC6. As shown in Figure 2, the coefficient of friction of NFC7 is substantially less than that of NFC6, and yet the NFC7 shows no measurable wear. Tests were harsher with the NFC7: 2-hr duration at either 2,000 rpm or 6,000 rpm, 50% duty cycle, up to 15 N load. A proprietary DLC coating did not perform as well. A Ni/polytetrafluoroethylene (PTFE) coating was obtained on test coupons, but testing was delayed. A nondisclosure agreement is being negotiated with a company that offers a low-temperature diamond coating process.

New Characterization Methods

A newly installed Hysitron nanoindenter was used to probe the mechanical properties of unworn and worn surfaces (Table 2). Transfer films, as expected, are quite soft, but the new NFC7 is surprisingly hard with high elastic modulus when compared to the other leading candidate material NFC6, or the lesser-performing N3FC. The NFC7 exhibits surprising constancy in hardness and elastic modulus for various loadings (1-5 mN).

TABLE 2. Nanoindenter Measurement of Mechanical Properties of Materials

<table>
<thead>
<tr>
<th>Sample and Region of Probing</th>
<th>Hardness (GPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain 4118 steel</td>
<td>13.8±1.3</td>
<td>234±20</td>
</tr>
<tr>
<td>Transfer film of H, tested</td>
<td>1.7±0.42</td>
<td>60±14</td>
</tr>
<tr>
<td>N3FC DLC</td>
<td>1.7±0.5</td>
<td>30±5</td>
</tr>
<tr>
<td>N3FC tested in H</td>
<td>5.3±2.5</td>
<td>35±15</td>
</tr>
<tr>
<td>N3FC DLC</td>
<td>6.4±2.6</td>
<td>44±22</td>
</tr>
<tr>
<td>N3FC12</td>
<td>9</td>
<td>66</td>
</tr>
<tr>
<td>NFC7 (area 1)</td>
<td>17.3±0.5</td>
<td>122±1</td>
</tr>
<tr>
<td>NFC7 (area 2)</td>
<td>16.6±0.5</td>
<td>111±3</td>
</tr>
<tr>
<td>NFC6</td>
<td>7.8±0.8</td>
<td>69±54</td>
</tr>
</tbody>
</table>

Conclusions and Future Directions

Longer-duration room-temperature testing was performed on existing (NFC6) and new (proprietary DLC and Argonne NFC7) materials, with excellent results for the latter. Installation of the new elevated-temperature tribometer is 80% complete, with shakedown tests performed in N₂ but not meeting specifications in H₂. Pending successful modifications and acceptance tests, we will finish up testing of promising materials at typical in-service temperatures. A series of tests of newly received Ni/PTFE test specimens will be performed.

TABLE 1. Friction Coefficients of Materials in Ambient-Pressure Hydrogen
The original goal of “Large Compressors: Transmission, Terminals, Geological Storage” is being broadened to include the section “Forecourt Compressors: Forecourt,” and discussions have been started with two suppliers of non-centrifugal hydrogen compressors who have products in the field that are exhibiting the need for frequent scheduled and unscheduled maintenance. This revised goal will involve conducting longer-term sliding tests on materials used in forecourt compressors for “bone dry” use (e.g., polyether-ether-ketone and carbon-tetrafluoroethylene instead of nickel alloys, as has been done so far). We will continue nanoindentation studies to elucidate the possible relationship of surface mechanical properties to tribology friction and wear, and will apply the focused-ion-beam method to understand how H₂ can affect near-surface and subsurface failure.

**FY 2010 Publications/Presentations**

III.19 Advanced Sealing Technology for Hydrogen Compression

<table>
<thead>
<tr>
<th>TABLE 1. Technical Targets for Hydrogen Compression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Category</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Reliability</td>
</tr>
<tr>
<td>Energy Efficiency</td>
</tr>
<tr>
<td>Capital Investment ($M)</td>
</tr>
<tr>
<td>(based on 200,000 kg of H2/day)</td>
</tr>
<tr>
<td>Maintenance (% of Total Capital Investment)</td>
</tr>
<tr>
<td>Contamination</td>
</tr>
</tbody>
</table>

Accomplishments

- Several seal designs were evaluated in static and dynamic tests. The variations included the radial clearance, presence or absence of face bumps, preload level, and the axial length.
- Tests were conducted both with air and helium as the substitute gas for hydrogen. The effect of inlet pressure and speed were evaluated. The gas temperature was varied from the ambient to 500°F. The results confirmed that the flow factor, or seal leakage, decreased as the inlet pressure was reduced or the speed was increased.
- Presence of the face bumps decreased leakage, while preload had only a minor effect. Longer seals did not necessarily improve the seal performance. Seal leakage was significantly reduced at higher temperatures. A smaller leakage was obtained with helium as compared with air. The seal performance and durability improved when all surfaces that would come into contact were also coated with the Korolon® 7 coating.
- A continuous 3.5-hour test confirmed excellent durability for the seals as no wear or erosion were observed on the seal components after the test and the flow factors remained constant throughout the testing period.

Introduction

The objective of this project is to develop and demonstrate 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 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**

The initial dynamic testing was carried out with four seal configurations in progressive settings in order to safely run to full operating speed and high inlet pressures. The static and dynamic performance of each seal configuration was first evaluated with a loose radial clearance and no face bumps. The flow factor was reduced as the speed was increased from 0 to 60,000 rpm due to centrifugal growth of the rotor and the developed hydrodynamic pressure. The results also confirmed that the leakage was higher for the static seal as compared to the dynamic conditions. The seal leakage increased as the inlet pressure was increased from 20 to 100 psi (see Figure 1).

Since the first set of tests were successfully performed with loose radial clearance seals and no face bumps, the face bumps were then installed without preload, using the same radial clearance as before. Both the static and dynamic performance of this seal configuration was then evaluated. The seal leakage was reduced as the speed was increased and as the inlet pressure was reduced. In the next series of test, the face bumps were preloaded while the radial clearance remained the same as before. The results were similar to those for the other two seal configurations described above.

As the last configuration for this series of parametric study, the seal radial clearance was reduced while the face bumps were kept loose without preload. The
dynamic performance of the four seal configurations under the same testing conditions was further compared as a function of inlet pressure at a fixed operating speed of 60,000 rpm, and as a function of operating speed at a fixed inlet pressure of 100 psi. The seal leakage was reduced when the face bumps were installed in the seal assemblies, while preloading the face bumps had no effect on the seal performance. The most significant contribution to the seal performance was from the radial clearance between the sealing surface and the test journal - the smaller the radial clearance the less seal leakage. The seal configuration with loose radial clearance and loose face bumps was selected for further testing to evaluate the seal performance under various conditions.

**Elevated Temperature:** To characterize the seal performance at elevated gas temperatures, four heat torches were installed at the air inlet of the high-speed test rig. The static and dynamic performance was evaluated first when the heaters were off. The heaters were then turned on and the temperature was set at 500°F. After the temperature reached the steady-state value, the seal performance was evaluated under static conditions and then under dynamic conditions at various speeds. The seal leakage was significantly reduced at the higher temperature.

To protect the seals from being damaged, the testing procedure was revised and the inlet pressure was kept above 70 psi during dynamic testing. Figure 2 compares the dynamic performance of the seals under ambient, 250°F, and 500°F temperatures. The leakage was reduced as the speed and temperature were increased and as the inlet pressure was reduced.

**Testing with Helium:** The seal performance was evaluated under ambient and elevated temperatures with helium as a substitute gas for hydrogen. While it was desired to test with helium subjected to higher inlet pressures up to 250 psi, the pressure was limited to about 120 psi due to heating by the heat torches used. The leakage was reduced as the temperature increased. The flow factor with helium was smaller than that with air under the same conditions at 500°F.

Dynamic tests with helium were conducted next at various temperatures; however, significant buzzing came from the inside of the test rig at ambient temperature. The seals were removed and examined after the test was completed. Significant erosion had occurred at the overlapped trailing and leading edges of both inner and outer smooth foils of the outboard mounted seal. However, the inboard mounted seal showed no visible damage. Therefore, it was decided to coat not only the sealing surface of the smooth top foils, but also the two touching surfaces of the inner and outer smooth foils with thinner Korolon® coating. The new seals were also tested at 250°F and 500°F. The additional coating reduced buzzing during testing and prolonged the seal life. Figure 3 shows the dynamic test results with and without the additional coating and compares the dynamic performance of the seals with helium at different temperatures. Similar to air, both temperature and speed help reduce the seal leakage.

**Different Coatings:** The smooth foils in the tests described above were coated with Korolon® 900. To compare the seal performances with different coatings, new seals were made and coated with Emralon® and Teflon®. The dynamic performance of the three coatings at operating speeds of 50,000 and 60,000 rpm at 70 psi were compared. For each coating, the leakage increased as the inlet pressure increased, and decreased as the operating speed increased. The leakage of the Korolon® coated seals was slightly larger than that from the other two coatings. However, these tests were conducted at ambient temperature only; the Korolon® coating has been designed for and has demonstrated excellent performance at elevated temperatures.

**Longer Axial Length Seals:** In order to further improve the seal performance, the seal design was modified. The axial length of the smooth foils was...
III. Hydrogen Delivery

Durability Testing: Long-term durability testing was conducted to verify seal life. Two standard axial length seals with Korolon® 900 coating were tested with air under ambient temperature at an operating speed of around 40,000 rpm and an inlet pressure of about 50 psi. The flow factor as a function of time during the 3.5-hour test was constant. The seal foil temperatures remained low and the flow factor stayed steadily below 0.007. The seals were checked after the test and showed no wear marks; therefore, the seals were capable of running continuously for an extended period of time.

Conclusions and Future Directions

Several seal designs were evaluated in static and dynamic tests. The variations included the radial clearance, presence or absence of face bumps, preload level, and the axial length. Tests were conducted both with air and helium as the substitute gas for hydrogen. The effect of inlet pressure and speed were evaluated. The gas temperature was varied from the ambient to 500°F. The results confirmed that the flow factor, or seal leakage, decreased as the inlet pressure was reduced or the speed was increased. Smaller clearance values decreased the leakage through the seals. Presence of the face bumps decreased leakage, while preload had only a minor effect. Longer seals did not necessarily improve the seal performance. Seal leakage was significantly reduced at higher temperatures. A smaller leakage was obtained with helium as compared with air. The seal performance and durability improved when all surfaces that would come into contact were also coated with the Korolon® 7 coating. A continuous 3.5-hour test confirmed excellent durability for the seals as no wear or erosion were observed on the seal components after the test and the flow factors remained constant throughout the testing period. The following tasks are planned for next year:

- Prepare the final report

FY 2010 Publications/Presentations

III.20 Rapid Low-Loss Cryogenic Hydrogen Refueling

Objectives

- Demonstrate rapid refueling of cryogenic vessels.
- Refuel cryogenic vessels even when warm and/or pressurized.
- Refuel at high density (>80 kg/m³).

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(j) Other Refueling Site/Terminal Operations

TABLE 1. Progress toward Meeting DOE Hydrogen Delivery Technical Targets

<table>
<thead>
<tr>
<th>Pressurized LH₂ pump</th>
<th>DOE Targets for Forecourt Compressors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Units</td>
</tr>
<tr>
<td>Reliability</td>
<td>-</td>
</tr>
<tr>
<td>Compression Efficiency</td>
<td>%</td>
</tr>
<tr>
<td>Installed Capital Cost</td>
<td>k$/kg/hr</td>
</tr>
<tr>
<td>H₂ Fill Pressure</td>
<td>Peak psi</td>
</tr>
</tbody>
</table>

Accomplishments

- Identified pressurized liquefied hydrogen (LH₂) as a viable solution for cryogenic vessel refueling.
- Acquired LLNL institutional approvals for pump purchase and installation.
- Identified commercial LH₂ pump that will deliver required performance.

Introduction

Cryogenic pressure vessels have demonstrated highest performance for automotive hydrogen storage, with considerable advantages in terms of weight, volume, and cost [1,2]. One of the outstanding challenges for cryogenic pressure vessels is refueling. Today’s hydrogen storage technologies (compressed and liquid hydrogen) operate at fixed temperature. Cryogenic pressure vessels, however, drift across the phase diagram depending on the level of use. The challenge is demonstrating rapid, inexpensive refueling that minimizes evaporative losses regardless of the initial thermodynamic state of the vessel.

Approach

We have identified a promising technology for cryogenic pressure vessel refueling: a liquid hydrogen pump. This pump takes liquid hydrogen at low pressure (near atmospheric) and delivers it as high-pressure (3,000-12,000 psi) low temperature (30-50 K) high-density (>80 kg/m³) hydrogen that can be directly dispensed into a cryogenic pressure vessel, even when warm and/or pressurized. In this project we plan to purchase a LH₂ pump, install it in the LLNL campus, and demonstrate its virtues for rapid and efficient cryogenic vessel refueling.

Results

Cryogenic vessel temperature and pressure are strong functions of use patterns. After a cryogenic hydrogen fill, pressure vessels will remain cold and unpressurized if frequently driven due to (nearly) isentropic hydrogen expansion during gas extraction, thereby enabling efficient refueling from conventional low pressure (~100 psi) LH₂ Dewars. Extended periods of parking, however, will warm up and pressurize the vessel due to heat transfer from the environment. Refueling warm vessels with low pressure LH₂ is slow and produces considerable evaporative losses. A better solution is needed for practical cryogenic pressure vessel refueling.

Liquid hydrogen pressurization appears a viable solution. A pump may take LH₂ from a low pressure...
Dewar and deliver it at 30-50 K and 3,000-10,000 psi, enabling direct dispensing into even warm and/or pressurized vessels while minimizing evaporative losses.

A potential issue with direct dispensing from a LH$_2$ pump is the variability in the amount of hydrogen in a “full” tank as a function of initial conditions. While a cold tank can be filled to full capacity, a warm vessel can only be refueled to lower capacity to avoid evaporative losses when thermal equilibrium between the hydrogen and the vessel is reached. Fill variability may be acceptable to consumers because it is self-regulating: an infrequently driven vehicle is filled partially, but also requires less fuel because it is typically unused. A frequently driven vehicle has a cold vessel that can be filled to capacity, enabling long driving range.

Pressurized cryogenic refueling may also reduce station capital cost and hydrogen delivery cost. Unlike compressed gas dispensing, pressurized cryogenic dispensing does not require a cascade or refrigeration (Figure 1). The simpler station configuration reduces capital cost and makes the overall cost of liquid hydrogen dispensing comparable to the cost of compressed gas dispensing, even after considering liquefaction cost [3].

We have now identified a pump that satisfies the requirements for rapid cryogenic pressure vessel refueling. The pump takes advantage of LH$_2$ compressibility to deliver high density H$_2$ (over 80 kg/m$^3$, Figure 2) at rapid refuel rates (100 kg/hr) and with low evaporative rates (<3%). Evaporated hydrogen is not vented. Instead, it is recirculated into the station LH$_2$ Dewar, helping maintain its pressure.

LLNL is currently negotiating a contract with the manufacturer. Current plans call for pump installation (along with a large 3,000 gallon Dewar) at LLNL by early 2012.

**Conclusions and Future Directions**

- Rapid, low-loss refueling of cryogenic vessels is possible through pressurized LH$_2$ dispensing.
- Pressurized LH$_2$ dispensing reduces station cost by avoiding compressor, cascade, and refrigerator.
- Overall delivery cost of pressurized LH$_2$ is comparable to compressed gas, even after including the cost of liquefaction.
- Future work includes important tasks:

![Image of station equipment needs for 700 bar compressed H$_2$ dispensing and pressurized LH$_2$ dispensing](source: Argonne National Laboratory)

**FIGURE 1.** Graphical comparison between station equipment needs for 700 bar compressed H$_2$ dispensing and pressurized LH$_2$ dispensing (from Argonne National Laboratory [3]).
Aceves – Lawrence Livermore National Laboratory

III. Hydrogen Delivery

- Purchase and install a pressurized cryogenic pump.
- Demonstrate rapid refueling of (even warm or pressurized) cryogenic pressure vessels with low evaporative losses.
- Explore effect of higher pressure on evaporative losses, refueling speed and maximum vessel capacity.

References


FY 2010 Publications/Presentations


2. High Density Hydrogen Storage in Cryogenic Capable Pressure vessels, Salvador Aceves, Invited presentation, Purdue Hydrogen Symposium, Purdue University, Indiana, April 2009.


III.21 Range Optimization for Fuel Cell Vehicles

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Project Start Date: October 1, 2009
Project End Date: September 30, 2010

Objectives

- Develop the fuel cell vehicle (FCV) range optimization model.
- Compare onboard storage technologies.
- Support the DOE integrated analysis on storage and range issues.

Technical Barriers

This project addresses the following three barriers from the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(A) System Weight and Volume from the Storage section
(B) System Cost from the Storage section
(B) Stove-piped/Siloed Analytical Capability from the System Analysis section

Technical Targets

This project optimizes the driving range for FCVs. Insights gained from the study can be applied toward assessment and planning of research and development (R&D) activities on onboard hydrogen storage in meeting the following DOE 2010 hydrogen storage targets [1]:

- Cost: $4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Accomplishments

- Baseline analysis suggests that the optimal FCV range for the very near term is estimated to be 297-544 miles, depending on up to 10% variation on key parameters.
- Sensitivity analysis demonstrates the robustness of the optimization. A 10% variation on each of 16 key parameters results in -5.7% to +6.2% of change in the optimal range and the optimal onboard usable fuel capacity.
- Quantified the functional relationship between optimal range, storage cost, storage density, and fuel availability. In general, the optimal range is found to increase with lower storage cost or higher storage density, but decrease with better fuel availability.
- Based on the range optimization model, several storage technologies are compared in the transitional market context based on an integrated consumer value metric.
- Demonstrated the benefit of range optimization in informing policy making. Compared to the optimal range, the standard range assumption leads to an overestimate of FCV commercialization barrier by over $8,000 per vehicle. Such a significant overestimate of this transition barrier can seriously mislead policy making but can be corrected by range optimization.

Introduction

The driving range of FCVs needs to be properly determined for accurately assessing the market barriers and cost-effectiveness of this vehicle technology [2-5]. While an overestimated range means an overestimated cost of onboard storage, an underestimated range leads to exaggeration of refueling hassle especially in the early transition period when fuel availability is very limited. Either overestimation or underestimation of the driving range leads to exaggeration of commercialization barrier for FCVs and could mislead policies.

If FCVs become commercialized, it is logical and likely that the private sector will design the range to maximize the value for FCV customers. This suggests optimization of FCV range for proper representation of FCVs in analyses where various vehicle technologies are compared and the future vehicle market is projected. Currently, the FCV range commonly assumed in many analyses is based on engineering constraints and simple analogy to conventional vehicles [6], but not on optimization that reflects the storage technology status.
and fuel availability for FCVs. It is unclear to what extent the ongoing non-optimal range assumptions affect the FCV barrier assessment. It is necessary to revisit the issue by optimizing the FCV range in the context of transitional markets.

### Approach

The FCV range is optimized from the perspective of maximizing consumer value or minimizing total vehicle ownership cost. As a benefit to consumers, increasing the FCV range reduces the stress and time of accessing hydrogen stations, the wasted fuel in searching for stations and the time at the station. On the cost side, a longer FCV range results in loss of legroom or cargo space and higher storage system cost and vehicle price. The optimal range is defined as one where the marginal benefit equals the marginal cost. In preparation for the optimization, the stress and time of refueling are estimated based on calibration to 5,850 light-duty vehicles and appear to be more consistent with survey estimates than conventional analytical methods that consider only travel time cost [7]. Refueling travel time is calculated by assuming optimal station locations [8,9]. Onboard storage technologies are characterized based on published information from the hydrogen storage projects funded by U.S. DOE [1,10]. Value of vehicle interior space is currently based on published estimate that is based on statistical analysis of vehicle design and pricing data [11].

### Results

- The baseline analysis shows the optimal FCV range for the very near term ranging from 297 to 544 miles, depending on up to 10% variation on key parameters. The baseline case is intended to represent the near term characterized by very limited hydrogen station deployment and current technology status for onboard storage. For hydrogen availability, the percentage of stations providing hydrogen is assumed to grow from 1% at the present to 10% in 10 years. Onboard storage technology is assumed to be available at $15.6/kWh and 0.6 kWh/L.

- The barrier of limited range and fuel availability is described by the extra range cost relative to conventional gasoline vehicles, including storage hardware cost, loss of interior space, refueling travel stress and time, wasted fuel, dispensing time and station time overhead. The baseline case results show the extra range cost for a near-term FCV owner is more than $20k (Figure 1). Storage system cost, loss of interior space and refueling travel stress and time contribute to most of the extra range cost.

- Sensitivity analysis demonstrates the robustness of the optimization. A 10% variation on each of 16 key parameters results in -5.7% - +6.2% change in the optimal range and the optimal onboard usable fuel capacity (Figure 2).

- The relationship between optimal range, storage cost, storage density, and fuel availability is quantified. In general, the optimal range is found to increase with lower storage cost or higher storage density, but decrease with better fuel availability.

- Different storage technologies are compared based on range cost and infrastructure cost (Figure 3)
for the near-term scenario. Based on current technology status and near-term infrastructure deployment, cryo-compressed appears to be overall the most cost-competitive, even though its infrastructure cost is higher than compressed gaseous technologies. The chemical hydride technology based on liquid hydrogen carrier (LCH$_2$) is slightly more cost-competitive than compressed gaseous hydrogen. The two compression technologies, with pressures of 350 bar and 700 bar, do not differ substantially from each other in terms of total range and infrastructure costs. The chemical hydride technology based on sodium borohydride (SBH) has a good balance of storage system cost and density, resulting in a relatively low range cost, but its high infrastructure cost makes it the least cost-competitive among the five technologies. It should be noted that these comparisons reflect the near-term technology and infrastructure status and do not reflect the improvement potential of the technologies.

- The barrier overestimation by non-optimal range design can be significant. Compared to the optimal range, the standard range assumption leads to an overestimate of range cost by over $8,000 per vehicle. Such a significant overestimate of barrier can seriously mislead policy making and should be corrected by range optimization (Figure 4).
- The scenario analysis based on the DOE Scenario 3 shows that the FCV range does not necessarily exhibit a monotonic increase or decrease over time. It decreases initially and grows later in response to the relative development pace of storage technology and infrastructure (Figure 4). In reality, product design constraints and consumer expectation set by previous products may prevent the designed range from significantly decreasing. However, what is important is that by reaching the initial critical level of fuel availability, FCV range can be reduced to save costs if little progress is made on onboard storage. It also suggests that after the critical fuel availability level, a higher FCV range is realistic if onboard storage is significantly improved.

### Conclusions and Future Directions
- It is very likely that the non-optimal FCV range currently assumed in analyses has led to exaggeration of this market barrier. Compared to the estimated optimal range, the currently assumed FCV range is found to be too low, which reduces the cost of onboard storage hardware but will require early FCV owners to make more frequent trips to the very few stations that provide hydrogen. The collective effect is a range cost overestimation by over $8,000 per each early FCV owner. In integrated market analyses, such an overestimation would put FCVs into biased disadvantage. It should and can be corrected with range optimization that trades off onboard storage cost with refueling inconvenience.
- The optimal FCV range is found to be a function of fuel availability, onboard hydrogen storage cost and density. The optimal range increases with technological progress of onboard storage, because lower storage cost or higher storage density makes it cost-effective to have additional range in order to reduce refueling frequency. The optimal range decrease with refueling infrastructure deployment, because better fuel availability makes it worthwhile to reduce the range in order to save upfront storage cost.
- The FCV range should be adaptive to the developments of onboard storage technology and refueling infrastructure, for two reasons. First, as we have shown, the optimal FCV range is a function of storage cost, storage density and fuel availability. Second, all these three factors will likely change significantly during the transition period.
• High cost and low density onboard storage and limited fuel availability cause a serious market barrier for FCVs, even if the FCV range is optimized. To eliminate such a barrier, both improving onboard storage and deploying refueling infrastructure will help, but given the uncertainty of technology development and the diminishing contribution to fuel availability of more stations, building up the initial small-scale refueling network should be of higher priority.

• On future study, the methods or observations from this study should be utilized for integrated models. The optimization model can be used to track the progress of onboard storage R&D activities. More research is recommended to better understand the value of vehicle interior space. The optimization model can be expanded to other vehicle technologies, including electric vehicles and plug-in hybrid vehicles. Other factors may also need to be included in optimizing the range, such as weight, efficiency and leakage.

References


IV. HYDROGEN STORAGE
IV.0 Hydrogen Storage Sub-Program Overview

Introduction

Hydrogen Storage activities in Fiscal Year (FY) 2010 continued to focus on research and development (R&D) of low-pressure, materials-based technologies applicable to both stationary and transportation applications. For transportation, the key objective is 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. Materials projects are focused in three main areas: metal hydrides, chemical hydrogen storage materials, and hydrogen sorbents.

FY 2010 saw continued close coordination between the Office of Science’s basic research activities and Energy Efficiency and Renewable Energy’s (EERE’s) applied R&D portfolio. Twenty-five fundamental studies on hydrogen storage materials are being supported by the Office of Science. Within EERE, several projects were completed this past year and no new projects have been initiated. In summary, the storage portfolio currently comprises projects involving 39 universities, 13 companies, and 14 federal laboratories (Figure 1).

Goal

The sub-program’s primary goal is to develop and demonstrate viable hydrogen storage technologies for transportation and stationary fuel cell applications.

Objectives

The sub-program’s ultimate targets for transportation applications are intended to facilitate the introduction of hydrogen-fueled propulsion systems across the majority of vehicle classes and models, whereas the 2010 and 2015 intermediate targets will allow some hydrogen-fueled vehicle platforms to meet customer performance expectations. In pursuit of high-level goals and targets for hydrogen storage, there are many requirements to achieve technical success, including improvements in volume, weight, cost, durability, cycle life, and transient performance. The full set of hydrogen storage targets for light-duty vehicles can be found at: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_on-board_hydro_storage.pdf. These targets are based on the requirements of the application—not the current status of the technologies—and they account for differences in vehicle architecture between conventional vehicles and fuel cell vehicles.

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 without compromising space, performance, or cost. Advanced storage materials and concepts are needed to meet 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 FY 2010, the sub-program began to address storage options for stationary, portable, and backup power systems—to aid in the deployment of fuel cells in these early markets. A “hydrogen storage for early markets” topic was included in the FY 2010 Small Business Innovation Research solicitation, and a new project (at Hawaii Hydrogen Carriers LLC) on the use of low-cost metal hydrides in forklift applications was selected.

In October 2009, DOE issued a request for information to gather input from stakeholders on the requirements for fuel storage subsystems for early market fuel cell applications. In November 2009, DOE held a workshop on fuel storage requirements for early market applications. The input garnered from these activities will aid in identifying key challenges, priorities, and needs for fuel storage in early market, non-automotive applications and in development of future solicitations for research proposals in these areas.
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 the vehicle.

The current projected storage system gravimetric and volumetric capacities are shown relative to the 2010 and 2015 targets in Figures 2 and 3. On a routine basis the sub-program has system capacity projections made for the various on-board hydrogen storage technologies under development. Analytical models use the best available data for the technologies to project the gravimetric and volumetric capacities of complete on-board hydrogen storage systems that meet the required operational specifications. The capacity projections are periodically revised as new and more complete data become available and when improvements to system models are developed. Confidence in the accuracy of the projection improves with the maturity of the technology; for instance, there is higher confidence in projections for relatively mature compressed gas systems than for much less mature complex hydride systems. The range bars shown in Figures 2 and 3 represent the ranges of volumetric and gravimetric capacity projections for all the on-board storage technologies made during the given year. The point within the bars is the average capacity (mean) for the technologies analyzed within the given year.
FIGURES 2 and 3. 2010 status of projected hydrogen storage system gravimetric and volumetric capacities versus 2010 and 2015 on-board system targets. Note that all systems were sized to provide 5.6 kg of useable hydrogen and that the plotted data points are the average value for all systems analyzed during each year while the bars correspond to the range of maximum and minimum values obtained for the year. Also note that systems with predicted capacities exceeding the gravimetric targets do not meet other targets.
IV. Hydrogen Storage / Overview

**FY 2010 Accomplishments**

During FY 2010, a number of new materials were developed and the performance of earlier materials improved through the three material Centers of Excellence (CoEs) and independent projects. Formal down-select reports were published for the Metal Hydride Center of Excellence (MHCoE)\(^1\) and Chemical Hydrogen Storage Center of Excellence (CHSCoE)\(^2\) in FY 2009. Through FY 2010, approximately 81 distinct materials have been considered experimentally within the MHCoE, and work on about 75% of those has been discontinued, based on criteria developed by the MHCoE—including material reversible capacity, sorption thermodynamics, and kinetics. Through FY 2010, the CHSCoE has evaluated a total of approximately 130 materials and combinations of materials; research on 95% of those has been discontinued, due to issues related to storage capacities, release temperature, kinetics, and spent-fuel regeneration. The Hydrogen Sorption Center of Excellence (HSCoE) has investigated 210 hydrogen sorbent materials through FY 2010; R&D continues on about 20% and has been discontinued on about 80% of these sorbent materials.

In FY 2010, the HSCoE published the Materials Go/No-Go Recommendation Document.\(^3\) The report gives an overview of the research strategies that the center has pursued in developing hydrogen sorbents to meet the DOE technical targets and makes recommendations on which strategies and sorbent material classes DOE should or should not continue to pursue in the future. The objective of the HSCoE has been to develop hydrogen sorbent materials that can store hydrogen at close to ambient temperature and at moderate pressure with the potential to meet the DOE system performance targets. The center’s strategy has included developing high-surface-area sorbents with high volumetric capacity and developing materials with high binding energy to allow closer to ambient temperature adsorption and moderate pressure. The report categorizes the sorbent materials and sorption mechanisms into four classes: physisorbents, substituted/heterogeneous materials, multiple dihydrogen adsorption, and weak chemisorption (spillover). For pure physisorption, the center recommends continued development only on materials exceeding 2,500 m\(^2\)/g with pore sizes between 0.7 and 1.2 nm. For substituted/ heterogeneous materials, they recommend continued development of materials with properly coordinated elements in high-surface-area structures (e.g., uncoordinated metal centers in a framework material). In the area of materials with multiple dihydrogen sorption sites, experimental work is needed to synthesize materials with appropriate structures to validate theoretical predictions. Finally, for weak chemisorption materials, further research is recommended to improve reproducibility of materials synthesis and measurements, hydrogen sorption kinetics, and catalyst integration.

CoE efforts will be completed by the end of FY 2010 as planned. During this last year, much of their efforts are devoted to optimizing key parameters for the promising storage systems as well as generating required data for use by the HSECoE and analysis efforts to develop complete system models for the more promising materials. To capture the research carried out by the three CoEs and independent projects, DOE is establishing a searchable materials database. The database will be populated with material compositions, synthesis methods, measured properties, spent fuel regeneration schemes, and references. Predicted materials and properties from theoretical computational modeling will also be included. The database is expected to be available on the DOE Web site by January 2011.

Three key material properties needed for system models are the materials’ capacity, thermodynamics (e.g., heat of ad/absorption and/or heat of reaction), and sorption kinetics under different temperature and pressure conditions. Significant R&D is needed to modify or “tune” the properties of high-hydrogen-capacity materials toward the required range of operating temperatures and pressures. The optimum scenario is to utilize the waste heat of the powerplant (i.e., fuel cell or internal combustion engine). For example, if hydrogen could be released at acceptable rates at less than 80°C,

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the waste heat of the fuel cell could be utilized for endothermic desorption—avoiding the need to burn hydrogen to generate the needed temperature.

A useful alternative to depictions of gravimetric and volumetric capacity is to show capacity as a function of temperature. Figure 4 shows the current status of materials development 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 temperature are defined by the dashed lines (greater than 5.5 wt% H₂ for the 2015 target 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 temperatures across which hydrogen is discharged (or charged). The values shown in Figure 4 have been updated for new candidates identified during FY 2010 and will be further modified by DOE as advancements are made in this rapidly progressing field.

This past year the HSECoE made significant strides in developing complete system models for the three material classes and identifying engineering and material property gaps and research needs. In order to determine the impact of storage system performance on vehicle performance, the HSECoE developed the Hydrogen Storage Simulator (HSSIM) as well as a fuel cell power plant model. Preliminary models for metal hydride, chemical hydrogen, and adsorbent systems were also completed. The various models were coupled through a MATLAB/COMSOL/Simulink environment so that effects of changes in one model on the other models could be determined. For the three material classes, parametric models were identified for thermal modeling. Thermal modeling of the material based systems is critical, due to the exothermic/endothermic nature of the hydrogen uptake and release reactions. The center was also able to develop acceptability criteria for the material classes for use in selecting materials with suitable properties in on-board automotive storage systems. To establish a baseline, a well-
characterized material from each class (NaAlH₄, NH₃BH₃ and AX-21) was selected for the initial system modeling to determine current system status versus the DOE performance targets for on-board hydrogen storage. Figure 5 shows a representative spider chart for a metal hydride system. The spider chart clearly indicates areas where there are knowledge gaps (i.e., zero values) as well as engineering and material property deficiencies. For example due to the material's low gravimetric and volumetric capacities, the system is unable to meet the gravimetric and volumetric system targets. Also, due to the combination of the material's intrinsic uptake kinetics and the system's heat transfer properties, the modeled system is unable to meet the refill-time target. The models can therefore be very useful in identifying areas to focus engineering R&D and material properties requiring additional development.

**FIGURE 5.** Spider chart for a representative modeled metal hydride system against the DOE 2010 system performance targets, showing technical and/or knowledge gaps in gravimetric and volumetric densities and cycle life.

**Metal Hydrides**

- Five distinct pathways for forming alane (AlH₃) from hydrogen gas and aluminum powder under relatively mild conditions were developed (Brookhaven National Laboratory).
- An electrocatalytic additive that approximately doubled the rate of electrochemical production of alane was identified (Savannah River National Laboratory [SRNL]).
- An efficient, low-temperature and low-pressure route to rehydrogenate spent LiAlH₄ in dimethyl ether was developed (University of Hawaii, University of New Brunswick).
- Stable, reversible capacity greater than 10 wt% in LiNH₂ was demonstrated through the introduction of nitrogen into the hydrogen phase (University of Nevada, Reno).
- The first example of a “kinetically coupled” destabilized system (LiBH₄/Mg₂NiH₄) with favorable thermodynamics (∆H=15 kJ/mol H₂ and ∆S=62 J/mol H₂) was discovered (HRL Laboratories).
- Additives to increase hydrogen release rates from Mg(BH₄)₂ and 2LiNH₂/MgH₂ were developed and demonstrated (Sandia National Laboratories [SNL]).
- Improved desorption kinetics through metal hydride incorporation into aerogels were demonstrated (United Technologies Research Center, HRL Laboratories, University of Hawaii).
- Partial reversibility of several metal borohydrides under mild conditions was demonstrated (University of Hawaii).
Chemical Hydrogen Storage Materials

- Demonstrated a new ammonia borane (AB) first-fill process with higher purity and yield and completed reactor scale up capable of providing 100-gram batches of high-purity AB to center partners (Pacific Northwest National Laboratory [PNNL]).
- Significant rate enhancements with reduced borazine formation and a high mat-wt% H2-release (up to 11.4%) were achieved with 20 wt% ionic-liquid/AB mixtures at 110°C (University of Pennsylvania).
- High release rates for liquid AB at temperatures as low as 70°C with non-platinum group metal catalysts were demonstrated (Los Alamos National Laboratory [LANL]).
- Impurities and their formation rates were quantified in hydrogen released from AB, which led to demonstration that impurity formation may be mitigated through proper choice of process conditions (LANL, PNNL).
- A one-pot AB spent-fuel regeneration cycle using hydrazine was developed with an overall yield through reduction steps exceeding 90% (LANL).
- The one-pot AB spent-fuel regeneration cycle was demonstrated to work for multiple spent-fuel forms, including spent-fuel from AB in ionic liquids (LANL).
- Costs analyses were performed that indicate the one-pot AB spent-fuel regeneration cycle substantially reduces process costs but may have higher raw material costs than a previous AB spent-fuel regeneration processes (Dow).
- Resource studies were carried out that indicates the U.S. boron supply is adequate to meet boron requirements for AB fuel for projected vehicle market penetration scenarios (US Borax).
- Demonstrated syntheses of endothermic/exothermic cyclo-carbon-boron-nitrogen compounds, pathways for regeneration of spent-fuel, first-fill syntheses, and measured thermodynamic parameters that have corroborated computational studies on these molecules (University of Oregon, University of Alabama).

Hydrogen Sorption Materials

- The HSCoE Materials Go/No-Go Recommendations Report was published with five specific recommendations for continued sorption materials R&D; the report provided tabulated data on 36 specific materials the center has investigated, and research on 26 of these has been discontinued (National Renewable Energy Laboratory [NREL]).
- Boron-substituted carbon materials were synthesized and demonstrated to have increased hydrogen binding energy as a function of coverage (isosteric heats of 9–11 kJ/mol) agreeing with theory predictions (The Pennsylvania State University, University of Missouri, Air Products and Chemicals, Inc., NREL).
- Polyetheretherketone material treated with CO\textsubscript{2} and steam at 900°C was demonstrated to have greater than 5 wt% excess hydrogen adsorption capacity with a binding energy of about 8 kJ/mol at 77 K and 20 bar (Duke University).
- An isoreticular framework material (PCN-68) was synthesized with a Brunauer-Emmett-Teller surface area of 5,109 m\textsuperscript{2}/g and 7.2 wt% excess hydrogen adsorption capacity at 77 K and 50 bar (Texas A&M University).
- Cs and Rb-intercalated graphite with narrow “slit-pore” geometries of 5.3 to 5.8 Å were shown to have nearly constant isosteric heats of adsorption (at low coverage) of 14 and 12 kJ/mole (Caltech).

System Engineering

- Completed programming of HSSIM, which will improve the speed of analyses and enhance the assessment of the tradeoffs involved in the use of different technologies (NREL, Ford, General Motors).
- Coupled vehicle, fuel cell power plant, and on-board storage system models through MATLAB/COMSOL/Simulink environment so that on-board system performance impacts on vehicle...
performance can be readily determined (NREL, Ford, General Motors, United Technologies Research Center, PNNL, SRNL).

- Developed candidate material matrix and acceptability criteria for the three material classes (LANL, United Technologies Research Center, Ford, BASF, General Motors, PNNL, L’Université du Québec à Trois-Rivières, SRNL).
- Developed and demonstrated a novel acoustic fuel gauge sensor for use with hydrides (LANL).
- Developed preliminary complete system models with baseline materials for the three material classes for comparison against DOE performance targets (LANL, PNNL, Jet Propulsion Laboratory, Caltech, L’Université du Québec à Trois-Rivières, General Motors, United Technologies Research Center, SRNL).

Compressed and Cryogenic Tanks

- Demonstrated a third generation cryogenic vessel with verified zero evaporative losses for day dormancy of more than eight days. The conversion of para-$\text{H}_2$ to ortho-$\text{H}_2$ was shown to double the dormancy for a nearly full vessel (Lawrence Livermore National Laboratory).

Testing, Materials Properties, and Analysis Cross-Cutting

- Performed system-level analysis of six hydrogen storage technologies, addressing all aspects of onboard storage targets including capacity, charge/discharge rates, greenhouse-gas emissions, safety, and cost. Technologies analyzed or updated included 350-bar and 700-bar compressed hydrogen, cryo-compressed hydrogen, liquid hydrogen, MOF-177 sorption systems, activated carbon sorption systems, and AB in ionic liquids chemical systems (Argonne National Laboratory [ANL]).
- Conducted independent cost assessments of MOF-177 sorption ($12/kWh), liquid hydrogen ($8/kWh), cryo-compressed hydrogen ($12/kWh), and 350-bar ($13/kWh) and 700-bar ($20/kWh) compressed hydrogen systems, all with 5.6 kg of useable hydrogen (TIAX LLC).
- Evaluated four potential mitigation strategies for hazards associated with flammable hydrogen storage materials; several were found to be promising (SRNL).
- Found polymer matrices to be a potential hazard mitigation strategy for materials-based systems by demonstrating a 70% reduction of heat generation and formation of little to no oxidation products when flowing air through a reactive metal hydride bed encapsulated within polystyrene (SNL).

Budget

The President’s FY 2011 budget request includes $40 million for hydrogen fuel R&D, of which $20 million is planned for hydrogen storage—compared with the FY 2010 congressional appropriation of $32 million for hydrogen storage. The reduction is primarily reflected in the completion of the three materials centers that are ending in FY 2010 in accordance with their five year plan. In FY 2011 the Hydrogen Storage sub-program will continue to focus on hydrogen storage materials discovery, new concepts, and systems analysis, as well as on continued system engineering R&D. The sub-program will also consider hydrogen storage requirements for early market applications and rebalance the portfolio to address near-term and longer-term R&D needs.
IV. Hydrogen Storage / Overview

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**FY 2011 Plans**

The technology portfolio for Hydrogen Storage emphasizes materials R&D to meet system targets for on-board and early market applications. The three Materials CoEs are ending in FY 2010 according to their five-year plans. In FY 2011 detailed reports of the research efforts carried out within the CoEs over their five year lives will be published and the materials data made available through an on-line searchable database. This information will be accessible to researchers, the fuel cell industry, and the general public. With the end of the three Materials CoEs, research and development on advanced hydrogen storage materials with improved material volumetric capacity, hydrogen uptake and discharge kinetics, overall system efficiency, durability, and life cycle cost will continue through independent projects. While a focus on light-duty vehicle applications will continue, increased emphasis will be placed on new materials and novel concepts to meet performance requirements for early market applications. In FY 2011, understanding of the hydrogen storage needs and performance requirements for early market applications will be further developed. Additionally, increased emphasis will be placed on developing lower-cost physical storage technologies that have the potential to meet customer requirements for some vehicle platforms for near-term commercialization. Specifically, the sub-program will coordinate with other efforts (e.g., Vehicle Technologies, Defense Advanced Research Projects Agency, etc.) on development of approaches to produce low-cost carbon fiber for composite cylinders. System engineering and analyses will continue through the HSECoE and ANL. Coordination with basic science efforts, including theory, characterization, and novel concepts, will continue during FY 2011. Coordination with the National Science Foundation and Advanced Research Projects Agency–Energy will also be investigated through activities such as workshops and joint meetings.
Introduction

The DOE Metal Hydride Center of Excellence (MHCoE) comprises 10 universities (Caltech, Georgia Institute of Technology, Stanford, University of Hawaii, University of Illinois-Urbana Champaign, University of Nevada-Reno, University of New Brunswick, University of Pittsburgh, The 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) and two industrial partners (HRL Laboratories, and United Technologies Research Center). SNL is the lead laboratory, providing technical leadership for the Center and a structure to guide the overall technical program and to advise the DOE.

The purpose of the MHCoE is to develop hydrogen storage materials with engineering properties that allow the use of these materials in a way that satisfies the DOE/FreedomCAR Program system requirements for automotive hydrogen storage. The Center is a multidisciplinary and collaborative effort with technical interactions divided into two broad areas: 1) mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials) and 2) materials development (in which new materials are synthesized and characterized). 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 show 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. The four areas are summarized below.

Project A (Destabilized Hydrides) is led by Prof. Bruce Clemens, Stanford University. The objective of this project is to controllably modify the thermodynamics of hydrogen sorption reactions in light metal hydrides using hydride destabilization strategies. The technical approach involves altering the thermodynamics of the metal hydride by forming a stable alloy in the dehydrogenated stage. This effectively destabilizes the hydride, 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 minimize the required hydrogen diffusion distance by decreasing particle size and by incorporating the metal hydride reactants in nano-engineered scaffolds.

Project B (Complex Anionic Materials) is led by Prof. Craig Jensen (UH). The objective 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 the past year 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 (inorganic materials containing–NH2 and–NH moieties, respectively) for onboard hydrogen storage. The technical approach is to reduce thermal requirements of these materials by alloying, to understand and elucidate the chemical pathways by which these materials release and absorb hydrogen, and to determine the initial engineering issues (thermal cycling) of these materials.

Project D (Alane, AlH3) is headed by Dr. Jim Wegrzyn of BNL. The objective of Project D is to understand the sorption and regeneration properties of AlH3 for hydrogen storage. The technical approach has been to synthesize the various structural forms of AlH3, and characterize the structure and hydrogen sorption properties of these forms. The emphasis the past year has been on regenerating AlH3 from Al, using solution-based and electrochemical methods. Project D also examines the properties and reversibility of LiAlH4.

In addition to these formal “Projects”, a Theory Group (TG), coordinated by Dr. Mark Allendorf (SNL), supports all of the experimental efforts in the Center. The TG makes use of first-principles methods to predict new materials and their thermodynamic properties, and suggests new directions for experimental investigations and interpretation of results. The TG consists of researchers at five institutions: SNL, U. 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 synergy with the experimental efforts.

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 for practical, on-board storage system applications. These barriers are reproduced below from the onboard Hydrogen Storage section of the Multi-Year Research, Development and Demonstration Plan (MYRDDP):

(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 MYRDDP are addressed, our main emphasis has been 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 following report submitted to DOE:
Selected MHCoE Technical Highlights for Fiscal Year (FY) 2010

During the past year, the MHCoE has published 65 papers (29 of these collaborations between MHCoE partners) in the leading journals of chemistry, physics, materials science and crystallography. In addition, MHCoE scientists delivered 76 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.

Selected highlights from the MHCoE technical work over the period March 2009 to June 2010 are presented in the following. We point out that the five-year scheduled lifetime of the MHCoE ends in 2010. Please consult the annual reports from individual MHCoE partners for specific details about technical activities in 2010, and the MHCoE final report which covers the five-year history of the Center.

MHCoE Technical Highlights (March 2009 to June 2010)

1. Five distinct pathways were identified for forming AlH₃ adducts from H₂ + Al, thereby increasing prospects for AlH₃ regeneration. (BNL)
2. An electro-catalytic additive was discovered that increased the rate of electrochemical production of alane. (SRNL)
3. A highly efficient, low-temperature and low-pressure method to regenerate LiAlH₄ from (LiH + Al[Ti]) using dimethyl ether was developed. (UH and UNB)
4. The cycling capacity of LiNH₂ was increased to 10 wt% by introducing 20% nitrogen into the hydrogen gas phase. (UNR)
5. The first example of “kinetic coupling” in the LiBH₄/Mg,NiH₄ destabilized system was discovered. The ΔH (15K J/moleH₂) and ΔS (62 J/moleH₂K) are the lowest reported so far for a reversible system. (HRL)
6. The structure of the important intermediate MgB₁₂H₁₂ in Mg(BH₄)₂ storage reactions was established by neutron vibrational spectroscopy studies. (NIST)
7. The rate of hydrogen release from Mg(BH₄)₂ was dramatically increased by adding TiF₃/ScCl₃. (SNL)
8. The rate of hydrogen absorption kinetics for the 2LiNH₂ + MgH₂ system was increased by introducing KH, confirming prior work by P. Chen. (SNL)
9. The hydrogen desorption kinetics of Ca(BH₄)₂, and to a lesser extent Mg(BH₄)₂, were enhanced by incorporating the metal hydrides into a C-aerogel. (UTRC, UH)
10. Mild conditions (<200°C, <100 atm) have been found for the reversible partial (2.4 wt%) dehydrogenation of Mg(BH₄)₂, which circumvents the unwanted formation of Mg(B₁₂H₁₂). Analogous effects are seen for LiSc(BH₄)₄, NaSc(BH₄)₄, and KSc(BH₄)₄. (SNL)

Special Recognitions & Awards

1. The MHCoE received a DOE Hydrogen Program 2010 “Special Recognition Award,” In Recognition of Outstanding Contributions to the Department of Energy.” This award was made June 8, 2010.

2. DOE Hydrogen Program Research Award was given to Ragaiy Zidan for his Electrochemical Studies of Alane Regeneration. The award was made June 8, 2010.

Acknowledgements

It is our pleasure to acknowledge funding for the MHCoE from the DOE Fuel Cell Technology Program.
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 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, AlH3, and/or LiH/Al to LiAlH4 at moderate pressures in non-conventional solvents.

Technical Barriers

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

- System Weight and Volume
- Charging/Discharging Rates
- Thermal Management
- Lack of Understanding of Hydrogen Physisorption and Chemisorption
- \( \text{IV.A.1b  Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides} \)

Technical Targets

The work on this project is currently exclusively devoted to materials that have demonstrated available hydrogen capacities of 7.9-15 wt% hydrogen. We have developed a system for the full reversible dehydrogenation of Mg(BH4)2 to MgB2 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 LiAlH4 (7.9 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 DOE targets.

Accomplishments

Borohydrides

- Demonstration of the reversible hydrogenation of MgB2 to Mg(BH4)2 with cycling of 12 wt% hydrogen.
- Nano-association of Mg(BH4)2 in a carbon aerogel found to improve dehydrogenation kinetics.
- Mild conditions (<200°C, <100 atm) found for the reversible dehydrogenation of 2.4 wt% hydrogen from Mg(BH4)2 as well as (~2.0 wt%) from LiSc(BH4)4, NaSc(BH4)4, and KSc(BH4)4.

Hydrogenation in Non-Conventional Solvents

- Demonstration of the full recharging of Ti-doped LiAlH4 by the direct hydrogenation of Ti-doped LiH/Al in liquefied dimethyl ether at room temperature under 100 bar of Me2O/H2. Calcautions show that this recharging process approaches 60% WTT efficiency.

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 end we have examined anionic transition metal borohydride complexes as hydrogen storage materials. 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. 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 and increase stability. We have also found that the alkali metal salts of anionic transition metal borohydride complexes such LiMn(BH₄)₂ undergo rapid dehydrogenation at moderate (<150°C) temperatures. In some cases, only very minor the amounts of the undesirable, diborane side product are produced. However, we have not found the full 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 mixtures of Group I hydrides and transition borides proved unsuccessful. However, hydrogen uptake was found to occur at 400°C and 90 atm in experiments in which MgB₂ was present. Analysis of the product mixtures by X-ray diffraction (XRD) showed that the transition metal component was un-reactive while the MgB₂ was hydrogenated to Mg(BH₄)₂. The hydrogenation also occurred when starting with only ball-milled MgB₂. Our experiments provided the first demonstration of the full reversibility MgB₂ to Mg(BH₄)₂. In consideration of the >14 wt% hydrogen that is potentially cyclable with this system, it has become the chief focus of our efforts in the area of borohydrides.

In collaboration with the University of New Brunswick, we are also developing new approaches utilizing supercritical fluids and non-conventional solvents for the direct synthesis of AlH₃ and LiAlH₄. LiAlH₄ releases 7.9 wt% hydrogen according to the two reactions seen in equations 1 and 2.

$$3 \text{LiAlH}_4 \rightarrow \text{Li}_2\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \quad (1)$$

$$\text{Li}_2\text{AlH}_6 \rightarrow 3 \text{LiH} + \text{Al} + 1.5\text{H}_2 \quad (2)$$

The second reaction is endothermic ($\Delta H = +25$ kJ/mol H₂) but the first reaction is exothermic ($\Delta H = -10$ kJ/mol H₂). 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 LiAlH₄ cannot be recharged and there have been no reports of its use for reversible hydrogen storage. However, the unfavorable thermodynamics of Eq. 1 may be altered by carrying out the reaction in solution, with the solvation of LiAlH₄ contributing to an endothermic $\Delta H$ value. In 1963, Ashby et al. reported that a mixture of LiH and activated Al in tetrahydrofuran (THF) solvent reacted with 350 bar H₂ at 120°C to produce LiAlH₄. While this method results in the ultimate formation of LiAlH₄ from LiH, Al and H₂, it is impractical because of the requirements of high temperature and high pressure during the synthesis as well as subsequent heating for the removal the THF adduct. An improvement in the synthesis of the THF adduct was achieved by researchers at Brookhaven National Laboratory by using Ti additives to significantly lower the required pressure and temperature. However, the prolonged baking in vacuo that is required to remove THF results in the dehydrogenation of the majority of a Ti-activated product. We have discovered that this difficulty can be eliminated by utilizing liquefied dimethyl ether (Me₂O) as the reaction solvent. It is sufficiently coordinating to support the nascent LiAlH₄ in the reaction environment, yet also volatile enough to be removed easily once it has served this purpose. Through this approach, LiAlH₄ can be synthesized at room temperature under moderate pressures of H₂ (80-100 bar) in the presence of very low amounts of Ti catalyst (0.5-0.2 mol%). On completion of reaction, the volatile Me₂O solvent and excess H₂ are vented leaving only fine, dry Ti-doped LiAlH₄ in 95% yield. Thus we have found a highly efficient method for the direct synthesis of LiAlH₄ at low pressure and room temperature. Preliminary analysis conducted at Argonne National Laboratory has indicated that WTT energy efficiency of our regeneration process is great than 60% and thus approaches the DOE targets.

**Approach**

Having demonstrated the reversible elimination of over 11 wt% hydrogen from Mg(BH₄)₂, we wish to develop methods for hydrogen cycling in this system under less forcing conditions. In order to accomplish this, we required a more detailed understanding of the dehydrogenation reaction pathway. Thus we have monitored both the dehydrogenation and re-hydrogenation reactions by XRD and magic angle spinning boron-11 nuclear magnetic resonance spectroscopy (MAS ¹¹B NMR) and conducted quantitative thermal volumetric pressure-composition-temperature measurements. We have also attempted to improve the kinetics and/or thermodynamics of the dehydrogenation of Mg(BH₄)₂ through nano-confinement of the hydride in a carbon aerogel.

Our highly efficient, room temperature direct synthesis of LiAlH₄ in liquefied Me₂O shows great promise as a practical method for the re-hydrogenation of LiH/Al to LiAlH₄. We have found that nearly the entire 7.9 wt% theoretical cycling capacity can be restored in the first cycle of re-hydrogenation. However, the cycling capacity dramatically drops off over the first five cycles of dehydrogenation/re-hydrogenation. In order to overcome this limitation, we have explored the extension of the maximum cycling capacity of Ti-doped LiAlH₄ through variation of the dopant concentration, recharging conditions, and variation dopants.
Results

Task 1. Characterization of the Active Titanium Species in Ti Doped NaAlH\textsubscript{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

We have merged the Task 4 and 5 efforts and examined whether, as we found for MgH\textsubscript{2}, the kinetics of the dehydrogenation of Mg(BH\textsubscript{4})\textsubscript{2} could be improved through nano-confinement. Following the exposure of the aerogel to the molten diethyl ether adduct of Mg(BH\textsubscript{4})\textsubscript{2}, the coordinated diethyl ether was removed by heating at 220°C en vacuo for 3 h. Mg(BH\textsubscript{4})\textsubscript{2} loadings of the aerogel 57–63 wt\% were achieved by this method. Figure 1, provides a comparison of the XRD patterns of the Mg(BH\textsubscript{4})\textsubscript{2} loaded aerogel with those observed for Mg(BH\textsubscript{4})\textsubscript{2} powder that was scraped from the surface of the aerogel. The diffraction peaks of the Mg(BH\textsubscript{4})\textsubscript{2} associated with the aerogel are clearly seen to be broader and much smaller. This indicates that the Mg(BH\textsubscript{4})\textsubscript{2} associated with the aerogel has nano dimensions. As seen in Figure 2, the 11B NMR spectrum of the Mg(BH\textsubscript{4})\textsubscript{2} incorporated aerogel contains only a single peak at the chemical shift of -41.5 ppm, thus verifying that Mg(BH\textsubscript{4})\textsubscript{2} is the only boron containing species present in the material. The nano-Mg(BH\textsubscript{4})\textsubscript{2} showed good kinetics during the first dehydrogenation. As seen in Figure 3, 2.7 wt\% H\textsubscript{2} was eliminated at 270°C in ca. 30 min. Overall, 4.94 wt\% H\textsubscript{2} was evolved as the temperature was increased to 400°C. Re-hydrogenation was carried out under 11-15 MPa of H\textsubscript{2} at 500°C for 10 h. The observation of a much slower rate for the second cycle of dehydrogenation strongly suggests that the nano-Mg(BH\textsubscript{4})\textsubscript{2} was not incorporated into the pores of the aerogel and was just associated with its surface.

Task 5. Synthesis and Evaluation of Novel Borohydrides

In order to confirm the uptake of over 11 wt\% hydrogen occurs in the high pressure hydrogenation of MgB\textsubscript{2}, the dehydrogenation of a sample of the Mg(BH\textsubscript{4})\textsubscript{2} product was monitored using an automated thermal volumetric analyzer (Sievert’s type apparatus). The dehydrogenation profile (seen in Figure 4) shows the release of 11.4 wt\% hydrogen. Longer reaction times would quite likely result in higher levels of hydrogenation MgB\textsubscript{2} and thus cycling of 14 wt\% hydrogen.

![FIGURE 1. Comparison of the XRD patterns of co-synthesized, bulk and nano-Mg(BH\textsubscript{4})\textsubscript{2}.](image)

![FIGURE 2. MAS 11B NMR spectrum of carbon aerogel associated nano-Mg(BH\textsubscript{4})\textsubscript{2}.](image)

![FIGURE 3. First dehydrogenation of carbon aerogel associated nano-Mg(BH\textsubscript{4})\textsubscript{2}.](image)
B NMR studies of the dehydrogenation of Mg(BH$_4$)$_2$ have revealed that the dehydrogenation process involves multiple steps. We have found that the early steps do not require heating above 250°C and result in the release of 2.4 wt% hydrogen. The products of the dehydrogenation at this lower temperature have not yet been fully characterized. However, it is clear at that, in contrast to the large mixture of boranes that results upon high temperature dehydrogenation, the products resulting from the low temperature dehydrogenation of only MgH$_2$ and a single borane species. We have found that this species can be cleanly hydrogenated back to Mg(BH$_4$)$_2$ at 200°C under 100 atm of hydrogen. This represents a major step towards practically from the extreme (400°C and 900 atm) conditions under which we initially achieved re-hydrogenation of Mg(BH$_4$)$_2$.

The molecular structure of KSc(BH$_4$)$_4$ (seen in Figure 5) was determined as part of our continuing collaboration with the University of Geneva. We have now determined the crystal structures of the Li, Na, and K salts of [Sc(BH$_4$)$_4$]$^{1-}$. We have found that heating LiSc(BH$_4$)$_4$, NaSc(BH$_4$)$_4$, and KSc(BH$_4$)$_4$ to 250°C also results the elimination of significant amounts of hydrogen (2.4, 2.1, and 1.8 wt%, respectively) and give rise to a product mixture that can be re-hydrogenated to the starting borohydride at 200°C under 100 atm of hydrogen.

**Task 6. Recharging of Light Metal Hydrides in Non-Conventional Media**

Cycle performance experiments were carried out for the LiAlH$_4$ material doped with 0.05 mol% TiCl$_3$. The initial dehydrogenation of this material was seen to release 7.9 wt% hydrogen. Following the first re-hydrogenation in liquid dimethyl ether, the dehydrogenation half cycle was again found to release 7.9 wt% hydrogen. However, this value dropped to 5.9 and 4.1 wt% H in the third and fourth dehydrogenation half cycles, respectively. In an attempt to stabilize the cycling hydrogen capacity, we investigated the effect of the substitution of TiCl$_3$ with other dopants (e.g. ScCl$_3$ and CeCl$_3$). Our results indicate that the catalytic performance of ScCl$_3$ supersedes that of CeCl$_3$, but does not reach that of TiCl$_3$. We also explored whether the use of TiCl$_3$ supported on alumina (Al$_2$O$_3$), would enhance hydrogen cycling performance. As seen in Figure 6, the Ti-supported catalysts were consistently found to lower the H$_2$ desorption temperature of the hydride to ~125°C (opposed to 180°C for the undoped LiAlH$_4$). However, after dehydrogenation and subsequent re-hydrogenation, the hydrogen capacity dropped to 4.0 and 0.0 wt% in the second and third cycle respectively. Analysis of the sample after the third cycle dehydrogenation by transmission electron microscopy (TEM)/energy dispersive X-ray (EDX) showed that Ti was not uniformly distributed; there were areas where no Ti was detected (Figure 7). It is possible that Ti falls off the support upon cycling thereby reducing its effectiveness as a catalyst.

**Conclusions**

Our continuing studies of Mg(BH$_4$)$_2$ have confirmed the uptake of over 11 wt% hydrogen occurs in the...
high pressure hydrogenation $\text{MgB}_2$ to Mg($\text{BH}_4$)$_2$ and indicate that an optimized system might allow cycling of $>14$ wt% hydrogen. Our attempts to lower the temperature required for the hydrogen cycling in the Mg($\text{BH}_4$)$_2$/MgB$_2$ system through catalytic enhancement and nano-confinement of the hydride did not prove successful. However, nano-Mg($\text{BH}_4$)$_2$ was found to exhibit dehydrogenation kinetics that were significantly enhanced beyond those of bulk Mg($\text{BH}_4$)$_2$.

$^{11}$B NMR studies of the dehydrogenation of Mg($\text{BH}_4$)$_2$ at 250°C results in the release of 2.4 wt% hydrogen. The products that are obtained from the low temperature dehydrogenation can be cleanly hydrogenated back to Mg($\text{BH}_4$)$_2$ at 200°C under 100 atm of hydrogen. Dehydrogenation of LiSc($\text{BH}_4$)$_2$, NaSc($\text{BH}_4$)$_2$, and KSc($\text{BH}_4$)$_2$ under similar conditions also results the elimination of significant amounts of hydrogen (2.4, 2.1, and 1.8 wt%, respectively) and give rise to product mixtures that can be re-hydrogenated to the starting borohydride at 200°C under 100 atm of hydrogen. Thus earlier studies of the dehydrogenation anionic transition metal borohydrides under more forcing conditions were premature in concluding that this family of hydrides are “irreversible.”

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 in liquefied Me$_2$O. Although the method is highly efficient method for the re-hydrogenation of LiAlH$_4$, cycling studies have shown the system’s hydrogen capacity dramatically drops off over the first five cycles of dehydrogenation/re-hydrogenation. Attempts to remedy this problem through substitution of TiCl$_3$ other dopants (e.g. ScCl$_3$ and CeCl$_3$) and TiCl$_3$ supported on alumina (Al$_2$O$_3$) have not proven successful.

**Future Directions**

**Borohydrides**
- Adjustment of conditions to maximize trade off between cycling capacity and reaction conditions (temperature/pressures) required for reversible dehydrogenation of Mg($\text{BH}_4$)$_2$, LiSc($\text{BH}_4$)$_2$, NaSc($\text{BH}_4$)$_2$, and KSc($\text{BH}_4$)$_2$.

**Hydrogenation in Non-conventional Solvents**
- Explore maintenance of cycling capacity of doped LiAlH$_4$ through variation of the dopants.
- Further evaluation of WTT efficiency of the dimethoxyethane/LiAlH$_4$ system to be examined in collaboration with Argonne National Laboratory.
FY 2010 Publications/Presentations

Publications


Presentations


8. “Catalysts in Complex Hydrides”; Craig M. Jensen. NANO-MAT Workshop, University of Oslo, Norway; October 20, 2009.


**Patents**

Objectives

- Develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.
- Synthesize and study aluminoborane compounds and other lightweight, high-capacity boron hydrides for hydrogen storage.
- Perform detailed characterization of the decomposition mechanisms, desorbed gaseous species and structures of the synthesized compounds.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan:

(D) Durability/Operability

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(E) Charging/Discharging Rates

(J) Thermal Management

Introduction

The 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 aluminoborane compounds such as AlB$_4$H$_{11}$ and other high-capacity, lightweight boron hydrides.
- Study the crystal structures and the decomposition mechanisms using multiple techniques such as interrupted PCT tests, NMR, infrared (IR), 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 Oak Ridge National Laboratory (ORNL), SNL, and National Institute of Standards and Technology (NIST).

**Results**

Aluminoboranes AlB$_4$H$_{11}$, AlB$_5$H$_{12}$, and AlB$_6$H$_{13}$ were reported by Himpsl and Bond in 1981 [1], but these compounds have eluded the attention of the worldwide hydrogen storage research community for more than a quarter of a century. They have very attractive properties for hydrogen storage: high hydrogen capacity (i.e., 13.5, 12.9, and 12.4 wt% H, respectively) and attractive hydrogen desorption temperature (i.e., AlB$_4$H$_{11}$ decomposes at ~125°C). In collaboration with ORNL, the Jet Propulsion Laboratory (JPL) and the California Institute of Technology (Caltech), we synthesized and studied AlB$_4$H$_{11}$ for hydrogen storage. AlB$_4$H$_{11}$ is an amorphous white solid that starts to release hydrogen around 125°C as demonstrated by both thermogravimetric analysis (TGA) and PCT tests. Mass spectroscopy analysis showed relatively clean desorption with a small amount of diborane (<1 mole%) [2]. A TiCl$_3$ catalyzed AlB$_4$H$_{11}$ desorbed 6.5 wt% H when it was heated to 220°C under 0.1 bar hydrogen pressure during a PCT test. The desorbed residue remained as amorphous. Re-hydrogenation was performed at 200°C, 100 bar hydrogen for the first run and 97 bar of hydrogen for the second run. About 2.5% hydrogen was re-absorbed each time based on the hydrogen pressure drop during the re-hydrogenation PCT tests (Figure 1). The observed reversibility (hydrogen absorption) during PCT tests was further confirmed by both IR and NMR analysis which both showed that signals associated with AlB$_4$H$_{11}$ re-appeared after the re-hydrogenation runs. The results clearly show that AlB$_4$H$_{11}$ is one of the very few boron-containing materials which show reversibility at mild conditions. DSC measurements also show that AlB$_4$H$_{11}$ dehydrogenates around 125°C with a broad endothermic peak, thus it is thermodynamically reversible (Figure 2). All these results together clearly show that is a very attractive candidate for reversible hydrogen storage. The key is to increase the reversibility weight% and improve both hydrogenation and rehydrogenation kinetics.
Based on the AlB₄H₁₁ synthesis experience, we explored the syntheses of other aluminoborane compounds such as AlB₆H₁₄ and AlB₁₀H₁₄ at OSU. Their syntheses require the both B₄H₄ and B₂H₆ as the starting materials – both are tedious to make. Tetraborane (B₄H₁₀) was prepared by a solid-liquid reaction of KB₄H₄ with BCl₃ at -78°C for 90 min followed by stirring at room temperature for 20 min according to the procedure reported by Hill et al. [3]. KB₄H₄ was prepared by the reduction of BH₃tetrahydrofuran (THF) with K-Hg amalgam. KB₄H₄ was washed with CH₂Cl₂ several times and recrystallized from THF solvent to remove all the impurities. A number of trials showed that it is very difficult to obtain pure B₂H₆ by this method. Inconsistent stirring (due to the high viscosity) was the main issue in this reaction which never proceeded to the completion. Apparatus and special methods were designed and reaction conditions were optimized to try to obtain pure tetraborane; but a small amount of BCl₃ impurity was always found in the end product. Since the boiling points of BCl₃ and B₂H₆ are very close, it’s very hard to separate them. The BCl₃ impurity affects the synthesis of AlB₆H₁₄ considerably by reacting with Al(BH₄)₃ to produce -BHCl₂ species. Hence this procedure cannot be used to synthesize pure B₂H₆ by this method. Another method involved a reaction between [N(n-But)₄][B₃H₈] and liquid BBr₃ at 0°C for 1h. This is an efficient method as it was easy to separate tetraborane from other products and the yield was 60%. KB₄H₄ was converted to a corresponding tetrabutyl ammonium compound by reacting with tetrabutyl ammonium bromide in THF. The tetraborane was then reacted with Al(BH₄)₃ in a benzene solution that was stirred for 67 h. The solution was then turned to a viscous liquid which was further heated to 100°C for 27 h to obtain an insoluble pale yellow color solid. Solvent was evaporated under dynamic vacuum for overnight to obtain AlB₄H₁₁. The product was characterized by XRD, IR and DSC. The XRD pattern revealed that it was an amorphous material (polymeric) similar to the literature result. The IR spectrum and DSC profiles closely resemble to those of AlB₄H₁₁. Detailed analysis is in progress.

OSU (Prof. Sheldon Shore) has some decaborane (B₁₀H₂₀) (probably the only source in the world). We explored its reaction with Al(BH₄)₃ to see whether the aluminoborane compounds can be extended beyond the Himpsl-Bond compounds (AlB₄H₁₁, AlB₆H₁₂ and AlB₁₀H₁₄). Decaborane has four bridging hydrogens compared to two for diboran. Reaction of Al(BH₄)₃ with decaborane (B₁₀H₂₀) was tried in 1:2, 2:1 and 4:1 mole ratios respectively. The 1:2 reaction gave a yellow solid but the 2:1 and 4:1 gave pale yellow solids with high yields (>80%). To confirm that the solids contain both Al and boron species, the solids were hydrolyzed and solution ¹¹B NMR and ²⁷Al NMR indicated the elemental presence. Elemental analysis of the product of the first reaction indicated that the Al:B ratio is 1:8 and there is 40% of carbon incorporated in the solid, which comes from the benzene solvent (¹¹H-MAS NMR indicated a peak at 7 ppm corresponding to benzene-type species). IR analysis indicated that the bridge hydrogens of the decaborane disappeared completely and a broad B-H peak emerged. ¹¹B MAS NMR of the solid showed a broad peak from 20 to -45 ppm that is centered at -15 ppm. ²⁷Al MAS NMR shows two Al peaks at 80 and 35 ppm. As the amount of Al(BH₄)₃ increased, more IR peaks corresponding to those observed in AlB₄H₁₁ become more evident in the 2:1 and 4:1 ratio reactions. Elemental analysis and solid state NMR characterization of the solids obtained from the 2:1 and 4:1 reactions are underway. Our results show that this family of aluminoborane compounds has a broad chemistry base and all of them form amorphous solids, which is very encouraging news.

The boron-cage compound (NH₄)₂B₁₀H₁₀ contains 11 wt% hydrogen and it is a crystalline compound. TGA measurements show that its desorption started ~190°C and ~9% weight loss was observed up to 400°C. PCT study showed a desorption of 8 wt% H at 400°C which is in reasonable agreement with the TGA result. Simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS) analysis performed at SNL showed a small amount of ammonia release at temperatures between ~200°C and 280°C while H₂ release was observed from ~200°C all the way up to 1,000°C. No diborane was observed during the STMBMS analysis. STMBMS results show that the ratio of hydrogen to ammonia gas depends on the orifice size and the percentage of hydrogen in the gas mixture increases with the orifice size. At 35 mm orifice confinement, the ammonia in the desorbed H₂ gas from (NH₄)₂B₁₀H₁₀ was 3.3 mole% (Figure 3). Rehydrogenation of 1.8 wt% was observed at a mild condition (240°C and 93 bar hydrogen pressure) even without any catalyst. The ammonia formation needs to be addressed. The reversibility at mild conditions is very attractive, but the total amount of hydrogen released before the cage collapsing is relatively low.

(NH₄)₂B₁₀H₁₀ is another boron-cage compound we studied for potential hydrogen storage. STMBMS analysis also showed a small amount of ammonia release at temperatures between ~200°C and 560°C. Its behavior is very similar to that of (NH₄)₂B₁₀H₁₀. STMBMS
analysis showed both hydrogen and ammonia release at 200-365°C and pure H₂ at higher temperatures (Figure 4). No diborane was observed. Again the ratio of hydrogen to ammonia gas depends on the orifice size and the percentage of hydrogen in the gas mixture increases with the orifice size. At 35 mm orifice confinement, the ammonia in the desorbed H₂ gas from (NH₄)₂B₁₀H₁₂ was 0.9 mole%. The DSC curve (Figure 5) clearly shows endothermic desorption for the first step which can potentially be reversible based on thermodynamics. Similar to (NH₄)B₁₀H₁₈, the ammonia formation needs to be addressed and the total amount of hydrogen released before the cage collapsing is relatively low.

Non-cage boron compounds such as MₓB₃H₈ may be less stable and easier for dehydrogenation and rehydrogenation. To explore this class of compound, we have developed a safe and convenient method for the synthesis of the starting material, NaB₃H₈ (Figure 6). Using this compound, we have also developed a convenient and safe method for the synthesis of ammonium octahydrotriborate (NH₄B₃H₈) which has an very high H content (20 wt%). We were able to identify its crystal structure for the first time for both NaB₃H₈ and NH₄B₃H₈. More characterization is in progress. These compounds can potentially serve as both metal hydrides and chemical hydrides.

To synthesize more boron-containing lightweight hydrides for hydrogen storage, we need to synthesize starting materials such as B₉H₁₆, B₁₀H₁₉, and NaB₃H₈. One of the very active chemical reagents is aminodiborane (NH₂B₂H₅) that can be used to synthesize many compounds. It was first found serendipitously and then prepared through a tedious procedure using diborane gas at -130°C with a low yield in 1,938 [4,5]. Except for its structure determination, no further studies of its reactions or properties have been reported in the past 70 years, mostly due to its

![Figure 3](image3.png) **FIGURE 3.** STMBMS gas evolution rate of (NH₄)₂B₁₀H₁₂ showing hydrogen release in two steps and small amount of ammonia release associated with the first step.

![Figure 4](image4.png) **FIGURE 4.** STMBMS gas evolution rate of (NH₄)₂B₁₂H₁₂ showing hydrogen release in two steps and small amount of ammonia release associated with the first step.

![Figure 5](image5.png) **FIGURE 5.** DSC curve of (NH₄)₂B₁₂H₁₂ showing endothermic desorption which is essential for reversibility.

![Figure 6](image6.png) **FIGURE 6.** Crystal Structure of Unsolvated NaB₃H₈ (Na: violet, B: pink, H: grey)
unavailability. We recently developed a practical synthesis of aminodiborane using a new ambient temperature, catalyst-free reaction between ammonia borane and tetrahydrofuran borane [6]. The facile synthesis of aminodiborane will make this long-sought active chemical reagent readily available for both inorganic and organic syntheses. From aminodiborane, we synthesized an inorganic butane analogue NH₄BH₄-NH₃BH₃, which is a potential hydrogen storage material with 16.9 wt% hydrogen. It has been predicted as an intermediate during thermal decomposition of NH₃BH₃ [7,8]. Thus, its properties are relevant to NH₃BH₃ studies as well as hydrogen storage research. This compound is a white solid at room temperature with a melting point of 62°C. Further study of its properties is in progress.

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 several vacuum wet-chemistry synthesis lines in Prof. Sheldon Shore’s laboratory, a group of dedicated researchers, the unique boron chemistry expertise and inorganic chemistry expertise in the group (especially single crystal structure identification expertise and NMR and IR expertise), 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 include AlB₆H₁₁, AlB₄H₁₄, (NH₄)₂B₆H₁₃, (NH₄)₂B₃H₁₀, Na₃B₄H₆, NH₃B₄H₉, NH₂B₃H₅, NH₄BH₃NH₂BH₃, and new aluminoborane compounds made with B₂H₆. A few of these compounds showed endothermic desorption at low temperatures, thus they are good candidates for further study as potential reversible hydrogen storage materials. We have observed reversibility at mild conditions for AlB₆H₁₁, which is very remarkable for a compound containing only Al, B and H.

We will perform more detailed study of these compounds for hydrogen storage in collaboration with ORNL, JPL/Caltech, Sandia, and NIST. Several compounds have been sent to ORNL, NIST, Sandia, and Ford for various analyses and testing. We will focus on more promising candidates as the properties of these compounds are tested.

Special Recognitions & Awards/Patents Issued


FY 2010 Publications/Presentations


References

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 Fuel Cell 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 materials with high hydrogen capacity and promising thermodynamics and kinetics properties, and understanding metal hydride regeneration issues. The targets being addressed include:

- System Gravimetric Capacity: 0.06 kgH₂/kg system
- System Volumetric Capacity: 0.045 kgH₂/L system
- Fill Time (for 5 kg): 5 minutes

Accomplishments

Our major accomplishments in Fiscal Year (FY) 2010 are summarized below:

- Performed multi-phase equilibrium theoretical studies on LiBH₄, Mg(BH₄)₂ and 2LiBH₄ + MgH₂. Found that Li₂B₁₂H₁₂ and MgB₁₂H₁₂ species play important roles during decomposition. Revealed a pressure-dependent mechanism governing the reaction pathways of 2LiBH₄ + MgH₂.
- Predicted that the decomposition of LiBH₄, Mg(BH₄)₂ and 2LiBH₄ + MgH₂ is accompanied by low levels of gas-phase impurities. In contrast, 2LiNH₂ + C, LiBH₄ + C, and Mg(BH₄)₂ + C are associated with large levels of impurities because of the strong thermodynamic stability of CH₄ and other hydrocarbons.
- Completed comprehensive prototype electrostatic ground state (PEGS) predictions of Ti(BH₄)₅, M[PB₂H₈]ₓ for M = Li, Na, K, Mg, Ca; x=1, 2.
- Confirmed remarkable catalysis of 2LiNH₂/MgH₂ by KH and KNH₂. Demonstrated that in the presence of catalysts, the absorption is >90% complete within minutes at 200°C.
- Improved the desorption kinetics of Mg(BH₄)₂ using various additives. Found that in the presence of 4 mol% TiF₅/ScCl₃, 9.6% H₂ is released at 300°C in several hours.
- Observed low-temperature (<100°C) hydrogen evolution from Ti(BH₄)₅. However, the material was down-selected (removed from further study) due to irreversible hydrogen release.
- Developed a destabilization approach for releasing H₂ from [B₁₂H₁₂]²⁻ compounds at lower temperatures, confirming prior Metal Hydride Center of Excellence (MHCoE) theory.
- Experimentally demonstrated almost complete conversion of Li₃B₁₂H₁₆ and Na₃B₁₂H₁₂ to LiBH₄ and NaBH₄ in the presence of corresponding hydrides at high H₂ pressures.
• Successfully synthesized and studied hydrogen storage characteristics of several alkali and alkaline-earth bis(borano)hypophosphites of general formula \( M[PB_2H_8]_x \). \( Na[PH_2(BH_3)_2] \) was removed from further study due to formation of \( PH_3 \) and \( B_2H_6 \), along with \( H_2 \).

• Using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) detected significant amounts of ammonia during the decomposition of \( M'M''(BH_4)_x \cdot yNH_3 \) and \( M'M''(BH_4)_x(NH_2)_y \) (\( M' \) and \( M'' = Li, Na, Ca and/or Mg \)). Found that small amounts of added \( LiH \) and \( MgH_2 \) significantly decrease the amounts of ammonia released.

**Introduction**

There are currently no materials that fully meet the DOE hydrogen storage performance targets. In order to address this problem, we at SNL have undertaken the prediction, synthesis and characterization of new high-hydrogen content complex metal hydrides for use as reversible hydrogen sorption materials. Also, 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 guiding these efforts, as well as understanding kinetic and regeneration issues for metal hydrides. In addition, we provide technical leadership and collaborate extensively with our partners in the 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. The new materials are characterized by various traditional spectroscopic and diffraction techniques, including Fourier transform infrared (FTIR), Raman, nuclear magnetic resonance (NMR), mass-spectrometry, X-ray and neutron diffraction. The kinetics of hydrogen release are investigated using residual gas analysis (RGA), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Sieverts and pressure-concentration-temperature measurements.

**Results**

**Borohydrides**

During the current fiscal year our major focus has been on exploring the hydrogen sorption properties of magnesium borohydride and several transition metal borohydrides. We isolated the low-temperature \( Mg(BH_4)_2 \) phase and found that upon desorption in vacuum up to 7.8 wt\% \( H_2 \) is released. In the presence of a complex \( TiF_3/ScCl_3 \) additive, the amount of \( H_2 \) released increases to 9.6 wt\%. The doped \( Mg(BH_4)_2 \) sample also shows dramatic enhancement in the kinetics of hydrogen release compared to milled \( Mg(BH_4)_2 \), as shown in Figure 1.

The decomposition of \( Mg(BH_4)_2 \) to \( MgH_2 \) can be represented as the first step (I) of the multi-step process (I–III):

\[
\begin{align*}
6Mg(BH_4)_2 & \rightarrow 5MgH_2 + MgB_12H_{12} + 13H_2 \\
5MgH_2 & \rightarrow 5Mg + 5H_2 \\
5Mg + MgB_12H_{12} & \rightarrow 6MgB_2 + 6H_2
\end{align*}
\]

With \( TiF_3/ScCl_3 \) additives, there is X-ray diffraction (XRD) evidence for the presence of \( Mg \) and \( MgF_2 \) in addition to \( MgH_2 \). The presence of \( MgH_2 \) and \( Mg \) indicates that both reactions (I) and (II) are occurring to some extent. \( MgF_2 \) implies partial reaction of \( TiF_3 \) with \( Mg(BH_4)_2 \), possibly forming \( Ti \)-containing borohydride species which can then readily decompose to release hydrogen. However, the \( TiB_2 \) species were not observed in our study. We confirmed significant conversion of \( MgB_2 \) to fully hydrogenated \( Mg(BH_4)_2 \) for samples with and without additives.

We continued our efforts towards the understanding the role of dodecahydro-closo-dodecaborates in dehydriding/rehydriding reactions of metal borohydrides. In collaboration with our colleagues at the National Institute of Standards and Technology, we reported the structural aspects of the \( M_2B_{12}H_{12} \) series

**FIGURE 1.** Hydrogen Desorption from Doped and Undoped \( Mg(BH_4)_2 \)
(M=alkali metal). We also confirmed the MHCoE Theory Group prediction that MB₁₂H₁₂ compounds (M=Mg, Ca) can be destabilized in the presence of the corresponding metal hydrides. However, attempts to hydrogenate mixtures of CaB₁₂H₁₂ and CaH₂ into Ca(BH₄)₂ at 550-500°C and hydrogen pressures up to 900 bar were unsuccessful. Interestingly, under the same conditions both LiB₁₂H₁₂ and NaB₁₂H₁₂ react with the corresponding metal hydrides to form LiBH₄ and NaBH₄.

Stabilization of transition metal borohydrides through addition of alkali metal atoms has been explored both computationally and experimentally. Theory results for Li₅Ti(BH₄)₃ and Na₅Ti(BH₄)₃ indicate the compounds are unstable with respect to decomposition into LiBH₄, or NaBH₄, respectively. Although decomposition of pure titanium borohydride is calculated to occur spontaneously, in agreement with the observation of rapid decomposition at room temperature, it may be possible to stabilize the compound by incorporation within high surface area nano-frameworks.

Zak Fang in the MHCoE (University of Utah) recently reported up to 5 wt% H capacity at 90°C in the 3LiBH₄-TiF₃ system. We explored various molar ratios in the LiBH₄-TiF₃ and NaBH₄-TiF₃ systems. However, we found no indication that mixed Li-Ti-BH₄ or Na-Ti-BH₄ phases form, which is in agreement with theoretical predictions. We used various ball-milling techniques and found that high-energy milling at room temperature is not appropriate as a synthetic technique for mixed borohydride species in these systems, presumably due to facile decomposition of the in situ-formed Ti(BH₄)₃. Temperature-programmed desorption (TPD) studies of the LiBH₄-TiF₃ and NaBH₄-TiF₃ composites show that most of the H₂ is released at temperatures between 20 and 175°C. However, at 175°C the hydrogen uptake of the dehydrogenated LiBH₄-TiF₃ and NaBH₄-TiF₃ materials is below 1 wt%. Thus, neither of the two is suitable for reversible hydrogen storage applications.

An alternative approach to decrease the desorption temperatures of main group metal borohydrides is through “hydridic-protic” interactions in the presence of ammonia or metal amides. This FY we explored several mixed borohydride-ammonia and borohydride-amide compounds, M'M''(BH₄)ₓ(NH₃)y and M'M''(BH₄)ₓ(NH₂)y (where M' and M''= Li, Na, Ca and/or Mg). We isolated Mg(BH₄)ₓ(NH₃)y and confirmed prior MHCoE results that the major gaseous product of the reaction is hydrogen. Rehydrogenation attempts on the products of desorption of Mg(BH₄)ₓ(NH₃)y and MgCa(BH₄)ₓ(NH₂)y were performed at 90 MPa H₂ pressure and 350°C. The XRD investigation of the samples after rehydrogenation showed that the starting materials do not form under these conditions. However, our TPD measurements indicate that the rehydrogenated products release 3.5 (Mg-system) and 2.8 wt% H (Mg-Ca system) upon heating from room temperature to 350°C, suggesting partial reversibility in both systems. Another problem with the ammonia adducts is the contamination of hydrogen with impurity NH₃ gas. In an attempt to decrease the amount of ammonia released from the initial borohydride-ammonia materials, we isolated Mn(BH₄)ₓ and reacted the material with gaseous NH₃. Transition metals are known to display high affinity towards amine ligands. We found that the as-synthesized Mn(BH₄)ₓ sample can absorb two or more moles of ammonia at room temperature; however most of the NH₃ is released upon heating the adduct above 120°C.

In the area of mixed borohydride-amide materials we investigated several compositions in the M'M''(BH₄)ₓ(NH₂)y systems (where M' and M''= Li, Na, Ca or Mg). We focused only on the systems where new phases are formed during the ball-milling process. We explored various molar ratios of the binaries in several lightweight borohydride-amide materials. Powder XRD data revealed that the ball-milling of these binary and ternary precursors resulted in the formation of a series of related M'-B-N-H (M'= Li, Na and/or Ca) phases. All tested binary borohydride-amide phases release a significant amount of ammonia upon heating, typically starting at temperatures <100°C. Significant mass losses were found by TGA/differential scanning calorimetry (DSC) in the LiBH₄-Mg(NH₂)y and Mg(BH₄)ₓ-LiNH₂ systems, which indicates to significant impurity gas formation. In contrast, Ca(BH₄)ₓ-LiNH₂ and Ca(BH₄)ₓ- NaNH₂ decompose to produce H₂ as the major product of the reaction. Ca(BH₄)ₓ-LiNH₂ system is more promising of the two materials and shows the first peak of H₂ release between 80 and 210°C in the STMBMS data of Figure 2. Ammonia is released in several steps between 40 and 310°C. RGA and STMBMS investigations of several ternary Ca(BH₄)ₓ-LiNH₂-LiH and Ca(BH₄)ₓ-LiNH₂-MgH₂ compositions showed that the amount of ammonia can be significantly reduced when the corresponding metal hydrides are added before the ball-milling step.
RGA of the milled Mg(BH$_4$)$_2$-LiNH$_2$ sample revealed that ammonia is the major product at relatively low temperatures (up to 140°C). Upon heating to 180°C, both H$_2$ and NH$_3$ are released, while at 290°C and above hydrogen is the major product. Small amounts of boron hydrides were also detected. The presence of significant amounts of ammonia at relatively low temperatures suggests this process is energetically favorable. Interesting enough, after the first dehydriding/rehydriding cycle, the amount of NH$_3$ released decreases dramatically. This is associated with a significant loss in capacity (>50%). We also studied the effect of small amounts of MgH$_2$ and LiH on the impurity gas formation from the Mg(BH$_4$)$_2$-4LiNH$_2$ system. Our tests on the ball-milled Mg(BH$_4$)$_2$-4LiNH$_2$-0.1MgH$_2$ and Mg(BH$_4$)$_2$-4LiNH$_2$-0.1LiH composites indicate a decrease in the amount of NH$_3$ formed, presumably through formation of reactive amide species. As far as the reversibility is concerned, none of the borohydride-amide materials we studied so far display full reversibility, even at high temperatures (up to 500°C) and H$_2$ pressures (up to 100 MPa).

**Phosphorous Materials**

Syntheses of the various salts of [PH$_2$(BH$_3$)$_2$] are known. However, most methods use phosphine, ammonia, and diborane, are performed at temperatures as low as -196°C, and take upwards of seven days to complete. To avoid these hazards, a new method was developed from commercially available starting materials:

\[
\text{NaBH}_4 + \text{PCl}_3 \rightarrow \text{Na}^+ + \text{H}_2 + \text{B} \uparrow + \text{HCl} + \text{P} \uparrow
\]

Differential scanning calorimetry of the sodium salt 1 was carried out in order to determine the heat of decomposition. A multi-step process between 150 and 200°C for Na[PH$_2$(BH$_3$)$_2$] yields a $\Delta H$ of approximately +1 kcal/mol at 10°C/min (Figure 3, left). Interestingly, this process appears to be heating rate-dependent. With fast heating rates (>5°C/min), a sharp endothermic event is observed before a large, and long-lived, exothermic event occurs yielding the aforementioned value for $\Delta H$. If the heating rate is slowed to 1°C/min, the sharp endothermic event becomes much less pronounced, and the exothermic signal intensifies (Figure 3, right). The multi-step process in the same temperature range (150-200°C) becomes overall exothermic with a measured $\Delta H$ of roughly -10 kcal/mol. We hypothesize that fast heating rates allow the sample to melt before decomposing, whereas, a slow heating rate causes sample decomposition before undergoing the endothermic melting process. TGA shows a weight loss of approximately 6% over the same temperature range. No additional mass loss was observed up to 500°C.

**FIGURE 3.** DSC of Na[PB] Decomposition Showing Dependence on Heating Rate
The 6% mass loss observed during the thermal decomposition of Na[PH$_2$(BH$_3$)$_2$] was initially attributed to H$_2$ loss. To confirm this assessment, analysis of the volatile compounds released from the solid material was performed using STMBMS. Large amounts of H$_2$ were detected as the sample was heated through the temperature range of 150-200°C along with PH$_3$ and B$_2$H$_6$. The signal for hydrogen was qualitatively larger compared to other volatile species but the amount of phosphine and diborane were not negligible. Clearly, the loss of phosphorus and boron from the solid material is detrimental to achieving a reversible material.

To identify additional products formed during thermal decomposition, samples of the sodium salt were heated under vacuum to 150°C for fixed time intervals and then analyzed by attenuated total reflection-FTIR spectroscopy, NMR spectroscopy, XRD, DSC, and TGA. Regardless of the time interval (1h, 2h, 3h, 6h, and 18h) at 150°C, each reaction gave the same product, identified as sodium borohydride (NaBH$_4$):

![Diagram of NaBH$_4$ formation](image)

The sodium salt crystallizes in the orthorhombic space group Ama2, with lattice parameters $a = 13.77\,$Å, $b = 7.91\,$Å, and $c = 4.50\,$Å. The structure was predicted using the PEGS method that combines a simplified electrostatic Hamiltonian and Monte Carlo simulated annealing to find prototype structures that are further refined using state-of-the-art first-principles techniques. The Rietveld-refined XRD spectrum is shown in Figure 4, and indicates excellent agreement with the measured powder diffraction spectra.

**FIGURE 4.** Rietveld refined powder XRD spectrum of 1 in space group Ama2. The difference curve (black trace) is below the observed data (red +), and spectra of the predicted structure (green trace).

Amide Materials

The (2LiNH$_2$+MgH$_2$) system has been selected as a near-term candidate for further development in the Engineering Center of Excellence. This material has convenient characteristics (i.e., pressure and temperature) for an operational storage system, with extensive cycle life of ~220 cycles. While the promising thermodynamic features and the high desorption rate of this material are attractive, its absorption rate is poor. The goal of this project is to search for adequate method to improve the sorption kinetics of this material. Previously we tested the traditional catalysts for hydrogen sorption, such as Pd, Pt, TiCl$_3$, Nd$_2$O$_3$, and found that none of them made significant improvements in the sorption behavior of the material. Up to now there has been no theory that can guide the discovery of effective catalysts for the amide materials. It is common that new catalysts are discovered unexpectedly. Recently, Dr. Ping Chen (DaLian Institute of Chemical Physics, Chinese Academy of Science) discovered a non-traditional catalyst, KH, that led to performance improvements. This motivated our investigation of potassium compounds, such as KH and KNH$_2$, as candidate catalysts for (2LiNH$_2$ + MgH$_2$).

**FIGURE 5.** Absorption profiles for (2LiNH$_2$+MgH$_2$), with or without KH addition (at ~4 mole %), at 180, 200 and 220°C and...
initial H₂ pressure of 150 bar. The solid lines are for those with KH added and the dashed lines are for those without KH. It can be seen that with the addition of KH, the absorption rapidly achieves >90% completion at 200°C and above and more than 70% at 180°C. The van’t Hoff plot for this material is shown in Figure 6. The formation enthalpy was measured to be 40 kJ/mol, very close to the previously reported value, 39.4 kJ/mol, indicating that the KH additive does not change the sorption thermodynamics. So far, we have been unable to detect any improvement on desorption of 2LiNH₂+MgH₂ in the presence of KH.

Theory Group Coordination

The Theory Group (TG) of the MHCoE makes use of first-principles methods to conduct materials discovery, provide thermodynamic and kinetic data for use by engineering and modeling efforts, and suggest new directions for experimentalists and interpretation of their results. The TG consists of researchers at the following institutions:

- Sandia National Laboratories (Mark Allendorf, TG Coordinator)
- Georgia Institute of Technology (Prof. David Sholl)
- National Institute of Standards and Technology (Dr. Ursula Kattner).
- University of Illinois/Champaign-Urbana (Prof. Duane Johnson)
- University of Missouri, St. Louis (Prof. Eric Majzoub)
- University of Pittsburgh (Prof. Karl Johnson)

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 synergy with experimentalists. The TG communicates through regular monthly conference calls involving all members of the team. This format has worked quite well and is followed up with a set of minutes and action items emailed to all participants. Depending on the topics under discussion, the TG also involves experimentalists from the various projects to provide insights into verification of theoretical predictions and suggestions for additional work by the TG.

Multiphase Equilibrium Modeling to Predict Impurity Gases and Phases

We computed the thermodynamic equilibrium including the possible evolution of gases other than H₂ in hydride systems based on LiNH₂, LiBH₄, Mg(BH₄)₂ and their mixtures with LiH, MgH₂, or C. Although the majority of research on materials for reversible storage of H₂ has focused on issues associated with hydrogen capacity, the generation or absence of gaseous impurities from any storage system could be decisive in the value of such a system for practical applications. The extensive literature that has applied first-principles calculations to searching for metal hydrides and their mixtures with attractive properties for reversible storage has typically assumed that H₂ is the only gas phase product. The approach we introduced here couples first-principles (density functional theory) methods, which are used to obtain the thermodynamic properties of solid phases of interest, and free energy minimization incorporating a broad range of gaseous and liquid species to obtain a comprehensive thermodynamic picture of the metal hydride decomposition chemistry. This concept will be a valuable addition to computational efforts designed to aid development of reversible storage applications by screening large numbers of materials.

One useful way to categorize the systems we studied is to assess the purity of H₂ that is available at equilibrium in each case. To this end, we define R to be the fraction of H₂ that is observed at equilibrium relative to the amount of H₂ that would be predicted in the gas phase if H₂ was the only gaseous species considered in a thermodynamic calculation. The variation in R as a function of temperature at 1 atm pressure is shown for each system we considered in Figure 7. Interestingly enough, the decomposition of 2LiBH₄ + MgH₂ is pressure dependent. For LiNH₂, LiBH₄, and 2LiBH₄ + MgH₂, R is very close to 1; that is, these examples are associated with very low levels of gas-phase impurities. The mixture LiNH₂ + LiH, in contrast, generates an appreciable level of N₂ and NH₃ when LiNH₂ decomposes, especially at temperatures above 700 K. All three of the mixtures we considered that included

![van’t Hoff Plot](image-url)
C, namely 2LiNH2 + C, LiBH4 + C and Mg(BH4)2 + C, are associated with very impure H2 except at high temperatures because of the strong thermodynamic stability of CH4.

Conclusions

- Performed multi-phase equilibrium theoretical studies on LiBH4, Mg(BH4)2 and 2LiBH4 + MgH2. Found that Li2B12H12 and MgB12H12 species play important roles during decomposition. Revealed a pressure-dependent mechanism governing the reaction pathways of 2LiBH4 + MgH2.
- Predicted that the decomposition of LiBH4, Mg(BH4)2 and 2LiBH4 + MgH2 is associated with low levels of gas-phase impurities. In contrast, 2LiNH2 + C, LiBH4 + C, and Mg(BH4)2 + C, are associated with very impure H2 because of the strong thermodynamic stability of CH4.
- Completed comprehensive PEGS predictions of Ti(BH4)3, M[PB2H8]x for M = Li, Na, K, Mg, Ca; x=1, 2.
- Confirmed remarkable catalysis of 2LiNH2/MgH2 by KH and KNH2. Demonstrated that in the presence of catalysts the absorption is >90% complete within minutes at 200°C.
- Improved the desorption kinetics of Mg(BH4)2 using various additives. Found that in the presence of 4 mol% TiF3/ScCl3, 9.6% H2 is released at 300°C.
- Observed low-temperature (<100°C) hydrogen evolution from Ti(BH4)3. However, the material was down-selected (removed from further study) due to irreversible hydrogen release.
- Developed a destabilization approach for releasing H2 from [B12H12]5- compounds at lower temperatures, confirming prior MHCoE theory.
- Experimentally demonstrated almost full conversion of Li2B12H12 and Na2B12H12 into LiBH4 and NaBH4 in the presence of corresponding hydrides at high H2 pressures.
- Successfully synthesized and studied storage characteristics of several alkali and alkaline-earth bis(borano)hypophosphites of general formula M[PB2H8]x. Na[PH2(BH3)2] was removed from further study due to formation of PH3 and B2H6, along with H2.
- Using STMBMS, detected significant amounts of ammonia during the decomposition of M'M''(BH4)x·yNH3 and M'M''(BH4) x(NH2)y (where M' and M''= Li, Na, Ca and/or Mg). Found that small amounts of metal hydrides significantly decrease the amounts of ammonia released.

Special Recognitions & Awards/Patents Issued

1. Director Klebanoff accepted a DOE Hydrogen Program 2010 “Special Recognition Award,” made to the entire MHCoE, “In Recognition of Outstanding Contributions to the Department of Energy.” This award was made June 8, 2010.

FY 2010 Publications/Presentations


IV.A.1e Aluminum Hydride Regeneration

Objectives

Develop an onboard vehicle storage system meeting DOE’s targets that uses aluminum hydride for storing hydrogen:

- Produce aluminum hydride material with a hydrogen storage capacity greater than 9% gravimetric (kg-H₂/kg) and 0.13 kg-H₂/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 kg-H₂/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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(D) Durability/Operability
(E) Charging/Discharging Rates

Technical Targets

The current 2010 and 2015 hydrogen storage targets are listed in Table 1 along with our 2010 status using AlH₃. The well-to-wheels efficiency listed in Table 1 under the column for 2010 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. Argonne’s analysis assumes 70-wt% aluminum hydride slurry, and uses trimethylamine (TMA) 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 40-wt% aluminum hydride slurry. The 0.036 gravimetric storage parameter listed in Table 1 is a measured value from 40-wt% slurry consisting of 9-wt% aluminum hydride particles.

### TABLE 1. Progress in Meeting Technical Hydrogen Storage Targets

<table>
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<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010/2015 Target</th>
<th>2010 Status</th>
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<td>Gravimetric</td>
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<td>Volumetric</td>
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<td>55%</td>
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<tr>
<td>Refueling Time</td>
<td>min</td>
<td>3/2.5</td>
<td>To Be Determined</td>
</tr>
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</table>

Accomplishments

Progress was realized in Fiscal Year (FY) 2010 towards meeting DOE’s hydrogen storage targets by demonstrating the following three steps for the synthesis of AlH₃:

**Step 1: formation of NR₃-AlH₃ by direct hydrogenation**

- Five alane adducts formed by direct hydrogenation under mild conditions.
- Alane adducts also formed by reacting amine directly with alane.

**Step 2: transamination exchange NR₃ for triethylamine (TEA)**

- Transamination demonstrated starting with dimethylethylamine (DMEA) and TMA.

**Step 3: separation of TEA-AlH₃**

- Separation of TEA-AlH₃ successful with ~70% AlH₃ recovery (additional optimization is necessary to improve yields to achieve the target).
**Approach**

The research direction under the Metal Hydride Center of Excellence 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 approach towards meeting the three-minute refueling target.

**Results**

In FY 2010 we continued to explore low-energy methods to regenerate AlH₃ from Ti-catalyzed aluminum and hydrogen gas. In the past we demonstrated, in the presence of hydrogen gas and an inert solvent, the direct reaction of catalyzed aluminum with many tertiary amines to form amine-alane adducts. The practice of Ti doping to catalyze the reversible formation of aluminum-based hydrides has been the subject of many studies. These catalyzed materials are known to possess improved reaction kinetics in regards to the formation of alane complexes and reversibility when compared with those formed with undoped materials. Our current model suggests that arrangements of Ti atoms on the surface of Al promote the chemisorption of hydrogen and the formation of transitory alane species. Based upon these calculations, it is believe that any alane formed on the surface of titanium-doped aluminum, survives long enough to react with a Lewis base, such as DMEA, to form an alane adduct. The alane adduct detaches from the aluminum surface and is significantly more stable than molecular AlH₃. Previously, we demonstrated the formation of dimethylethylamine alane (DMEAA) through the direct hydrogenation of Al* and DMEA in one of three solvents (Et₂O, tetrahydrofurran or toluene) using the following reaction:

\[
\text{DMEA} + \text{Al}^* + \frac{3}{2}\text{H}_2 \rightarrow \text{AlH}_3 \cdot \text{DMEA} \quad (1) \text{ Step 1}
\]

Attempts to produce a pure DMEAA adduct through direct hydrogenation without a solvent were not successful. DMEAA can also be synthesized by a direct reaction between AlH₃ and DMEA in a number of solvents including excess DMEA, Et₂O, tetrahydrofurran or toluene using the following reaction:

\[
\text{DMEA} + \text{AlH}_3 \rightarrow \text{AlH}_3 \cdot \text{DMEA} \quad (2)
\]

This year the focus was placed on recovering the alane from the amine-alane adduct with particular attention given to the (DMEA) adduct. The recovery of intact AlH₃ from most amine-alane adducts is difficult since the temperatures required for adduct separation are typically greater than the AlH₃ decomposition temperature (~100°C). The one known exception is triethylamine-alane (TEAA), which can be separated under a partial vacuum at 70°C. In this effort, we demonstrate that although TEAA is not easily formed by direct hydrogenation, it can be formed by an amine exchange reaction (transamination) using DMEAA and TEA. This gives us a low-energy regeneration reaction which initially involves the direct formation of DMEAA from DMEA, catalyzed aluminum (Al*), and H₂ gas under moderate conditions (Eq. 1). This step is followed by transamination with TEA (Figure 1), and then finally the separation of TEAA for the recovery of alane (Figure 2):

\[
\text{AlH}_3 \cdot \text{DMEA} + \text{TEA} \rightarrow \text{AlH}_3 \cdot \text{TEA} + \text{DMEA} \uparrow \quad (3) \text{ Step 2}
\]

\[
\text{AlH}_3 \cdot \text{TEA} \rightarrow \text{AlH}_3 + \text{TEA} \uparrow \quad (4) \text{ Step 3}
\]

**Step 2: amine exchange (transamination)**

![FTIR spectra confirming the exchange of DMEA with TEA](image)

**Figure 1.** Fourier Transform Infrared (FTIR) Spectra Confirming the Exchange of DMEA with TEA.
CONCLUSIONS AND FUTURE DIRECTIONS

At the close of this project we have concluded that many alanes of tertiary amines may be synthesized at relatively modest hydrogen temperatures and pressures. However, the technical barriers of improving yields and slurry mass loadings need to be addressed before an alane storage system can meet all of DOE’s hydrogen storage targets. These barriers define the future direction of alane research at BNL, and are listed as follows.

• Improve the well-to-tank efficiency from the estimate of 40-55% with TMA to the target efficiency of 70% with DMEAA.

Combining step 2 + 3: Separation of DMEA-AlH₃

• DMEA-AlH₃ separated by combining steps 1 & 2
• Analysis of recovered AlH₃ (XRD and decomposition) suggests ~35% AlH₃ with 65% Al when steps 1 & 2 are combined
• Improvements expected with optimization & washes to remove unwanted material

Figure 3 shows the recovery of aluminum hydride by starting with DMEAA synthesized using Equation 2, and then combining steps 2 and 3 together for the recovery of aluminum hydride.

Special Recognitions & Awards/Patents Issued

1. Jason Graetz was awarded the “Presidential Early Career Award for Scientists and Engineers” (PECASE) for innovative research in hydrogen storage for automotive fuel-cell applications, 2009.

FY 2010 Publications/Presentations


IV.A.1f  Reversible Hydrogen Storage Materials – Structure, Chemistry, and Electronic Structure

Objectives

- Advance the understanding of the microstructural characteristics of complex light-weight metal hydrides to ascertain controlling mechanisms.
- Develop and apply reliable theoretical methods to assess potential complex metal hydrogen-storage materials, including key issues limiting material performance.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.)3 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(E) Charging/Discharging Rates

Technical Targets

**Catalytically Enhanced Hydrogen Storage Systems:** This project uses a combined theoretical and experimental approach to gain a fundamental understanding of the role of the catalytic species in several candidate complex hydride storage systems. Insights gained from these studies are applied toward identifying potential complex metal hydride storage systems as well as optimizing the design and synthesis of systems to meet or exceed the following DOE 2015 hydrogen storage targets:

- System gravimetric capacity in terms of usable, specific-energy from H₂ 1.8 kWh/kg.
- System volumetric capacity in terms of usable, specific-energy from H₂ 1.3 kWh/L.
- System fill time (for 5 kg H₂): 4.2 min (1.2 kg/min).

Accomplishments

The following accomplishments were made in this fiscal year:

- Improved electron tomography capability and used it to address the question of the dispersion of particles in nanoporous scaffolds.
- Showed in MgH₂ that there is no nanoparticle size effect for dehydrogenation enthalpies, although there is an effect on kinetic barriers with transition metal catalyst.
- Determined universal behavior for core-shell preference in binary nanoparticles.
- Demonstrated that the amount of Ti needed to activate the system is less than introduced initially.
- Established in the Ca(BH₄)₂ system the existence of numerous CaB₁₂H₁₂ polymorphs and the origin for the observed amorphous-structure in dehydrogenated material.

Introduction

The transition from a petroleum-based to a hydrogen-based fuel for automotive applications depends on finding a viable, reliable and economic means in which to store hydrogen on-board the vehicle. One option is the high-capacity lightweight, metal hydrides that includes aluminum, borohydrides, destabilized metal hydrides, binary hydrides, intermetallic hydrides, and modified lithium amides. This includes exploring the potential of making nanoscale systems and confining them within nanoporous structures to exploit the enhanced properties found in large surface area to volume conditions. However, the challenge was and remains that none of the candidate systems tested to date satisfy the thermodynamic and kinetic constraints imposed by the DOE targets.
Approach

State-of-the-art characterization tools, electron microscopy and X-ray diffraction for structural and phase characterization, energy dispersive and electron energy loss spectroscopy for chemical analysis, as well as atomic force microscopy to probe surface interactions, were employed to investigate the microstructural and microcompositional changes that occur in candidate material systems during the uptake and release of hydrogen. The characterization was coupled with first-principles, electronic-structure and thermodynamic theoretical techniques to predict and assess metastable and stable phases, as well as surface effects that can poison or limit kinetics. Electronic-structure and thermodynamic calculations were used to interpret and understand the experimental results on candidate systems. This combined theoretical/characterization effort provides fundamental insight to the processes governing hydrogen uptake and release.

Results

X-ray and electron diffraction of desolvated and dehydrogenated Ca(BH$_4$)$_2$ showed that after dehydrogenation the Ca(BH$_4$)$_2$ peaks are replaced with CaH$_2$ peaks only, no other crystalline phases were present. Electron diffraction from a single particle showed weak crystalline diffraction spots superimposed on a diffuse background, which is consistent with the particle being amorphous with a low volume fraction of small crystalline regions. Chemical analysis via electron energy loss spectroscopy, confirmed no significant compositional modifications occurred during dehydrogenation.

To interpret these experimental results, theoretical calculations of Ca(BH$_4$)$_2$ hydride and dehydride reactions that included possible intermediate CaB$_{12}$H$_{12}$ states were performed. A key finding was the discovery of the existence of numerous polymorphs of CaB$_{12}$H$_{12}$ that, at low temperatures, would lead to formation of a stable intermediate phase. It was demonstrated via ab initio molecular dynamics that these polymorphs arose from the varying bond length of Ca-Ca cations (as opposed to the Ca-B and B-B contained in the stable B$_{12}$H$_{12}$ unit). Significantly, a mixed state of several polymorphs explained the experimental diffraction pattern; that is, around 2θ = 22° more than two CaB$_{12}$H$_{12}$ polymorphs were needed to produce the weight at that scattering angle. Consequently, the weighted diffraction signal would produce a pattern that appears amorphous, as observed experimentally. The X-ray diffraction pattern along with the signals from the different polymorphs is shown in Figure 1. Phase segregation as well as complete extraction of all available hydrogen was possible only at higher temperatures.

To explore the interaction of molecular hydrogen with an aluminum surface with and without surface Ti atoms, a thin film of Al was deposited on Si(111) substrates both with and without a partial monolayer (0.02 ML) of Ti. Unlike the Al-only films, which exhibited no change when exposed to H$_2$, vacancy islands appeared and increased both in number and size under H$_2$ exposure of the Ti-dosed surfaces, Figure 2. The vacancy islands, an indication of hydrogen absorption by the Al, were one atom deep and randomly distributed across the surface. Shortly after the vacancy islands appeared, surface AlH$_x$ monomers formed next to a vacancy island. As exposure continued and the number of surface monomers increased, grouping of AlH$_x$ complexes formed. Future experiments will...
explore the interactions between Ti, the vacancy islands, and the AlHx complexes. The final series of experiments will explore how the responses differ if the surface is contaminated. In support of these scanning tunneling microscopy experiments, first principles calculations are being conducted to determine the surface projected electronic density of states to make a direct connection to the experimental results.

One possible strategy to improve the thermodynamics of the hydrogenation and dehydrogenation reactions is to reduce the particle size into the nanoscale regime. To explore this possibility, the size effect on desorption enthalpies of nanoparticles vs. bulk were calculated for MgH2-based systems with and without catalyst atoms of Ti and V. The results, reported in Table 1 show there is NO thermodynamic size effect for hydrogen release (except at very small [<10] atom clusters), although there is a catalytic effect with dopant in both bulk and nanoparticle cases.

An important aspect of developing nanoparticle hydrogen-storage systems is to employ light-weight scaffolds with nano-sized pores to control particle size and prevent agglomeration. A key question in using such scaffolds is determining if the storage medium actually impregnates the scaffold during the synthesis. To address this issue we have developed and applied compositional electron tomography to convert conventional two-dimensional compositional images to three-dimensional tomographs of scaffolds containing hydrogen storage materials. These tomographs enable visualization of the impregnated scaffold from any viewing angle. An example of a selection of snapshots from an electron tomogram of silver clusters that had been impregnated in a metalorganic framework are shown in Figure 3; silver is not a candidate system it is used here simply to demonstrate the technique capability.

Nudged Elastic Band calculations are being conducted to explore the kinetic barriers of hydrogen desorption from the [110] rutile surface of MgH2 with and without catalytic-dopants of Fe, V and Ti. Due to the large size of ball-milled and similar samples, we believe that surface calculations for facets are sufficient to obtain quantitative estimates of kinetic barriers. It is found that for H2 desorption, the lowest-energy structures involve dramatic local reconstructions around the catalyst site, with Ti (V) preferring a coordination number of 8 H (7 H) atoms. Thus, as one hydrogen molecule dissociates, hydrogen from the interior is drawn to the surface catalyst atom site so that the process can continue. This can be seen for V in the images shown in Figure 4a. The effects of nanosize and support interactions on H desorption are shown in Figure 4b and this shows the difference between the different catalytic-dopants and the effectiveness of Ti versus V at reducing the kinetic barriers, while no advantage was found by going “nano” with samples for dehydrogenation energies, i.e., no size-effects for thermodynamics.

Conclusions and Future Directions

- The core-shell behavior in transition-metal nanoparticles is governed by cohesive energy (or surface energy) and size differences, which predicts all observed structures.
- No nanoparticle size effect for dehydrogenation enthalpy exists although there is a reduction in kinetic barrier with catalyst.

![Figure 2](image2.png)

Figure 2. Scanning tunneling micrograph of an Al surface with 0.2 monolayer of Ti deposited on the surface following dosing with molecular hydrogen.

![Figure 3](image3.png)

Figure 3. Tomographic snapshots of Ag clusters inside metalorganic framework. (b) and (c) show zoomed images of the nanoparticles.

<table>
<thead>
<tr>
<th></th>
<th>Mg30H62</th>
<th>Mg30TiH62</th>
<th>Mg30VH62</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nanoparticle</strong></td>
<td>246</td>
<td>175</td>
<td>190</td>
</tr>
<tr>
<td><strong>Bulk (011) Rutile</strong></td>
<td>256</td>
<td>187</td>
<td>205</td>
</tr>
</tbody>
</table>

Table 1. Dehydrogenation energy (kJ/mol-H2) from nanoparticle surface site vs. bulk surface site (defined has being bonded to two metal sites).
The role of Ti on clean Al surfaces appears to be to enhance the dissociation of molecular hydrogen to atomic hydrogen. Our continuing effort will focus on completing the following activities:

- Continue the study of the reaction of H$_2$ with clean and poisoned Al surfaces with and without catalytic species. We will explore creating small islands of Ti, as opposed to isolated Ti atoms, and, if successful reacting them to form Al$_{1-x}$Ti$_x$ islands. The interaction of H$_2$ with these islands will then be investigated. Electronic-structure methods will be used to support these surface-science experiments and to aid the interpretation of the experimental results.
- The electron tomography method will be used to identify the location of MgH$_2$ in a scaffold (collaboration with University of Hawaii) and LiBH$_4$ melt-infiltrated into nanoporous carbon (University of Missouri).
- The electronic structure studies involving the following systems will be continued:
  - Stability of bulk Ca(BH$_4$)$_2$ and clusters of Mg and MgH$_2$.
  - Nanocluster structures of MgH$_2$ and NaAlH$_4$ with and without interactions to a carbon support (approximating interactions with aerogels).
  - The effects of nanosize and support interactions on H desorption.

**FY 2010 Publications/Presentations**

9. Presentation at the 2010 March Meeting of the American Physical Society, Portland, OR.


14. D.D. Graham, J. Graetz, J. Reilly, J. Wegrzyn, and I.M. Robertson. Location of Ti catalyst in the reversible AlH$_3$ adduct of triethylenediamine, Accepted, J. Physical Chemistry


IV.A.1g Electrochemical Reversible Formation of Alane

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Project Start Date: October 1, 2006
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. Alane AlH₃ was identified as material of potential to meet the DOE targets.
• Avoid the impractical high pressure needed to form AlH₃.
• Avoid the chemical reaction route of AlH₃ that leads to the formation of alkali halide salts such as LiCl or NaCl.
• Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form AlH₃.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(R) Regeneration Processes

Technical Targets

In this project studies are being conducted to lower cost and improve efficiency of the electrochemical method to form AlH₃. This material has the potential to meet the 2015 technical target for on-board hydrogen storage as shown in Table 1.

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>2015 Target</th>
<th>AlH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Capacity</td>
<td>0.055 kg H₂/kg System</td>
<td>0.1 kg H₂/kg AlH₃</td>
</tr>
<tr>
<td>Volumetric Capacity</td>
<td>0.04 kg H₂/L System</td>
<td>0.149 kg H₂/L AlH₃</td>
</tr>
</tbody>
</table>

Accomplishments

• Continued to produce gram quantities of alane with high purity.
• LiAlH₄ was also used to produce alane.
• The amount of dendrites was reduced by using LiAlH₄.
• Yield was increased and higher electrochemical cell efficiency was achieved.
• An electro-catalytic additive was discovered and found to greatly enhance the electrochemical process.
• Started improving efficiencies in every step of the regeneration method and achieved success.
• A pressurized electrochemical cell is being constructed for close material regeneration cycle and the use of more efficient separation.

Introduction

The DOE is supporting research to demonstrate viable materials for on-board hydrogen storage. Aluminum hydride (alane, or AlH₃), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g H₂/L and a desorption temperature of ~60°C to 175°C (depending on particle size and the addition of catalysts) has the potential to meet the 2010 and 2015 DOE targets.

In this report improvements to the electrochemical method to produce alane are discussed. Although many attempts in the past were made to make alane electrochemically [1-3] none of these attempts have isolated or characterized alane. These attempts were not directed at hydrogen storage. Our group is the first to demonstrate a reversible cycle utilizing electrochemistry and direct hydrogenation, where gram quantities of alane are produced, isolated and characterized [4]. Our regeneration method is based on a complete cycle that uses electrolysis and catalytic hydrogenation of spent aluminum Al(s).

DOE Hydrogen Program 394 FY 2010 Annual Progress Report
Approach

Electrochemical methods have been developed at SRNL to produce alane [4]. These methods avoid the impractical high pressure needed to form AlH₃ and the chemical reaction route of AlH₃ that leads to the formation of alkali halide salts such as LiCl. The process utilizes an electrolytic potential to drive the chemical reaction to form AlH₃. However, AlH₃ will be oxidized in an aqueous environment, forbidding the use of all protic solvents. For this reason, the use of a non-aqueous solvent system is required.

The electrolysis is carried out in an electrochemically stable, aprotic, and polar solvent such as tetrahydrofuran (THF) or ether. MAIH₄ (M = Li, Na) is dissolved in a polar solvent, forming an ionic solution. For example, sodium alanates dissolved in THF is used as an electrolyte.

NaAlH₄ / THF ↔ Na⁺ / AlH₄⁻ / THF

Though not directed at the regeneration of alane, elaborate research and extensive studies on the electrochemical properties of this type of electrolyte have been reported [5-6].

In addition ways to improve the electrochemical methods were considered, leading to the addition of chemicals that accelerate alane production. At this moment this species is referred as the electrocatalytic additive (ECA). Electrochemical techniques such as electrolysis, cyclic voltammograms (CV), and electrochemical impedance spectroscopy (EIS) were used to evaluate the effect of the ECA.

Results

Alane has continued to be produced in grams quantities, using the electrochemical method described in Zidan et al [4]. This method was improved by modifying the electrochemical cell setup and the electrochemical process. Increase in the alane production was obtained by increasing cell size, electrode size, minimizing resistance (by reducing electrode distance), and prolonging the electrolysis. Dendrites formation at the counter electrode has been reduced by the use of LiAlH₄ instead of NaAlH₄. Both solutions of NaAlH₄ in THF and LiAlH₄ in THF contain triple ions complexation. However, solutions of NaAlH₄ in THF produce more tightly solvated ions (Na⁺ and AlH₄⁻) than solvent separated ion pairs (Na⁺[AlH₄]⁻) whereas solutions of LiAlH₄ in THF contains more solvent separated ion pairs (Li⁺[AlH₄]⁻) than solvated ions (Li⁺ and AlH₄⁻) [6-7]. Consequently, there are less free ions in the solution of LiAlH₄ than in the solution of NaAlH₄ which can lead to less formation of Li₃AlH₆ and Al (dendrites). A new modified system is being developed to further reduce the dendrites formation. This system consists of a pressurized electrochemical cell in which a higher H₂ pressure is used to increase the H₂ in the solution in order to displace the reaction of Li to LiH avoiding in this way the reaction to form Li₃AlH₆. In addition, the electrochemical method was improved by the use of an ECA.

To test the effect of the ECA two cells were prepared using LiAlH₄ and triethylenediamine (TEDA) in THF and including the ECA in one of the cells. TEDA was incorporated in the solution to visually detect the formation of alane as AlH₃-TEDA (white precipitate) during the experimental test. AlH₃-TEDA was easily separated by filtering and weighted. Figure 1 shows the initial state of each cell and after 10 min of electrolysis. This figure clearly shows that cell 2 (cell with ECA) contains a larger amount of AlH₃-TEDA. Also, it should be notice that a minimal amount or no dendrites were produced in the counter electrode in either cell.

Figure 2 shows 10 min of bulk electrolysis at 2.1 V for alane production using the two comparative cells described above. The high potential used during the electrolysis was required to produce enough alane in those 10 min for visualization purpose and eventually yield comparison. This figure shows an increase of 80% in the current when the ECA was used. The total charge for cell 2 was twice the total charge obtained with cell 1. The amount of yield of AlH₃-TEDA was doubled when the ECA was used on cell 2. CVs for both cells are presented in Figure 3. It should be noted that the open circuit voltage (OCV) for cell 2 is shifted to -1.5 V from the original cell #1 (OCV = -1.9). This means that the overpotential required for cell 2 is less when performing the electrolysis at 2.1 V. Consequently, lower energy is required for cell 2 to produce AlH₃-TEDA, which implies that cell 2 is more efficient because it has more current with less energy input.

EIS was performed on the cells with and without the ECA. Figure 4 shows that real part of the impedance, which represents the resistance of the cells, is about 112 Wcm² for both cells. This shows that the ECA does not have a significant effect in the resistance (or conductivity) of the solution. That is, the ECA is not acting as an electrolyte. Consequently, the increase in current and efficiency discussed above are an electrocatalytic effect of the added species.

In additions to the improvements described above methods have been developed to extract alane from THF. These methods involve the heating and vacuum distillation of THF adducted alane solutions with subsequent crystallization of alane in toluene or other non coordinating solvents.

Conclusions and Future Directions

• The electrochemical cell setup was modified and larger quantities (grams) of alane were produced.
FIGURE 1. Two electrochemical cells showing the formation of AlH₃-TEDA. Cell 1 without the ECA (a) before and (b) after 10 min of electrolysis; and cell 2 with the ECA (c) before and (d) after the 10 min of electrolysis.

FIGURE 2. Comparison of the bulk electrolysis for the production of AlH₃-TEDA using two electrochemical cells: with and without the ECA.
The use of LiAlH$_4$ helped to reduce the dendrites formation. An electro-catalytic additive was discovered and found to greatly enhance the electrochemical process by increasing the cell efficiency and the alane production. Ongoing work and future direction include:

- Use of a pressurized electrochemical cell to further reduce the dendrites formation.
- Examine catalysts in accelerating formation and regeneration.
- Use other techniques (e.g. nuclear magnetic resonance, prompt gamma activation analysis and Raman) to quantify and characterize AlH$_3$.
- Design and construct a larger electrochemical cell capable of producing larger quantities of AlH$_3$.
- Develop closed and efficient AlH$_3$ extracting system based on new solvents.
- Optimize all parameters needed for producing several grams of AlH$_3$ efficiently.
- Explore, reversibly, forming other high capacity complex hydrides such as Mg and Ca-based complex hydrides using electrochemical methods.

**Special Recognitions & Awards/Patents Issued**

1. 2010 DOE Hydrogen Program Team Award in Storage. This award recognizes Dr. Ragaiy Zidan and his team at SRNL for their outstanding contribution to the development of electrochemical methods to regenerate alane.

**FY 2010 Publications/Presentations**

1. R. Zidan, Aluminum Hydride (Alane), in M. Hirscher (Ed.), Handbook of Hydrogen Storage: New Materials for...


References


IV.A.1h Neutron Characterization and Calphad in Support of the Metal Hydride Center of Excellence

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Contract Number: DE-AI-01-05EE11104
Project Start Date: April 1, 2005
Project End Date: October 1, 2010

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 Fuel Cell 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 H₂/L

Accomplishments
Key accomplishments for Fiscal Year (FY) 2010 are listed below for hydrogen-storage materials of interest to the MHCoE:
- The structures of SrB₁₂H₁₂ and BaB₁₂H₁₂, heavier alkaline-earth analogs to MgB₁₂H₁₂, were solved by a combination of X-ray diffraction (XRD), neutron vibrational spectroscopy (NVS), and density functional theory (DFT) calculations.
- NVS measurements of amorphous, partially solvated MgB₁₂H₉ yield a vibrational density of states suggestive of the predicted stable crystalline structure.
- Quasielastic neutron scattering (QNS) measurements of NaBH₄, KBH₄, and Cs₂B₁₂H₁₂ allowed us to characterize, in detail, the rotational dynamics of the corresponding BH₄⁻ and B₁₂H₁₁⁻ anions.
- NVS measurements of the direct high-pressure hydrogenation of Li₂B₁₂H₁₂ + 10LiH and Na₂B₁₂H₁₂ + 10NaH mixtures indicate the near complete formation of LiBH₄ and NaBH₄, respectively.
- Small-angle neutron scattering (SANS) measurements of partially LiBH₄-loaded carbon aerogels are consistent with the preferential filling of smaller pores and/or surface film formation.
- The structures of two new synthesized complex hydrides, Li₂{(BH₄)₂NH₃BH₃} and Ca{(BH₄)₂(NH₃BH₃)₂}, where solved by XRD.
- Neutron reflectometry of dehydrogenated of MgH₂ thin films suggests the formation of porous Mg.
- The thermodynamic Calphad database for Li-Mg-Ca-B-Si-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 NaBH₄, KBH₄, SrB₁₂H₁₂, BaB₁₂H₁₂, MgB₁₂H₁₂, xTHF (THF = tetrahydrofuran), Li₂(BH₄)₂(NH₃BH₃), Ca(BH₄)₂(NH₃BH₃), and LiBH₄ 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.

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, 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 continued our collaboration with Sandia National Laboratories (SNL), the Jet Propulsion Laboratory, the California Institute of Technology (Caltech), and the University of Maryland to investigate the structures and bonding in the alkali and alkaline-earth dodecahydro-closo-dodecaborates, which are possible intermediates in borohydride decomposition. Adding to our previously determined Li₂B₁₂H₁₂, Na₂B₁₂H₁₂, and Ca₂B₁₂H₁₂ structures, we have solved the isomorphic P₃1c structures of the heavier alkaline earth analogs of MgB₁₂H₁₂, namely SrB₁₂H₁₂ and BaB₁₂H₁₂ by a combination of XRD, NVS, and DFT calculations. The MgB₁₂H₁₂ structure still eludes us since it has been impossible as of yet to synthesize the totally anhydrous compound. NVS results for MgB₁₂H₁₂, partially solvated by ~0.5 THF/MgB₁₂H₁₂ suggests some similarity with the predicted structure of Ozolins, et al., [1] but definitive results await a solvent-free sample.

We have collaborated with SNL and Caltech to investigate the hydrogenation behavior of A₂B₁₂H₁₂ + 10AH mixtures (A=Li and Na) because of the A₂B₁₂H₁₂ intermediate’s high stability during the cycling of alkali-metal borohydrides. Spectral comparison by NVS of hydrogenated Li₂B₁₂H₁₂ + 10LiH and Na₂B₁₂H₁₂ + 10NaH mixtures with pure LiBH₄ and NaBH₄ compounds indicates that 773 K and 90 MPa H₂ is sufficient to transform the reactant mixtures into the pure borohydride compounds.

We have collaborated with the universities of Maryland and Michigan to unravel the details of BH₄⁻ rotational dynamics in both the ordered and disordered phases of NaBH₄ and in the disordered phase of KBH₄ by QNS [2]. Model fits of the QNS data indicate that the BH₄⁻ tetrahedron in the NaBH₄ ordered phase rotates with a combination of two-site and three-site reorientations that preserve its crystallographic orientation. Data for the disordered phases are well described by a model assuming nearest-neighbor BH₄⁻ jumps from one corner to another of a cube formed by eight hydrogen positions of half occupancy. Distinguishing between likely mechanisms for reorientation was made possible by collecting data at sufficiently high Q values. The derived activation energies for reorientation for the NaBH₄ low-temperature and high-temperature phases are 13.4±0.8 and 11.9±0.5 kJ/mol, respectively, and 14.6±0.5 kJ/mol for the KBH₄ high-temperature phase.

We have collaborated with HRL Laboratories, Lawrence Livermore National Laboratory, and the universities of Maryland, and Michigan to characterize the properties of LiBH₄ nanoconfined in carbon aerogels. SANS measurements for LiBH₄-filled and partially-filled 15 nm aerogels (Figure 1) indicate significant scattering differences at the higher momentum transfer (Q) values and similar scattering behavior at intermediate Q values. This suggests that the smallest pores fill first with no change in apparent mesopore geometry with filling. Although NVS indicates
that the vibrational modes for LiBH$_4$ in a 13 nm carbon aerogel exhibit only a minor (~10%) broadening compared to those for bulk LiBH$_4$. QNS measurements of the BH$_4^-$ rotational jump frequency for nanoconfined LiBH$_4$ (Figure 2) indicate a step at ~360 K denoting the orthorhombic-to-hexagonal phase transition, which is nearly 30 K lower than the transition temperature for bulk LiBH$_4$. This suggests that nanoconfinement perturbs bulk thermodynamic properties.

We have collaborated with the University of Maryland and General Motors to synthesize and evaluate two new borohydride-ammonia borane complex hydrides, Li$_2$(BH$_4$)$_2$NH$_3$BH$_3$ (Figure 3) and Ca(BH$_4$)$_2$(NH$_3$BH$_3$)$_2$ [3]. Their structures were determined using a combination of XRD and DFT calculations. Both structures are composed of alternating layers of borohydride anions and ammonia borane. Examination of bond lengths indicates ammonia borane ligands are stabilized in the structures mainly via dihydrogen bonding and interactions with their surrounding cations. Our experimental results show that more than 10 wt% and 11 wt% hydrogen can be released from Li$_2$(BH$_4$)$_2$NH$_3$BH$_3$ and Ca(BH$_4$)$_2$(NH$_3$BH$_3$)$_2$, respectively. Negligible ammonia was detected compared to ammonia borane and its amidoborane derivatives. Further improvements are needed to reduce borazine emission. Cycling studies show that Li$_2$(BH$_4$)$_2$NH$_3$BH$_3$ and Ca(BH$_4$)$_2$(NH$_3$BH$_3$)$_2$ can be partially rehydrogenated under hydrogen pressures at high temperatures.

We have collaborated with the universities of Stanford and Maryland to help characterize hydrogen concentration profiles in thin Mg films. We have continued our measurements of the hydrogen cycling of a single (25 nm Pd-capped) 100 nm Mg layer on a sapphire substrate. Under typical conditions of 343-373 K and 0.1 MPa H$_2$, neutron reflectivity results indicate an expansion of the Mg layer upon hydrogenation to MgH$_2$. This expansion remains upon dehydrogenation of the MgH$_2$ layer, suggesting that the regenerated Mg layer possesses a porous morphology.

The thermodynamic Calphad database has been updated and expanded to include descriptions for the solid phases MgB$_{12}$H$_{12}$ and Li$_2$B$_{12}$H$_{12}$. Experimental data for the ternary hydride phases are extremely sparse. For developing the thermodynamic descriptions of these phases, data from first-principles calculations provided by members of the Theory Group were used to supplement the experimental data. 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
reported experimental dehydrogenation reactions differ greatly. This is caused by slow reaction kinetics and the potential for the formation of metastable reaction products. These complications result in reduced reliability of thermodynamic descriptions obtained from experimental desorption data. The dehydrogenation path of Mg(BH$_4$)$_2$ is depicted in Figure 4. The calculated reaction path of the desorption of Mg(BH$_4$)$_2$ gives an extremely favorable desorption temperature and released amount of hydrogen, however, this reaction has not been observed in experiments. This indicates that at least some of the reported dehydrogenation reactions are not equilibrium reactions.

The addition of nitrogen to the six component H-Ca-Mg-Li-B-Si databases results in the addition of 6 binary and 15 ternary sub-systems. The evaluation of the literature revealed that for the addition of nitrogen to the database, the descriptions of 49 intermediate phases and 16 gaseous species are needed, but very few data are available. Sufficient data are only available for 6 of the 49 intermediate compounds and 8 of the 14 gaseous species. The evaluation of the Gibbs energy functions of the complex borohydrides showed that the uncertainties from the experimental desorption data are significant. Similar or even larger uncertainties will affect the Gibbs energy functions of most of the nitrogen-containing phases. Therefore, the decision was made not to add nitrogen at this point to the database.

**Conclusions and Future Directions**

- Neutron methods and Calphad computations have provided crucial, non-destructive characterization and predictive tools for the MHCoE.
- X-ray and neutron powder diffraction, neutron spectroscopy, and DFT calculations continued to provide a powerful combination for characterizing the structures and bonding of the dodecahydro-closo-dodecaborates. Spectroscopy was particularly useful to test predicted structures. Work is still in progress to synthesize and characterize anhydrous crystalline MgB$_{12}$H$_{12}$.
- We characterized the rotational dynamics of BH$_4^-$ anions in bulk compounds as a baseline for comparison with the dynamics found for nanoconfined compounds. Changes in rotational dynamics due to nanoconfinement may signal changes in thermodynamic properties.
- We continued to characterize various aspects of nanoconfinement in an attempt to understand its effect on the hydrogen cycling of LiBH$_4$ and indeed observed non-bulk-like effects. We will continue to use SANS to understand the relationship between pore morphology and filling behavior of nanoconfined storage materials.
- We synthesized two examples of a new family of complex hydrides, the borohydrde ammonia boranes, that may have potentially favorable cycling behavior for hydrogen storage.
- We continued to characterize the hydrogen cycling of Mg thin films by neutron reflectometry to understand the fundamental mechanisms involved.
- The thermodynamic Calphad database for Li-Mg-Ca-B-Si-H was expanded to include more gas phase species and ternary hydride phases. Creating a database with Gibbs energy functions from first principles calculations and incorporating it with Calphad descriptions of solution phases will combine the strengths of both methods.

**FY 2010 Publications/Presentations**


References

IV.A.1i Metal Borohydrides, Ammines, and Aluminum Hydrides as Hydrogen Storage Materials

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

Objectives

ORNL is conducting research to develop the
chemistry for a reversible hydrogen storage system
based on complex hydrides, chosen mostly from the
metal borohydrides and ammine/amides/imides of
metal borohydrides, with particular emphasis on the
aluminum complexes of these materials.  These materials
are expected to achieve the DOE/FreedomCAR
performance targets for 2010 as well as 2015.  Research
at ORNL focuses on high hydrogen content materials
(>10 wt%).

Technical Barriers

This project addresses the following technical
barriers from the Hydrogen Storage section of the
Fuel Cell Technologies Program Multi-Year Research,
Development and Demonstration Plan for Fiscal Year
(FY) 2010 and FY 2015:
(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.  The materials in Table 1
are related materials for reference or materials that have
been investigated by ORNL in the last year (percentages
in table below are for H₂ release only).  The DOE
system targets to which we want to compare are 4.5% hydrogen for 2010 and 5.5% hydrogen for 2015.  The material of interest must allow for a weight penalty for the container.

TABLE 1.  Progress towards Meeting Technical Targets

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula Weight</th>
<th>% Hydrogen (calc)</th>
<th>% Hydrogen Evolved (500°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(BH₄)₃</td>
<td>71.508</td>
<td>16.92%</td>
<td>12.7%</td>
</tr>
<tr>
<td>Al(BH₄)₃⋅2NH₃</td>
<td>105.570</td>
<td>17.19%</td>
<td>15.1%</td>
</tr>
<tr>
<td>Al(BH₄)₃⋅3NH₃</td>
<td>122.601</td>
<td>17.26%</td>
<td>15.9%</td>
</tr>
<tr>
<td>NH₃BH₃</td>
<td>30.865</td>
<td>19.59%</td>
<td>~12%</td>
</tr>
</tbody>
</table>

Accomplishments

Progress was made toward defining the structure
and understanding the mechanism of hydrogen release
from aluminum ammine borohydrides:
• NH₃ adducts of Al(BH₄)₃ are formed both in
  solution and under solvent-free conditions and the
  products depend on reaction conditions (solvent/
solvent-free).
• Quantity of hydrogen desorbed from aluminum
  ammine borohydrides indicates both NH₃ and BH₄⁻
  contribute to hydrogen evolution reaction, and the
  product formed in toluene solvent, Al(BH₄)₃⋅3NH₃⁻,
  evolves as much hydrogen as a function of
temperature as ammonia borane, NH₃BH₃.
• Structure of product formed during reaction of
  Al(BH₄)₃ with NH₃ in diethyl ether gives insight into
  the reaction mechanism for hydrogen desorption,
  and the use of deuterated ammonia (ND₃) shows
  first hydrogen evolved is deuterium hydride
  (indicating equal contributions from ND₃ and BH₄⁻).
• Solid state magic angle spinning-nuclear magnetic
  resonance (MAS-NMR) spectroscopy (collaboration
  with the California Institute of Technology
  [Caltech] and Jet Propulsion Laboratory [JPL]) of
  the hydrogen desorption reaction products show
  definitively that (1) Al metal is not a product and (2)
  a boron-nitride polymer is formed.

☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐
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 2015. ORNL is developing new materials, developing synthetic methods to prepare materials, and studying chemical reactions that will lead to materials that reversibly store hydrogen. Our research takes advantage of expertise in handling oxygen and moisture sensitive reagents, knowledge of reaction pathways in solution, and insight into mechanisms of reactions and catalytic pathways. The research at ORNL emphasizes high hydrogen content materials (>10 wt% hydrogen).

In past work the thermal decomposition of Al(BH₄)₃ was studied in some detail in an effort to determine the dehydrogenation mechanism. In these studies we concluded that Al(BH₄)₃ follows a step-by-step loss of BH₃ during pyrolysis, ultimately producing AlH₃ and diborane (or higher borohydride clusters) which undergo their own thermal decomposition to form hydrogen, aluminum and a (BH)n polymeric residue. At 150°C, diborane is the predominant product but hydrogen becomes the dominant product as the temperature is increased. At 300°C and higher, the rate of decomposition of AlH₃ and diborane to form products (H₂) is fast compared to loss of BH₃ from Al(BH₄)₃.

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 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 (FTIR) spectroscopy, X-ray diffraction (XRD), and elemental analysis by inductively coupled plasma atomic emission spectroscopy as well as solution NMR are available at ORNL to characterize solid reaction products, and Raman and solid-state NMR are available through collaboration with Metal Hydride Center of Excellence partners. During this year ORNL obtained a thermogravimetric analyzer (TGA) which is housed in a glove box (<1 ppm H₂O and O₂) with capability of analysis of the evolved gas by mass spectrometry. 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

Most of the experimental work in the last year has been concerned with characterization of the products of the reaction of ammonia with aluminum borohydride. We have previously reported that a rapid, solvent-free reaction occurs between Al(BH₄)₃ and NH₃

\[ \text{Al(BH₄)₃} + 2 \text{NH₃} \rightarrow \text{Al(BH₃)₂}2\text{NH₃} \]

The structure of the product is not known with certainty but it is thought to be a trigonal bipyramid with axial NH₃ ligands and equatorial BH₃ ligands. The separation of ammonia with aluminum borohydride in solvents gives different products from the solvent-free reaction. Al(BH₄)₃ was previously reported by Bird and Wallbridge [1] to react with anhydrous ammonia in a 1:2 ratio in the absence of solvent to form Al(BH₃)₃(NH₃)₂ which is believed to have a trigonal bipyramidal geometry about the Al(III) center with axial NH₃ groups. The theoretical hydrogen content of this material is 17.2 wt% and we have observed that hydrogen is evolved at a lower temperature than from the parent compound, Al(BH₄)₃. The total hydrogen evolved is 15.2 wt% upon heating to 550°C. From the large amount of H₂ evolved it is apparent that both the BH₄⁻ and NH₃ groups are reactive.

This Al(BH₃)₃(NH₃)₂ compound was also prepared using N-15 enriched ammonia, ¹⁵NH₃, and deuterated ammonia, ND₃. The normal isotopic composition ammonia and N-15 enriched compounds was supplied to our collaborators at JPL and CalTech for analysis by solid-state NMR. Solid-state NMR measurements of ²H, ¹¹B, and ²⁷Al as well as the ¹⁵N resonances were determined for the starting diamine as well as at various stages of dehydrogenation. At complete dehydrogenation the ¹⁵B MAS-NMR signal is clearly consistent with the formation of a (BH-NH₃)ₙ polymer, and there do not appear to be any clearly distinguishable intermediates with distinctly different resonances between the starting material and the final product. The ²⁷Al NMR indicates that Al metal is not a product of thermal degradation under the circumstances of gas evolution into a vacuum. Unfortunately the ¹⁵N NMR of the enriched ammonia adduct was not definitive.

Mass spectrometry of the evolved gas from the ND₃ derivative is particularly helpful in assigning observed peaks to individual chemical species. The initial hydrogen which is evolved has mass 3, indicating one hydrogen atom originates from ND₃ and one originates from BH₄⁻. We observe trace amounts of borazine, a cyclic six membered ring species in which three of
the hydrogen atoms are deuterium, (ND-BH)_4. It is interesting that up to approximately 200°C, there is no definitive evidence for exchange of hydrogen between B and N. The challenge of future work is stop the reaction at a stage that will allow the reaction to be reverse, and that will be the focus of work in the latter part of FY 2010.

The reaction of Al(BH_4)_3 with NH_3 in toluene gives a product which has an XRD pattern different from the ammonia adduct in the solvent free reaction; the elemental analysis of the product suggest the composition is Al(BH_4)_3•5NH_3. Bird and Wallbridge [1] indicate two moles of NH_3 react with aluminum borohydride in the stoichiometric ratio. However, the species [Al(NH_3)_6](BH_4)_3 in which aluminum is octahedrally coordinated by six ammonia ligands, is formed with excess ammonia. Both the FTIR spectrum and the XRD pattern of our product show the hexamine is not formed. High resolution XRD of this compound was obtained at the National Synchrotron Light Source at Brookhaven National Laboratory. A preliminary solution of the structure which was reported at the annual merit review meeting last year is now believed to be in error. The correct structure is now believed to have two coordinated borohydride groups and three coordinated ammonia groups along with one ionic borohydride group, [Al(BH_4)_2(NH_3)_3][BH_4]. The tentative structure is shown in Figure 1. Preliminary calculations by B. P. Hay [2] confirm that this structure is an energy minimum with additional stabilization provided by hydrogen bonding between the ionic borohydride group and the coordinated ammines.

The infrared spectra of the compounds we prepared from reaction of NH_3 with Al(BH_4)_3 either in the absence of solvent or using toluene as the solvent are roughly in agreement with the spectrum which was reported in the literature by Bird and Wallbridge for Al(BH_4)_3(NH_3)_2 or for Al(BH_4)_3NH_3. Figure 2 shows the normalized FTIR spectra of our two compounds along with the difference spectrum. As a first approximation, the spectra of the two compounds have a lot of peaks in common, and we anticipate that the structures of the two compounds are not vastly different. The infrared spectrum of [Al(NH_3)_6](BH_4)_3 as reported by both Bird and Wallbridge and by Semenenko is quite different from what we have observed, and along with the XRD serve as definitive evidence to prove that our compounds are not [Al(NH_3)_6](BH_4)_3. The spectrum of the material synthesized from toluene, Al(BH_4)_3(NH_3)_3, has less bands than the solvent free preparation. The high resolution XRD structure determination shown in Figure 1 has the chemical composition [Al(BH_4)_2(NH_3)_3](BH_4). It is anticipated that if this structure is correct, distinctive B-H stretching vibrations characteristic of uncoordinated borohydride will be observed, but these vibrations appear to be absent. Thus further

FIGURE 1. Structure of [Al(BH_4)_2(NH_3)_3](BH_4) with B and N atoms shown as green and blue spheres respectively. The position of H atoms was not refined.

FIGURE 2. The FTIR spectra of the solvent free preparation Al(BH_4)_3•2(NH_3) (green) and the synthesis from toluene [Al(BH_4)_2(NH_3)_3]BH_4 (red) are shown (KBr pellets, protected from air) Calculated difference spectrum (black) is shown at the bottom as negative peaks.
characterization of this very interesting and high hydrogen content material is warranted.

Conclusions and Future Directions

The adducts of ammonia with aluminum borohydride are high hydrogen content materials in which both the ammonia and borohydride groups contribute to hydrogen evolution, but the product depends on the reaction conditions:

- Refine the elemental analysis of the aluminum ammine borohydrides and precisely determine the amounts of gaseous products in the reaction of ammonia with aluminum borohydride in solvents (toluene and ether).
- Multinuclear solution and solid MAS-NMR of aluminum ammine borohydrides will be used to identify intermediates in desorption reactions.
- TGA with evolved gas analysis by mass spectrometry will be implemented to follow reactions of ammine metal borohydrides and identify intermediates.
- Continue study of aluminoboranes in collaboration with J.-C. Zhao, Ohio State University.

FY 2010 Publications/Presentations


References

2. B.P. Hay, unpublished results.
IV.A.1j Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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Contract Number: DE-AI01-05EE11105
Subcontractors:
California Institute of Technology (Caltech),
Solid-State NMR Facility, Pasadena, CA
Project Start Date: April, 2005
Project End Date: September, 2010

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 Fuel Cell 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

The clearest 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 H₂ content by weight in the engineered system. The material encapsulated in that system, obviously, must possess a higher content of H₂, perhaps in the 9-12% range. For several reasons, the Ca(BH₄)₂ system (theoretical 12 wt%) that was promising in prior years has shown several serious issues with its development. Turning to other systems as described below, some attention has been given to elucidating reaction processes and answering questions about capacities and charge/discharge rates (i.e., kinetics).

Accomplishments

- Via magic angle spinning – nuclear magnetic resonance (MAS-NMR) and thermo-volumetric methods, provided phase characterization, kinetics (i.e., diffusion behavior), and reversibility assessments in numerous systems (i.e., Mg-B-H, Ca-B-H + C-aerogel, Al-B-N-H).
- Investigated the effectiveness of specific additives (ScCl₃, TiF₃) on the desorption/absorption kinetics of the Mg(BH₄)₂ system by the use of MAS-NMR. Positive effects on the desorption kinetics were seen with 5 mol% of either additive, as well as an effect on the Mg(BH₄)₂ α to β phase transition and the production of borohydride (BH) intermediates.
- Determined that several pathways for boron products exist in the reaction pathways of hydrogen-metal BH systems. NMR is capable of determining the presence and activity of such products as MgB₂, MgB₁₂H₁₂, and amorphous boron “composites” within the Mg(BH₄)₂ system.
- Investigated the reactivity, capacity, and kinetic performance of the Al(BH₄)₃·2(NH₃) system. The total available H₂ capacity of this system has been shown to exceed 9% H₂ by mass at 350°C, with 7% available at 250°C.
- Continuing an Oak Ridge National Laboratory (ORNL)/Caltech/JPL study on the Al-B-N-H system, utilized ¹⁵N in the form of preparing labeled chemistries suitable for ¹⁵N NMR spectroscopy. Such detail proved necessary for elucidating the N-environments in the product, the precise chemical structure of which is still difficult to determine.

Introduction

Activities at JPL under the auspices of DOE’s Metal Hydride Center of Excellence (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, MgH₂, and LiBH₄, complex amide/imides, BH₃, and AlH₃-based hydrides as well as other promising samples provided by many MHCoE partners; significant attention in the latter part of the project has been paid to the metal BHs with Mg, Ca, Sc, and Al cations, as well as dual-cation systems. Along the way, the fundamental role of the B₁₂H₁₂₂⁻ anion and associated intermediate reaction pathways in preventing reversibility has been elucidated. Throughout, JPL has had 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 BHs 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, often providing insight into chemical processes, configurations, and reaction pathways otherwise impossible to determine via other analytical spectroscopic methods.

**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 as an investigation into the Mg(BH₄)$_2$ system enters its final phases; metal BHs from ORNL and Ca(BH₄)$_2$ from United Technologies Research Center (UTRC) have also been part of JPL’s recent collaborative role.

A comprehensive materials development and characterization project continues to be the central focus of JPL’s many roles in MHCoE. Of primary importance is the use of thermo-volumetric measurements to determine hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides. In addition, powder X-ray diffraction 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**

Under the guidance of MHCoE Project B (Complex Anionic Materials), JPL performed work relating to phase identification and reaction pathway discovery of various BHs. Samples of Ca(BH₄)$_2$ scaffolded with carbon aerogel were provided by partners at UTRC; these samples represented materials both as-made (38% by weight of the BH) and following several cycles of hydrogenation. JPL/Caltech were unable to determine a definitive effect on the use of C-aerogel as a scaffolding/encapsulation agent. In Figure 1, MAS-NMR shows the presence of the now familiar [B₁₂H₁₂⁻] intermediate as well as localized B-O bonding following several cycles of hydrogen absorption. Other than a partial peak shift, no improvement in performance was seen. It should be noted that the B-O bonding could be due to contamination of the parent sample by air.

Together with partners at Sandia National Laboratories, JPL/Caltech engaged in the study of the effects of various additives (ScCl₃, TiF₃) on the kinetics and reversibility of the Mg(BH₄)$_2$ system. Figure 2 shows a marked effect on the room-temperature stability of Mg(BH₄)$_2$, where an α to β phase transition is interpreted as a positive effect on reaction kinetics in this system due to the presence of the additives. Similarly, Figure 3 shows a high-temperature phase transition at 413 K, 40 K lower than the neat parent material; improved kinetics are a result. NMR has also elucidated the family of intermediates in this

![FIGURE 1. $^{11}$B MAS NMR spectra illustrating the presence of the \([\text{B}_12\text{H}_{12}]^{2-}\) intermediate as well as localized B-O bonding in the Ca(BH₄)$_2$ + C-aerogel system.](image-url)
system; Figure 4 suggests that the presence of additives in this system have differential effects on the possible intermediates.

JPL has continued to investigate novel Al-B-N-H chemistries with partner ORNL; during 2009-2010 the focus has been on the compound Al(BH$_4$)$_3$·2(NH$_3$)$_2$, which was synthesized at ORNL using wet chemistry methods. This material was characterized using JPL’s Sieverts’ apparatus. For the purposes of NMR investigation, versions of this system were also synthesized in the form Al(BH$_4$)$_3$·2(15NH$_3$)$_2$, as the 15N is a more NMR-active nucleus than the normal isotopic form. Several of these samples were reacted at ORNL and characterized using Caltech’s NMR facilities. Figure 5 shows the results of the desorption of the as-made material at JPL in two steps, allowing...
for intermediate NMR sampling; the total available H₂ content was greater than 9% by mass. Figure 6 shows the \(^1\)H and \(^{11}\)B NMR spectra of the samples reacted at ORNL; \(^{11}\)B MAS NMR of the samples show a trend similar to Mg(BH₄)ₓ•2(NH₃) cases where BH₄ units release hydrogen to form B-N-H polymeric species. Investigations of specific samples enriched with \(^{15}\)N show two distinct NH₃ bonding environments as well as apparent B-N-H bonding activity at higher temperatures (~200°C), but more study is required to resolve these details. As also shown in Figure 7, there is the suggestion of multiple Al bonding sites as well, suggesting perhaps a medium-range order to the material. Again, more study is desired. This material system continues to prove interesting, even though the formation of the dodecaborane intermediate still seems difficult to avoid.

**Conclusions and Future Directions**

As currently planned, this is the last year of record for JPL’s participation in the MHCoe project. As the effort closes out, JPL plans to continue...
certain specific lines of investigation while preparing closeout documentation and ensuring the archiving of information produced under this effort. Special attention will be given to feeding information to the Hydrogen Storage Engineering Center of Excellence, a parallel DOE project that also includes JPL.

**FY 2010 Publications/Presentations**


IV.A.1k Li-Mg-N Hydrogen Storage Materials

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Project End Date: June 30, 2010

Objectives

- Determine the sorption kinetics for the transition metal-catalyzed 2LiH+Mg(NH$_2$)$_2$+MgH$_2$ system under the full spectrum of temperatures and pressures required for hydrogen storage system design.
- Explore the effect of catalyst loading on both charge and discharge reaction pathways and kinetics as well as ammonia release.
- Identify reversible hydrogen storage compounds in the mixed metal/amide-borohydride system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan in descending order of impact:

- System Weight and Volume
- 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$_3$N$_2$, LiMgN and a minor amount of an unidentified phase [<5%]).
- All chemical modifications tested thus far, while significantly increasing desorption rate in the first cycle, have been shown to have no effect on sorption kinetics after the third cycle.
- A characteristic charging time (t$_{80}$) of 30 minutes, calculated for the isothermal charging results, is faster than those presented for this material elsewhere in the literature.
- Processing methods have been shown to greatly affect sorption kinetics and capacity with high energy processing leading to formation of NH$_3$ and loss of capacity (6.66 wt%) while lower energy processes minimizing NH$_3$ release and resulting in higher capacities (8.0 wt%) and sorption kinetics.
- Additions of TiN have been shown to increase the release temperature of NH$_3$ from 220 to 250°C.
- The formation of mixed bi-metallic amides/borohydrides have resulted in lower dehydrogenation temperatures and reduced ammonia release compared to the individual amide or borohydride materials.

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 2LiH/MgH$_2$/Mg(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 2LiH+Mg(NH$_2$)$_2$+MgH$_2$ which decomposes to LiMgN plus 8.1 wt% H$_2$ [1] with a calculated enthalpy of desorption of 32 kJ/mole H$_2$. This composition has
been reported to be reversible under fairly moderate conditions (160°C – 220°C for dehydriding, 160°C and 2,000 psi for rehydridding) [1]. This study of the LiMgN used an autoclave-type high-pressure charging apparatus and transient thermogravimetric 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.

Additionally, materials of the form $M^1M^2(BH_4)\text{y}(NH_2)_z$, where $M^1=\text{Li, Na, K and } M^2=\text{Mg, Ca, Ti and/or other}$ transition metals are of interest for their high hydrogen storage as well as potential novel phase properties. New materials of these di-anionic species such as Li$_2$BH$_4$(NH$_2$)$_2$, Mg$_2$NH$_2$, and Ca$_2$NH$_2$ have been identified, which have been found to discharge initial hydrogen from the amide complex at lower temperatures with the borohydride present.

**Approach**

**LiH/Mg(NH$_2$)$_2$**

The previously identified LiMgN material was studied by ball milling the precursor LiNH$_2$ and MgH$_2$ materials with the various modifiers 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 30:1, following the work of Lu [1]. A Seivert’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 pressure, and the composition of the modifiers used to activate the material.

**Mixed Amide/Borohydrides**

The synthesis of materials was accomplished by ball milling one component metal borohydride (Ca(BH$_4$)$_2$, Mg(BH$_4$)$_2$) with another metal amide (LiNH$_2$). This is also extended for metal amides (Ca(NH$_2$)$_2$, Mg(NH$_2$)$_2$) with lithium borohydride (LiBH$_4$). These precursors such as LiNH$_2$, LiBH$_4$, and Mg(BH$_4$)$_2$ are available commercially through Aldrich, with others such as Mg(NH$_2$)$_2$ and Ca(NH$_2$)$_2$, prepared by the ammoniation of Mg and Ca inside a high pressure reactor. Once the desired metal hydrides are ball milled, powder X-ray diffraction (XRD) was used as the initial screening tool. Furthermore, thermo-gravimetric analyses, in conjunction with mass spectroscopy, was used to verify mass loss vs. temperature and identify the gas decomposition products as a function of temperature. Fourier transform infrared (FTIR), Raman scattering and nuclear magnetic resonance were used to verify investigate the characteristics of new formed compounds.

**Results**

**LiNH$_2$/MgH$_2$ Kinetics**

Previously, this study reported the charge and discharge profiles for precursor materials LiNH$_2$ and MgH$_2$ in a 1:1 mole ratio with 0.67 m% TiCl$_3$ 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 Mg$_x$N$_y$ partially substituted (Li,Mg)$_x$N$_y$ phase was detected using powder XRD. Other researchers have observed the presence of alternate discharge products in this system as well [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 were used to compare differing compositions, catalysts etc. A traditional kinetic analysis on the 0.67 m% TiCl$_3$ 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 isocconversional 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 various modifiers, material was prepared at the stoichiometric ratio of LiNH$_2$:MgH$_2$ (1:1) with 1.5 mol% TiCl$_3$, VCl$_3$, ScCl$_3$, NiCl$_2$, or TiN added. The initial decomposition data for the modified material are shown in Table 1. By adding a modifier, the initial hydrogen desorption temperature of the began between 105°C and 120°C, lower than the 135°C release temperature for the unmodified material. Compositional additions also greatly affect ammonia release. As seen in Table 1, the mixtures with TiCl$_3$, VCl$_3$, ScCl$_3$, and NiCl$_2$ released ammonia at temperatures lower or equal to the unmodified material, approximately 230°C. Through a metathesis reaction between LiNH$_2$, and transition metal chlorides, modification resulted in the formation of LiCl and a transition metal through the release of NH$_3$. For all additions other than TiN, the H$_2$ and NH$_3$ peaks were coincidental. TiN additions decoupled the these two peaks, substantially increasing the NH$_3$ peak by
20°C while maintaining the H₂ peak at 270°C. Lai-Peng Ma, et al. have reported that for the 2:1 LiNH₂:MgH₂, the defective metal-N pairs in transition metal nitrides (specifically TaN and TiN) act as active sites in favor of dissociating the N-H bond of the amide in the system, which then promotes the generation of reactant species [9]. This suggests that TiN is not only effective at reducing the temperature of hydrogen release but also as acting as an ammonia mitigant.

The bed discharge rates were calculated on a mass-specific basis, determining from data the quantity of hydride bed that would be required to store 5 kg of hydrogen. From these data, it was observed that after two sorption cycles (see Figure 1), the modifier composition has little effect on the discharging rate. This was determined to be due to the metathesis reaction between the metal chlorides and LiNH₂.

To optimize the cycling conditions, a desorption temperature study was conducted on the unmodified LiNH₂:MgH₂ mixture, as seen in Figure 2.

A strong effect of discharging temperature on the discharge rate is observed, with a more linear rate observed for the 200°C. The discharge rate associated with 200°C is a third of the 2010 DOE technical target of 3 gH₂/s.

**Mixed Amide/Borohydrides**

Figure 3 shows the TGA results of Ca(NH₂)₂, LiBH₄, and various mixtures of Ca(NH₂)₂/LiBH₄. The unmodified samples show a much higher onset of decomposition with respect to the mixtures. The addition of more Ca(NH₂)₂ resulted in a single decomposition similar to the starting amide material. This was also true for 3LiBH₄:Ca(NH₂)₂, which had a 2-step decomposition reaction, but at a significantly lower temperature than pure LiBH₄. These samples were characterized using mass spectroscopy and XRD. From mass spectroscopy, the addition of LiBH₄ reduces the release of ammonia and increases the amount of hydrogen released. Similar results were found with the addition of Mg(NH₂)₂, but the initial decomposition of

**TABLE 1.** Summary of TGA/residual gas analysis decomposition data of the as-milled 1:1 LiNH₂:MgH₂ samples without and with various additions while heating from 30°C to 400°C at 5°C/min.

<table>
<thead>
<tr>
<th>Compositional Modification</th>
<th>Theoretical H₂ Weight%</th>
<th>Total Weight% Released</th>
<th>Initial Hydrogen Release Temperature (°C)</th>
<th>H¹ (°C)</th>
<th>H² (°C)</th>
<th>H³ (°C)</th>
<th>Initial Ammonia Release Temperature (°C)</th>
<th>Ammonia Peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Modification</td>
<td>8.14</td>
<td>10.5</td>
<td>135</td>
<td>204</td>
<td>260</td>
<td>340</td>
<td>220</td>
<td>265</td>
</tr>
<tr>
<td>1.5 mol% TiCl₃</td>
<td>7.85</td>
<td>7.87</td>
<td>105</td>
<td>201</td>
<td>240</td>
<td>285</td>
<td>225</td>
<td>245</td>
</tr>
<tr>
<td>1.5 mol% VCl₃</td>
<td>7.46</td>
<td>6.5</td>
<td>115</td>
<td>190</td>
<td>245</td>
<td>290</td>
<td>225</td>
<td>250</td>
</tr>
<tr>
<td>1.5 mol% TiN</td>
<td>7.94</td>
<td>7.19</td>
<td>120</td>
<td>210</td>
<td>255</td>
<td>325</td>
<td>247</td>
<td>277</td>
</tr>
<tr>
<td>1.5 mol% ScCl₃</td>
<td>7.48</td>
<td>10.32</td>
<td>105</td>
<td>270</td>
<td>335</td>
<td>-</td>
<td>220</td>
<td>277</td>
</tr>
<tr>
<td>1.5 mol% NiCl₂</td>
<td>7.57</td>
<td>7.59 (by 300°C)</td>
<td>120</td>
<td>230</td>
<td>290</td>
<td>-</td>
<td>186</td>
<td>230</td>
</tr>
</tbody>
</table>

**FIGURE 1.** Rates of hydrogen discharge at 260°C into 1 bar of pressure during the first 30 minutes of each cycle for the unmodified (crosses), TiCl₃ (diamonds), VCl₃ (triangles), NiCl₂ (circles), ScCl₃ (asterisk), and TiN (squares) systems.

**FIGURE 2.** Rates of hydrogen discharge at 200, 220, and 260°C into 1 bar of pressure during the first 30 minutes of each cycle for the unmodified system.
the mixtures occur at a higher temperature. Isothermal Sievert's measurements were also conducted to evaluate the mixture's cyclic characteristics compared to their respective starting materials.

Conclusions

LiMgN

- Desorption of LiMgN at 200°C resulted in a constant discharge rate over four isothermal cycles.
- Discharge rate of a hydride bed at 200°C is a third of the 2010 DOE technical target of 3 gH₂/s.
- Desorption at 260°C and above leads to the loss of essential nitrogen.
- Metathesis reaction between LiNH₂ and metal chlorides resulted in the loss of nitrogen through ammonia release and the loss of capacity with the formation of LiCl.
- Desorption products were identified as a mixture of Li₅Ca(BH₄)ₓ(NH₂)ᵧ, Mg₃N₂, LiMgN with a minor amount, <5% of an unidentified phase.
- TiN shows promise as a modifier by increasing the temperature of ammonia release.

Mixed Amide/Borohydrides

- Ca(NH₂)₂ and Mg(NH₂)₂ have been successfully synthesized with >95% purity through direct ammoniation.
- Mixtures of Mg(BH₄)₂ and LiNH₂ have shown good absorption capabilities but limited kinetically on desorption through two cycles.

- Mixtures of Mg(BH₄)₂ and LiNH₂ contain multiple H₂ releases, with reduced release of NH₃.
- Raman has confirmed that a new compound is formed in mixtures of NH₃BH₃ to Ca(BH₄)₂ and LiNH₂.
- Initial results show desorption of H₂ as low as 150°C for the mixture of Ca(BH₄)₂:LiNH₂:NH₃BH₃.

Future Directions

- Complete temperature and pressure dependence on absorption rates.
- Test other catalysts to render faster kinetics, lower temperatures of operation (e.g. KH, LiH, LiBH₄, nano-Ti, etc…).
- Analyze the purity of the discharged H₂ as a function of temperature using FTIR.
- Identify structures and compositions of Li₅Ca(BH₄)ₓ(NH₂)ᵧ, Mg₃N₂, LiMgN with a minor amount, <5% of an unidentified phase.
- Synthesize and characterize LiMg(BH₄)ₓ(NH₂)ᵧ, LiCa(BH₄)ₓ(NH₂)ᵧ, and LiBH₄ as precursors for synthesis of Mg(NH₂)₂ and Ca(NH₂)₂ with LiBH₄.
- Characterize structures and compositions of LiCa(BH₄)ₓ(NH₂)ᵧ, Mg₃N₂, and LiMgN with a minor amount, <5% of an unidentified phase.

References

IV.A.11 Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

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Contract Number:  DE-FC36-05GO15068
Project Start Date:  October 1, 2005
Project End Date:   September 2010

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 Fuel Cell 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

- Determined causes for loss of cycle in Li₃N-H₂ system, using calculation of phase diagrams (CALPHAD) thermodynamic modeling and experiments.
  - It was determined that there was continuous loss of nitrogen from solid phases during the dehydrogenation cycle, leading to formation of rather stable LiH phase which traps the hydrogen at operating temperature of 528 K (255°C), consequently los of cycle life.
  - Significant cycle life improvements were achieved by using mixtures of H₂ and N₂ gases; using 80/20 molar mixtures of H₂/N₂; we obtained near starting Li₃N-H₂ reversible capacity of ~10 wt% H at 255°C after 516 cycles.
  - Critical phase reaction pathways determined using progressive incremental loading of hydrogen in Li₃N, supported by CALPHAD developed Li-N-H phase diagrams.
  - Determined the formation of the Li₃NH 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 cubic phase of Li₁₂₋ₓNH₁ₓ type was found.
  - Improved kinetics observed at higher pressures in the Li-N-H system.

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IV.A Hydrogen Storage / Metal Hydride CoE

Introduction

Trace amount (ppm levels) of gaseous impurities in ultra-high purity (UHP) hydrogen may lose in hydrogen capacity in solid state storage of hydrogen in complex hydrides. To evaluate these effects we performed extrinsic thermal cycling with impure hydrogen; these tests are rather long. We also performed thermal aging where necessary. 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, hydrogen is used in research laboratory for the development of metal hydrides. However, the commercial hydrogen will always have some very low level impurities (ppm levels); typically O₂, H₂O, CH₄, N₂, hydrocarbons, and others in hydrogen. Typical industrial grade hydrogen, that we used showed: “Hydrogen min % (v/v) 99%, others in industrial grade hydrogen, hydrogen. Typical hydrocarbons: 10 ppm, CO₂ ~10 ppm, CO ~10 ppm, water ~32 ppm, O₂ ~400 ppm, total hydrocarbons: 10 ppm, CO ~10 ppm, CO ~10 ppm, argon may be present, reads as oxygen.” We also used special 100 ppm O₂, 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 if there are trace amounts of impurities in the hydrogen. Parallel contamination studies are essential for evaluation impurity effect, before design of any hydride bed for a vehicular application containing complex hydride materials. 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 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 (MHCoE) 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 central problem is that Li₃NH will not reverse easily to either Li₄NH or Li₃N, at 255°C, leading to approximately 5.8 wt% H reversible capacity. In addition, a LiH phase forms during hydriding of Li₃N which is difficult to reduce back to Li₃N at 255°C. However, Huq et al. [1] showed that at ~320°C decomposition of LiH→Li,NH was possible. To elucidate the various phase transition mechanisms we developed ternary phase diagrams of Li-N-H at various pressures and temperatures.

We also found that during repeated cycling there was a loss of nitrogen in the system [2]. The data indicated that during the desorption cycle (under dynamic vacuum) we were desorbing nitrogen and hydrogen or possibly LiN gas. Thus, we decided to use mixtures of N₂-H₂ to compensate for the lost nitrogen. Nitrogen compensation cycling results that show up to 10 wt% H reversibility are discussed.

Approach

In this research, we are conducting experiments on cycling and aging tests of materials (as described in the above section) developed by the MHCoE 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 Li₃N 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 Nature paper [3].

We have studied the Li-N-H system in which an unusual improvement of hydrogen capacity is observed during pressure cycling at 528 K using mixed nitrogen/hydrogen gases. Without mixing in nitrogen, we observe a loss in hydrogen capacity, from ~10.2 to 3.1 wt% H after 501 cycles, during cycling due to the formation of a small amount of liquid lithium metal which forms a stable LiH phase during each cycle; this leads to a loss of nitrogen that significantly degrades the reversible hydrogen capacity of the Li,N-H system. In this paper we report results from data obtained by prolonged pressure cycling of Li₃N with H₂/100 ppm N₂ and 80/20 H₂/N₂ mixed gases. We observe a significantly enhanced reversible capacity of up to ~10 wt% H after 516 cycles with 80/20 H₂/N₂ mixtures, an improvement of ~7.1 wt% H as compared to using hydrogen with nitrogen additives. We attribute this enhancement to the reaction of nitrogen with liquid lithium during cycling as the Gibbs energies of formation of Li₃N (∆G° = -100.16 kJ/mol) are more negative than that of LiH phase (∆G° = -50.74 kJ/mol). We propose that there is continuous accumulation of the Li₃NH phase and minimizations of LiH formation as these materials...
are subjected to many cycles. The cyclic behavior mechanism of Li₃N with H₂/N₂ gas mixtures is quite a different phenomenon as compared to mechanisms occurring in classical hydrides.

Results

In this study we present the results of hydriding of Li₃N, with no catalyst, under different conditions. In our previous work (Chien et al. Ref. [2]) the results from Li₃N and industrial hydrogen with ppm levels of impurities were discussed. It was found that during pressure cycling of Li₃N with H₂ (under similar conditions as this study) there was a loss of nitrogen during cycling, and LiH formation increased with the number of cycles.

Pressure Cycling With Industrial Hydrogen

Pressure cycling under hydrogen without nitrogen additions showed a steady decline of the hydrogen capacity from ~10.1 to 3.2 wt% H after 501 cycles [2]. The mechanism suggested for this is the formation of LiH due to the loss of nitrogen, possibly in the form of LiN or NH₃, during the (dynamic vacuum) desorption cycle.

To mitigate the effect of lost nitrogen, we used mixtures of hydrogen and nitrogen to observe if the loss of hydrogen capacity was affected. Initially, we used 100 ppm levels of nitrogen in hydrogen. Then we increased the amount to 80/20 H₂/N₂ molar ratio, and finally to an excess of nitrogen 25/75 H₂/N₂.

Nitrogen Compensated Cycling Results

Initial experiments were performed by hydriding Li₃N with (2 bar) hydrogen mixed with 100 ppm nitrogen at 528 K followed by dynamic vacuum desorption for half hour each, in the cycling apparatus. The sample was then transferred to a Sieverts apparatus to obtain isotherms using UHP hydrogen gas after 345, and 853 cycles. Isotherms taken at 528 K and loading up to ~10 bar hydrogen showed that the cycling with 100 ppm nitrogen improved the hydrogen capacity as illustrated in Figure 1. We include data from our previous work designated as “1 cycle H₂,” which was taken after the “zeroth cycle.” When the hydrogen is added to Li₃N for the very first time, we refer to this as “zeroth cycle.” We obtained ~10.5 wt% H capacity, similar to reported by Chen et al. [2]. Then during the very next cycle, referred to as “1 cycle H₂,” the majority of the hydrogen could not be desorbed from the solids; only ~5.8 wt% H is reversibly absorbed. This is due to fact that the rest of hydrogen is trapped in LiH and Li₂NH phase that did not revert back to the Li₃N phase at 528 K. This “1 cycle H₂,” is used as a bench mark isotherm for comparison purposes. We now compare results obtained by cycling Li₃N with H₂-100 ppm N₂ mixed gases, up to 345 cycles, and noted an increase in capacity from 5.8 to ~7 wt% H. A further increase in the number of cycles to 853 led to a further enhancement from ~7 to ~8.5 w.% H (Figure 1). This trend in the increase of the capacity as a function of cycles is quite opposite to what we observed using hydrogen gas with no nitrogen.

In the next set of experiments, we increased the amount of nitrogen by mixing hydrogen with 20 mol% nitrogen (80/20 H₂/N₂ molar mixtures) for the reaction with Li₃N, and obtained an isotherm after 345 cycles as shown in Figure 2. The same sample was used to cycle up to 516 cycles whose results are also shown in Figure 2. In this case we include the data from “zeroth cycle,” from reference [2]. Results show that our 516 times cycled data with 80/20 H₂/N₂ is comparable with “zeroth cycle” data, showing ~10.5 wt% H reversible absorption capacity.

Later, the samples from both the H₂-100 ppm N₂ and 80/20 H₂/N₂ samples were subjected to 1,359 and 850 cycles respectively. We used the samples that were used earlier for these mixtures. However, the results showed a decrease in reversible capacity as compared to the “1 cycle” with industrial hydrogen (not shown, available from the principal investigator on request). Although reversible capacity is 7.2 wt% H after 1,359 cycles, these are better than “1 cycle” (~5.8 wt% H) with no nitrogen additions to hydrogen gas. The decrease at a high number of cycles is thought to be caused by oxygen contamination in the nitrogen gas.
X-ray diffraction (XRD) patterns of the products from desorbed samples obtained from the Sieverts experiments, after cycling, are presented in Figure 3. In the XRD pattern after “1 cycle” with industrial hydrogen, we detected Li₂NH as the major phase along with LiH and Li₂O as minor phases. After 501 cycles with industrial hydrogen, we found a significant increase in the LiH and Li₂O phases, and a decrease in the amount Li₂NH phase (noting that the reversible hydrogen capacity dropped to ~ 3.8 wt% H) [2]. Next, we compare the 516 cycle product from the 80/20 data with the 501 cycle data of industrial hydrogen. It can be seen in Figure 3c that the amount of Li₂NH is significantly higher than the 501cycled hydrogen and also the Li₂O phase is lower in amount, as indicated by the increased intensities of the Bragg peaks. Figure 4(d) show the XRD patterns from 850 cycled 80/20 H₂/N₂ gases, and Figure 4(e) form the 1,359 cycle H₂-100 ppmN₂, taken after the desorption isotherm, yielding similar powder patterns with much higher amount of Li₂O phase. It is possible that the increase in Li₂O phase was responsible for the decrease in H-capacities after prolonged cycling. A plausible reason for this is accidental trapping of air in the volume between the valve and the sample holder of the Sieverts apparatus during switching from the cycling to Sieverts apparatus. But it is surprising and coincidental that both the high cycled materials show similar XRD patterns.

To understand this phenomenon of increased reversibility we constructed ternary Li-N-H phase diagrams using the CALPHAD approach. Results from the FactSage software are shown in Figure 4. The Li-N-H phase diagram at 528 K and 2 bar hydrogen is shown in Figure 4(a). During absorption of hydrogen along the “Absorption pure H₂” line with the arrow pointing towards H, the phases formed in regions where the line intersects in the phase diagram progress as follows in Equation 1:

\[
\text{Absorption at 528 K, 2 bar H}_2 (\text{Figure 4(a)}):
\]

\[
\text{Li}_3\text{N}(s) + \text{H}_2(g) \rightarrow \text{Li}_3\text{N}(s) + \text{Li}_2\text{NH}(s) + \text{Li(liq.) (up to 2.5 wt% H)} \quad \rightarrow \quad \text{LiHp} + \text{Li}_2\text{NH}(s) + \text{gas (>~5 wt% H)}
\]

During desorption, along the H-Li₃N in Figure 4(b) under dynamic vacuum we ideally can go back in a reverse fashion. From the experiments, we note that the reversibility is not complete, in other words there persists always LiH phase as Li₂NH in the residual products. It can be noted that the maximum capacity reported so far is ~11 wt% H [2-6] in the Li₃N-H system. The LiH phase contains ~12.4 wt% H. Theoretically, Equation 1 shows ~8.58 wt% H but the trapping of hydrogen in the LiH phase increases the amount of hydrogen to about 11 wt% H as reported by Chen et al. [3,7,8]. The XRD patterns in Figure 4 are all taken after cooling the...
Cycling lithium nitride with hydrogen containing 100 ppm nitrogen gas showed improved hydrogen storage properties over that cycled without the nitrogen addition. Specifically, the reversible capacity approached ~10 wt% H after 516 cycles, and showed improved cycling stability. We propose that the ability of the nitrogen to have an effect in such small quantities is due to formation of Li,N which transforms to Li,NH. As the number of cycles increases, more Li,NH is formed that leads to an increased hydrogen capacity.

- Cycling with hydrogen containing 20 mol% nitrogen was able to improve the cycling stability over a large number of cycles and allowed the lithium nitride to maintain a capacity close to its starting capacity. A reversible capacity of ~10 wt% at 255°C was observed up to 516 cycles. However, the capacity decreased to ~5.8 wt% H at ~10 bar pressure after 850 cycles; we attribute this to oxidation of the particles due possible entrapment of air during sample transfer.
- CALPHAD modeling showed formation of pure lithium, which reacts with nitrogen to form Li,N in preference to Li,H. The modeling also enabled us to determine the path of reaction at different temperature and pressures.
- In a practical sense, when we load the hydrogen mixed with nitrogen, in batches, in a hydride bed (as opposed to continuous supply) there is always partial pressure of nitrogen gas, but the majority of hydrogen gas is absorbed in the solid complex hydride phases.
- Isothermal data collected using a 25/75 H2/N2 mixture showed that these high nitrogen concentrations tend to stop hydriding processes prematurely, which is thus not desirable.

**Conclusions and Future Directions**

- Cycling lithium nitride with hydrogen containing 100 ppm nitrogen gas showed improved hydrogen storage properties over that cycled without the nitrogen addition. Specifically, the reversible capacity approached ~10 wt% H after 516 cycles, and showed improved cycling stability. We propose that the ability of the nitrogen to have an effect in such small quantities is due to formation of Li,N which transforms to Li,NH. As the number of cycles increases, more Li,NH is formed that leads to an increased hydrogen capacity.

**FY 2010 Publications/Presentations**

1. J.-C. Crivello, M. Gupta, R. Černý, M. Latroche, and D. Chandra, “Density functional study of Li4NH and Li1.5NH1.5 as intermediary compounds during hydrogenation of Li3N,” PHYSICAL REVIEW B 81, 104113, 2010.
References


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 Fuel Cells section of the Fuel Cell 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

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 \( H_2 \) desorption temperatures and accelerating the kinetics. If successful, the project will address the following DOE technical targets, as outlined in the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DOE 2010 Target</th>
<th>Project Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Delivery Temperature</td>
<td>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)</td>
<td></td>
</tr>
</tbody>
</table>

Accomplishments

- Synthesized a suite of MOF and nanoporous carbon templates with <1 nm to 20 nm pore sizes.
- Developed and refined infiltration methods for simple metal hydrides, e.g. LiH, MgH\(_2\) using
organometallic precursor route, achieving loadings of up to 5.8 wt% Li.

- Demonstrated that both the thermodynamics and kinetics of melt-infiltrated LiBH₄ nanoparticles in 2-nm highly porous carbon are greatly improved with respect to bulk LiBH₄. The onset desorption temperature decreases from 460°C to 220°C (1 bar) and no B₂H₆ impurity is detected.
- Showed that no destabilization of LiH nanoparticles in MOF templates occurs relative to bulk, consistent with quantum Monte Carlo predictions.
- Predicted that (MgAlH₅)ₙ, where n = 1–8, are stable, suggesting that synthesis of this unknown compound in the form of nanoclusters within templates should be feasible.
- Computed the phase diagram of nanocluster NaAlH₄ from first-principles density functional theory (DFT) and nano-PEGS cluster prototypes.
- Predicted that small clusters of AlH₃ increase in stability dramatically, with 1 formula unit of AlH₃ predicted to have a decomposition enthalpy of about 150 kJ/mol H₂.

**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-saturated 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.

**Results**

**LiH@MOF Hydrogen Desorption**

The H₂ desorption behavior of LiH nanoparticles is not very different from the corresponding bulk-phase materials (Figure 1). Using 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 a series of processes occurring during nanoparticle-composite decomposition.

STMBMS data for EtLi infiltrated sample reveal that desorption of C₂H₄ occurs at temperatures between 50-200°C, indicating formation of LiH (Figure 1,
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The MOF template decomposes at ≈260-350°C. Hydrogen desorption from bulk LiH peaks at ≈580°C in this experiment (Figure 1, bottom). Similarly, H₂ desorption from MOF-confined LiH occurs at approximately the same temperature. This indicates that neither the thermodynamics nor the kinetics of nano-LiH are significantly altered by nanoconfinement. These observations are consistent with our quantum Monte Carlo calculations (see below), which suggest that only clusters as small as (LiH)ₙ, n=1,2 are destabilized. Moreover, these results indicate that, contrary to predictions based on a Wulff construction model [1] (see following), nanoscale LiH is not significantly stabilized by nanoscale confinement. Experiments to quantify the thermodynamic properties of the LiH@MOF are currently underway.

Controlling the Decomposition Pathway of LiBH₄ via Confinement in Highly Ordered Nanoporous Carbon

The decomposition behavior of LiBH₄ has been investigated in the presence of highly ordered nanoporous carbon (NPC) with columnar pores of average pore diameter 2.0 nm and a narrow size distribution with surface area and pore volume of about 594 m²/g and 0.35 cm³/g, respectively. The columnar pores are packed in a hexagonal geometry. X-ray diffraction and infrared spectroscopy measurements confirm that infiltrated samples result in non-crystalline LiBH₄ within the pore structure of the carbon. In contrast to previous studies of LiBH₄ confined in 12 nm and larger carbon aerogel pores, the non-crystalline LiBH₄ embedded in 2.0 nm pores not only results in the disappearance of the structural phase transition at around 100°C, and the melting transition, but also the significant decrease of the onset desorption temperature from 460°C to 220°C. Diborane release is suppressed or eliminated in the decomposition of non-crystalline LiBH₄ in the 2.0 nm pores, and only forms during the infiltration process.

FIGURE 2. DSC traces of (a) bulk LiBH₄, (b) physically mixed LiBH₄/NPC, and (c) pre-melted LiBH₄@NPC. The heating rate was 10°C/min.

Theoretical Modeling of Hydride Nanoparticles

Quantum Monte Carlo Modeling: Computational modeling of Li and (LiH)ₙ clusters (n = 1-20) clusters was completed, in which quantum Monte Carlo calculations were compared with the results of DFT obtained from a variety of functionals and the literature. These results enabled us to conceptually test the predictions of a Wulff construction model of hydride destabilization [2]. Comparing the diffusion Monte Carlo (DMC) predictions to the Wulff construction (Figure 3), we find that DMC predicts very little change in the hydrogen absorption energy over most values of n, with only LiH and (LiH)₂ destabilized relative to bulk. In contrast, the Wulff construction predicts that LiH is stabilized as its particle radius decreases below ~9 nm. In fact, of the hydrides examined by Kim et al., only MgH₂ and NaH are predicted to be destabilized at the nanoscale. Our previous DMC results for MgH₂ are consistent with this, although the destabilization occurs at much small particle sizes (<1 nm diameter). Unfortunately, we cannot perform comparable simulations for NaH clusters because of the lack of high-quality effective core potentials for sodium. Nevertheless, these results suggest that size affects the energetics of hydride nanoparticles only at extremely small sizes. The corollary, however, is that altered chemistry of hydrides, in particular a change in the thermodynamics observed by the group of de Jongh et al. [3], as well as changes in kinetics observed by several
groups, are connected in some way to the local chemical environment of the scaffold pores.

We also explored the possibility of alloying magnesium and aluminum to tune the hydrogen desorption energy. MgAlH<sub>5</sub> is a hypothetical compound, capable of storing up to 8.5% hydrogen by weight. However, DFT studies by Akbarzadeh et al. indicate that the bulk material is unstable relative to MgH<sub>2</sub>+Al+1.5H<sub>2</sub> [4]. We hypothesize that the stability of Mg-Al clusters will be intermediate between that of AlH<sub>3</sub> and MgH<sub>2</sub>, assuming that a stable cluster can form. In our initial DMC calculations, shown in Figure 4 for MgAlH<sub>5</sub> clusters with up to eight formula units, we find that the desorption energy scales quite differently from that of the Li clusters. This energy is highest for MgAl and progressively decreases until it reaches values near the appropriate range for hydrogen storage (~20-60 kJ mol<sup>-1</sup>) for an eight formula-unit cluster. These clusters are also of the correct size to be made within a MOF, having diameters around 1 nm. We are currently exploring different alloying concentrations to further enhance the tunability of these clusters and are initiating an experimental plan to determine if such clusters can be formed.

**Phase Diagram of Nano-Cluster NaAlH<sub>4</sub> from First-Principles DFT and Nano-PEGS Cluster Prototypes:** We have calculated the phase diagram of small clusters of atoms in the Na-Al-H ternary system using first-principles and determine the decomposition pathway of NaAlH<sub>4</sub> as a function of Na:Al ratio and cluster size up to 8 formula units. We included as decomposition products clusters of Na, Al, mixed NaAl, and ionic clusters AlH<sub>3</sub>, NaH, and NaAlH<sub>4</sub>. Cluster geometries for ionic clusters were obtained by relaxing prototype electrostatic ground state (PEGS) structures using density-functional theory calculations; vibrational free energy was also calculated for each of the clusters. We find that small clusters of AlH<sub>3</sub> increase in stability with smaller cluster size from enthalpies of around 51 to 160 kJ/mol H<sub>2</sub> for 8 and 1 formula units, respectively. In contrast, small clusters of NaH have an enthalpy of decomposition of about 70 kJ/mol H<sub>2</sub> and show no destabilization with size until the cluster is two formula units or smaller when they spontaneously decompose. Clusters of NaAlH<sub>4</sub> also show increasing stability with decreasing cluster size with an enthalpy of decomposition that increases from 80 kJ/mol H<sub>2</sub> for 8 f.u. clusters) to 150 kJ/mol H<sub>2</sub> for 1 f.u. clusters. Most interestingly, NaAlH<sub>4</sub> clusters are found to decompose directly into mixed metal AlNa clusters in one step. The lack of intermediate Na<sub>3</sub>AlH<sub>6</sub> in the decomposition path is in agreement with recent experimental work on nanoconfined NaAlH<sub>4</sub> in nanoporous carbons.

**Conclusions and Future Directions**

**Conclusions**

- Both thermodynamic and kinetic effects are observed when metal hydrides are confined within nanoporous templates.
- Simple hydrides (e.g. LiH and MgH<sub>2</sub>) are not destabilized until very small cluster sizes (<5 formula units). This is confirmed by both theory and experiment, invalidating the Wulff construction model for at least these two materials.
- Two complex hydrides we examined, NaAlH<sub>4</sub> and LiBH<sub>4</sub>, are kinetically destabilized by nanofocusing. In addition, thermodynamic destabilization is either observed (LiBH<sub>4</sub> at ~2 nm) or predicted (NaAlH<sub>4</sub> at 8 formula units, or ~1 nm), suggesting that both size and pore environment influence hydride stability.
Future Directions

- Complete an investigation of nanoscale LiBH$_4$ using both MOF and NPC templates with overlapping pore sizes so that the effects of size and pore chemistry can be systematically evaluated.
- Investigate LiBH$_4$ decomposition on graphene sheets for comparison with hard carbon framework experimental results.
- Complete Mg-Al-H cluster phase diagram (collaboration with MIT).
- Complete investigation of compositional tuning within the Mg-Al-H system.
- Complete and submit journal articles on:
  1) nanocluster thermodynamics of complex hydrides using nanoPEGS+DFT computational framework;
  2) experimental and theoretical tests of the Wulff construction model, using simple hydrides; and
  3) the influence of size and pore environment on complex hydride stability, using LiBH$_4$ as a model material.
- Complete infiltration of nanoporous hard carbons with Ca(BH$_4$)$_2$, Mg(BH$_4$)$_2$, and LiAlH$_4$.

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References

1. B. Dai et al.
Objectives

The objective of this project is to discover novel mixed hydrides for hydrogen storage, which enable the DOE 2010 system-level goals. 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. We will combine materials from distinct categories (e.g., chemical and complex hydrides) to form novel multicomponent 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).

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell 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 study is aimed at fundamental insights into new materials and the thermodynamic and kinetic aspects of hydrogen release and reabsorption from them. 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:

• Specific energy: 1.5 kWh/kg
• Energy density: 0.9 kWh/L

Accomplishments

• Used computational methods (density functional theory [DFT], prototype electrostatic ground state [PEGS], grand-canonical linear programming [GCLP]) to scan through and predict all possible reactions in Li-Mg-B-N-H system with reversible thermodynamics.
• New high-capacity reactions predicted, including those involving (NH₄)₂B₁₂H₁₂ (preliminary experimental verification underway).
• Used PEGS method to predict amido-borane structures. Good agreement with experiment where available (e.g., LiAB and KAB) and good prediction of structure for many other cases.
• NHBH₃NH₃BH₄ dianion as ammonia-borane (AB) intermediate product supported by DFT calculations.
• Computational prediction and experimental observation of new mixed BH₄/NH₂ compounds in Na and Ca systems.
Introduction

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. Specifically, we focus on combinations of materials from distinct categories (e.g., chemical and complex hydrides) to form novel multicomponent reactions.

Approach

We 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 elucidate the effect of dopants and nanoscale catalysts in achieving fast kinetics and reversibility. And, state-of-the-art storage experiments 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) hydrogen storage measurements and characterization, 2) state-of-the-art computational modeling, 3) detailed catalysis experiments, and 4) in-depth automotive perspective.

Results

First-Principles Prediction Of Novel Storage Reactions in the Li-Mg-B-N-H System

Metal borohydrides and amides exhibit some of the highest hydrogen capacities among the known solid-state materials. Compounds with Li, Mg, B, N, and H are particularly interesting as they involve numerous compounds of potentially high relevance for hydrogen storage:

1. Borohydrides: LiBH₄, MgBH₄, Li₂B₁₂H₁₂, MgB₁₂H₁₂
2. Amides and imides: LiNH₂, Mg(NH₂)₂, Li₃NH, MgNH, Li₃Mg(NH)₂, etc.
3. Borohydride-amide mixed compounds: Li₂BNH₄, Li₂BN₅H₁₀
4. Ammoniated borohydrides: Mg(BH₄)₂·2NH₃
5. AB and derivatives: BH₃NH₃, BH₃NH₂, LiBH₂NH₃, etc.
6. B-N-H and B-H compounds: B₂H₆, B₄H₁₀, B₁₂H₂₀, B₂₀H₁₆, (NH₄)₂B₁₂H₁₂, etc.
7. Various reaction products: elements (Li, Mg, B, N₂), metal hydrides (LiH, MgH₂), metal borides (MgB₂, MgB₄, MgB₇), metal nitrides (Mg₂N₃, Li₃N, LiMgN), boronitrides (BN, Li₃BN₅, LiMgBN₅), etc.

Using DFT methods, we have calculated the total crystal binding energies and vibrational free energies of all currently known compounds in the Li-Mg-B-N-H system (approximately 50 compounds). The structures of most of these compounds have been taken from the Inorganic Crystal Structure Database. To these, we have added the theoretically predicted compounds whose structures have been obtained using the PEGS search and other structure prediction methods. The calculated free energies have been used as inputs to the GCLP approach for determining reaction pathways in multinary systems [1]. Using the GCLP method, we have rigorously determined all the thermodynamically allowed reversible reactions in the Li-Mg-B-N-H system which involve the currently known (or predicted) compounds (some of these predictions may change with the discovery of new, currently unknown Li-Mg-B-N-H compounds). Our predictions for the DOE targeted range of temperatures and pressures are given in Table 1, and the corresponding van’t Hoff plots are shown in Figure 1.

Three of the five reactions in Table 1 were found by us in an earlier paper [2]. Two of these reactions (#2 and #3 in Table 1) involve Mg(BH₄)₂ and LiBH₄ as reactants and MgB₁₂H₁₂ and Li₂B₁₂H₁₂ as end products. In Ref. [2] we showed that both these reactions possess excellent thermodynamic properties that combine low reaction enthalpies with low entropies. They remain the two most-promising single-step reversible reactions in the Li-Mg-B-N-H system.

Interestingly, we now predict a novel two-step reaction involving ammonium dodekahydro-closo-dodekaborate as the starting material:

\[(\text{NH}_4)_2\text{B}_{12}\text{H}_{12} \leftrightarrow 2\text{BN} + 0.5\text{B}_{20}\text{H}_{16} + 6\text{H}_2 \leftrightarrow 2\text{BN} + 10\text{H}_2 + 10\text{H}_2\]

These reactions releases 11.3 wt% H₂ over both steps. At p=1 bar H₂ pressure, the first step (decomposition of (NH₄)₂B₁₂H₁₂ into BN, B₂₀H₁₆,
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TABLE 1. Predicted thermodynamically reversible hydrogen storage reactions that fall in (or near) the targeted temperature and pressure window of -40 to 80°C and 1 to 700 bar, respectively.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>H₂ wt%</th>
<th>ΔH°₂₉₈ (kJ/mol H₂)</th>
<th>ΔS°₂₉₈ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(NH₄)₂B₁₂H₁₂ ↔ 4BN + B₂₀H₁₆ + 12H₂</td>
<td>6.81</td>
<td>17</td>
<td>104</td>
</tr>
<tr>
<td>5Mg(BH₄)₂ + 2LiBH₄ ↔ 5MgH₂ + Li₂B₁₂H₁₂ + 13H₂</td>
<td>8.37</td>
<td>24</td>
<td>104</td>
</tr>
<tr>
<td>6Mg(BH₄)₂ ↔ 5MgH₂ + MgB₁₂H₁₂ + 13H₂</td>
<td>8.10</td>
<td>29</td>
<td>100</td>
</tr>
<tr>
<td>B₂₀H₁₆ ↔ 20B + 8H₂</td>
<td>6.95</td>
<td>33</td>
<td>111</td>
</tr>
<tr>
<td>5MgH₂ + MgB₁₂H₁₂ ↔ 6MgB₂ + 11H₂</td>
<td>7.46</td>
<td>44</td>
<td>115</td>
</tr>
</tbody>
</table>

FIGURE 1. The calculated van’t Hoff diagram for the thermodynamically reversible hydrogen storage reactions given in Table 1. Each line is labeled by the reactant or the combination of reactants. The red rectangle represents the targeted temperature-pressure window of -40 to 80°C and 1 to 700 bar, respectively.

and H₂) occurs at -120°C, while the second step (decomposition of B₂₀H₁₆ into B and H₂) proceeds at 20°C. In contrast to the conventional complex hydrides that contain metal cations and complex anions, the above reaction represents a new paradigm where the storage material contains both anionic and cationic complexes.

First-Principles Studies of Metal Amidoboranes

Metal amidoboranes, M(NH₄BH₄)₃ (M=metal atoms) or MAB, are interesting candidates for on-board hydrogen storage materials with promising properties, like high gravimetric capacity, low hydrogen release temperature, and the ability to suppress toxic borazine emission. But details about the intermediate products are largely unknown and these products are often categorized as amorphous. Armed with the PEGS+DFT methodology, we have searched for crystal structures of possible intermediate phases with [NHBH₄]₂, [NHBH₄], [NHBH₄]₃, polymer-[NHBH₄] anion groups in the decomposition of LiAB and CaAB. All of these anion groups were selected in analogy with the decomposition sequence and products for NH₄BH₄. However, all these reaction pathways produce high-endothermic hydrogen release enthalpies, which are far away from the experimental suggested nearly thermoneutral values, (-3~ -5 kJ/mol H₂ in LiAB and 3.5 kJ/mol H₂ in CaAB).

Recently, proposals in the literature have pointed towards the possibility of a new dianion group [NHBHNHBH₃], which might be formed in the decomposition of CaAB. For the cases of LiAB and CaAB, we used PEGS+DFT to predict crystal structures of this new metal-dianion intermediate compounds. For the static energies, these reaction pathways are much lower in energy than the above anion groups, lending credibility to the possible stability of the dianion group as an intermediate product. Hydrogen release enthalpies are calculated to be (static) 27.56 kJ/mol H₂ in LiAB and 27.33 kJ/mol H₂ in CaAB. Introducing the entropy effects from phonon calculations, the enthalpies are shifted down by a roughly constant amount, ~25 kJ/mol H₂ at 0 K and ~20 kJ/mol H₂ at 300 K. With these shifts due to vibrations, we successfully obtain calculated enthalpies that are in good agreement with the experimentally suggested nearly thermoneutral data at finite temperatures. This good agreement gives confidence in the ability of PEGS+DFT to determine MAB reaction products, and also provides strong evidence that the dianion phases are highly probable products in the decomposition of metal amidoboranes.

Exploration of Catalyst for Improved Hydrogen Absorption/Desorption Kinetics

Hydrogen evolution from complex hydrides is dictated by an inter-related sequence of chemical reaction steps including decomposition of the hydride, diffusion of hydrogen atom/ion and counter ions in the solid lattice, surface diffusion of these atoms/ions, recombination of hydrogen atoms, transformation of lattice phases, and desorption of hydrogen molecules. Reversing these step would lead to formation of the hydride. Improving kinetics in these reaction steps allows complex hydrides to evolve hydrogen under milder operating conditions (i.e. temperature and
pressure). For this funding period, we explore the concept that the hydrogen evolution kinetics can be facilitated by a catalyst external to the complex hydride. Furthermore, the effectiveness of the catalyst depends on the contact area between the catalyst and the complex hydride. Our hypothesis is that a light-weight, effective catalyst could be constructed with a known transition metal hydrogenation catalyst, that dissociatively adsorb and associatively desorb hydrogen molecules readily, highly dispersed on a carbon support on which hydrogen atoms can diffuse rapidly. By dispersing such a composite catalyst in a mixture with complex hydride, we can attain a high contact area between the catalyst and the hydride with minimal weight penalty. The contact points would serve both for hydrogen transfer between the catalyst complex and the hydride and as potential nucleation points for phase transformation of the hydride.

To test our hypothesis, we used a well characterized hydride, calcium borohydride Ca(BH$_4$)$_2$, that decomposes at a high temperature (380-420°C). It was mixed with a series of composite catalysts comprising non-precious metal nanoparticles and multi-walled carbon nanotubes (MWCNTs). Non-precious metals were used for lower costs, and MWCNT was chosen because of their low density and their aromatic nature permits facile hydrogen diffusion. The hydrogen desorption behavior of these mixtures was characterized by their hydrogen pressure-temperature profiles. The metal-decorated MWCNTs catalytic matrix was prepared by sonication-assisted impregnation. The metal precursor containing Co, Ni, or Fe (usually metal nitrates) was dissolved in a solvent and sonicated by their hydrogen pressure–temperature profiles. The metal-decorated MWCNTs catalytic matrix was prepared by sonication-assisted impregnation. The metal precursor containing Co, Ni, or Fe (usually metal nitrates) was dissolved in a solvent and sonicated with MWCNTs. The resulting solid mixture was thermally treated in a H$_2$-Ar stream, which converted (by decomposition and reduction) the loaded metal precursor to metal nanoparticles on the MWCNTs. The thermal treatment was carried out in a special sample holder that allows the reduced sample being transferred into a glove-box with no further surface oxidation.

Figure 2 shows the pressure change-temperature profiles for the pristine Ca(BH$_4$)$_2$ and the catalyst-Ca(BH$_4$)$_2$ mixtures. It was found that the addition of either carbon nanotubes or metal-decorated carbon nanotubes lowered the decomposition temperature of Ca(BH$_4$)$_2$ by 15-20°C. Among the Ni-, Fe-, and Co-MWCNT composites, Co-MWCNT was most effective and showed the lowest initial decomposition temperature.

The preliminary results show that the addition of the metal-decorated carbon nanotubes can lower the decomposition temperature of Ca(BH$_4$)$_2$ complex hydride. At this moment cobalt is the most promising among Co, Fe, and Ni, metals that were investigated. Future work will include optimization of the preparation parameters for the Co-decorated MWCNT matrix, as well as the parameters for operating the catalytic matrix for a more well-characterized complex hydride, for instance, NaAlH$_4$.

Several rate-controlling mechanisms have been proposed for the hydrogen desorption/recombination in complex hydrides. Overall, in order for hydrogen to desorb/recombine more efficiently, the hydride should have: (1) smaller particle size to obtain larger surface areas for gas phase exposure; (2) shorter diffusion length for its reaction species; (3) nucleation sites for the formation of the decomposition product phases.

The present catalyst composite can be further modified to better meet the above requirements. Our proposed reaction model involves complex hydrides in contact with the multi-functional catalytic matrix under development. The high surface area provided by the carbon nanotubes and the hydrogen spillover effect by the metal nanoparticles will increase the hydrogen gradient on the interfaces. The metal catalyst particles will serve as nucleation sites can enhance the kinetics of the subsequent reactions. Alternatively, product seeding could be attempted. For the complex hydrides with a low melting point, for example, NaAlH$_4$, a solid-liquid region can be retained between the interfaces of the hydride and the catalytic matrix by capillary action. Such region benefits the overall kinetics by facilitating the chemical bond breakage as well as the mass transfer of the product nuclei, which can be dispersed homogeneously via the liquid phase. In addition, carbon nanotubes, an excellent thermal conductor, can transfer heat effectively during the thermal decomposition of the hydrides. This working model cannot be realized if the hydride particles lose contact with the catalytic matrix, possibly due to the volume/morphology change in the hydride during its decomposition. Thus, to supplement the carbon nanotubes, two-dimensional graphene layers
will also be introduced into the catalytic matrix to help maintain the hydride/matrix interfaces.

Conclusions and Future Directions

- Extend computational search for all possible promising reversible reactions in Li-Ca-B-N-H system.
- Experimentally characterize storage properties/reactions of (NH₄)₂B₁₂H₁₂ and other predicted reactions.
- Extend experimental catalyst studies to (NH₄)₂B₁₂H₁₂ and other predicted promising materials.
- Continue computational exploration for: 1) novel BH₄/NH₂ compounds and reversible reactions, 2) mixed metal borohydrides, and 3) AB reaction products.

References

IV.A.4 Hydrogen Storage Materials for Fuel Cell-Powered Vehicles

Objectives

- Study new destabilized complex hydrides that have been predicted by first principles calculations to be suitable hydrogen storage materials.
- Develop methods for the synthesis, characterization, and modeling of new complex hydrides.
- Identify the most promising types of complex hydrides and develop new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures.
- Extend studies to include carbon materials, metal organic frameworks (MOFs), and possibly other nanostructured and porous materials as potential hydrogen storage materials using hydrogen spillover.
- Perform cycling studies to test the durability of destabilized complex hydrides and MOFs.
- Design, fabricate and test a hydride-based hydrogen storage system for fuel cell applications.

Technical Barriers

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

(A) System Weight and Volume
(D) Durability/Operability
(E) Charging/Discharging Rates

Technical Targets

This project is conducting fundamental studies of complex borohydride materials and other promising hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet DOE’s 2015 goal of 4.5 weight percent hydrogen storage for the system. The following table summarizes the targets:

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity: Usable, specific-energy from H₂ (net useful energy/max system mass)</td>
<td>kWh/kg</td>
<td>1.5</td>
</tr>
<tr>
<td>System Volumetric Capacity: Usable energy density from H₂ (net useful energy/max system volume)</td>
<td>kWh/L</td>
<td>1.2</td>
</tr>
<tr>
<td>Storage System Cost</td>
<td>$/kWh</td>
<td>6</td>
</tr>
</tbody>
</table>

Accomplishments

- We have determined that several destabilized borohydride systems based on Mg(BH₄)₂ can absorb hydrogen reversibly starting at temperatures less than 200°C.
- We used thermodynamic measurements, based on van’t Hoff plots to determine the reaction enthalpies of the destabilized systems.
- We have also determined that mixed catalysts are most effective in catalyzing the MgH₂ system and they may be effective for destabilized systems as well.
- We have determined the activation energies for the CaH₂/LiBH₄ system using the Kissinger analysis.

Introduction

Developing 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.

During the next several years 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
IV.A  Hydrogen Storage / MH-Independent Projects

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. We will also extend these studies to include carbon materials, MOFs and possibly other nanostructured and porous materials as potential hydrogen storage materials. There have been recent reports that some MOFs had a hydrogen storage capacity of 7.5 wt% H2 at 77 K and 70 bar. Unfortunately, the hydrogen adsorption capacities of most carbon materials at ambient temperature and pressure are quite low, generally being less than 1 wt%. Scientists are seeking materials that can absorb and release significant quantities of hydrogen near room temperature. Most recently it was found that IRMOF-8 could adsorb 4.0 wt% at room temperature and 100 bar using hydrogen spillover. This is significant because there is a good possibility that other MOFs could be made that might have even greater capacity at room temperature using the spillover technique. We will thus explore this possibility.

Once a suitable material has been identified for hydrogen storage it will be necessary to design, fabricate and test a hydride-based hydrogen storage system for fuel cell applications. A partner institution will be involved in this aspect of the research. This phase of the research will include using flow, reaction kinetics and thermal modeling, followed by system design, fabrication and performance evaluation.

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.

Thermogravimetric analyses (TGA) and temperature programmed desorption (TPD) were used to determine the thermal stability and the hydrogen capacity of the mixtures. The TGA analyses were done in a Lab System-Diamond TG/DTA. 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 pressure composition isotherm (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 IR Prestige-21 Fourier transform infrared spectrophotometer. This instrument operates in a single-beam mode and is capable of data collection over a wave number range of 7,800 cm⁻¹ ~ 350 cm⁻¹. Residual gas analyses 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

Last year we reported that the destabilized borohydride system described by the equation

\[ 6 \text{LiBH}_4 + \text{CaH}_2 \rightarrow 6 \text{LiH} + \text{CaB}_6 + 10 \text{H}_2 \]

absorbed hydrogen in a reversible manner. Further studies have been done to determine the effect of various additives on the desorption temperatures and activation energy of this system. The additives studied were TiCl₃, TiF₃, and TiO₂. It was found that the TiCl₃ additive lowered the dehydrogenation temperature more than the other additives. Furthermore, higher amounts of TiCl₃ were more effective in reducing the desorption temperature than lesser amounts. Kissinger plots were used to determine the activation energies of the catalyzed systems. The activations energies for mixtures containing 4, 10 and 25 mol% of TiCl₃ were 141, 126 and 110 kJ/mol, respectively.

The following six systems based on Mg(BH₄)₂ have also been studied to determine their reversibility and thermodynamic behavior:

- \[ 3\text{Mg(BH}_4)_2 + \text{CaH}_2 + 3\text{NaH} \rightarrow 3\text{NaMgH}_3 + \text{CaB}_6 + 10\text{H}_2 \]
- \[ 3\text{Mg(BH}_4)_2 + \text{CaH}_2 \rightarrow 3\text{MgH}_2 + \text{CaB}_6 + 10\text{H}_2 \]
- \[ 3\text{Mg(BH}_4)_2 + 3\text{Ca(BH}_4)_2 \rightarrow \text{CaB}_6\text{H}_{12} + 5\text{MgH}_2 + 13\text{H}_2 \]
- \[ 2\text{Mg(BH}_4)_2 + \text{NaH} \rightarrow \text{NaMgH}_3 + \text{MgB}_4 + 7\text{H}_2 \]
- \[ 3\text{Mg(BH}_4)_2 + \text{CaH}_2 + 1.5\text{Si} \rightarrow \text{CaB}_6 + 1.5\text{Mg}_2\text{Si} + 13\text{H}_2 \]
- \[ \text{Mg(BH}_4)_2 + 2\text{C} \rightarrow \text{MgB}_2\text{C}_2 + 4\text{H}_2 \]

The systems described in the first three equations are reversible with some releasing as much as 8 wt% hydrogen at temperatures beginning at less than 200°C (see Figure 1). The last three reactions did not show any well defined plateau region. Therefore, thermodynamic measurements were done only on the systems described by the first three equations. Cycling studies showed that these systems are only partially reversible. The hydrogen-holding capacities diminished to about
2 wt% upon continued cycling. Thermodynamic measurements, based on van’t Hoff plots showed that the reaction enthalpies were in the 82-88 kJ/mol range. Results are given in Figure 2. Thermodynamics and kinetics measurements were done using MgH₂ as a model system. The goal was to determine what catalysts work best in lowering reaction temperatures and increasing reaction rates. It was found that a mixture of two catalysts was more effective than either catalyst alone. Larger amounts of catalysts were more effective in lowering reaction temperatures but the hydrogen-holding capacity was significantly diminished as the amount of catalyst increased. Results are shown in Figures 3-4.

Conclusions and Future Directions

This work has shown that several destabilized borohydride systems based on Mg(BH₄)₂ can absorb hydrogen reversibly starting at temperatures less than 200°C. We have also determined that mixed catalysts are most effective in catalyzing the MgH₂ system and they may be effective for destabilized systems as well. In Fiscal Years 2010-2011, the following are planned:

- Prepare and characterize several Mg(BH₄)₂-based destabilized systems using ball milling, X-ray diffraction, TPD and TGA.
- Perform thermodynamic measurements, such as PCI analyses, on destabilized systems found to be reversible.
- Perform kinetics and modeling studies on the destabilized systems at constant pressure driving forces in order to establish the rate-controlling process.
- Use techniques such as residual gas analysis to determine if dehydrogenation is accompanied by the release of other gaseous byproducts.
- Use various catalysts and combinations of catalysts to lower reaction temperatures and increase reaction rates. MgH₂ will be used as a model system in these efforts.

FIGURE 1. TPD Profiles of the Mg(BH₄)₂ Destabilized Systems (TPD profiles were performed in an automated system controlled by LabVIEW-based software.)

FIGURE 2. Desorption Isotherms and Van’t Hoff Isochores for the Mg(BH₄)₂ System with Various Additives (The isotherms were done at 450°C. The van’t Hoff isochors were obtained from isotherms done at 350, 400, and 450°C.)
IV.A Hydrogen Storage / MH-Independent Projects

FY 2010 Publications/Presentations


6. Hongwei Yang and Andrew Goudy, “Kinetic and Modeling Study of Sodium Alanate at Constant Pressure Thermodynamic Driving Forces”, MRS Fall meeting, November 30 - December 3, 2009, Boston, MA.

7. Adeola Ibikunle, Tolulope Durojaiye and Andrew Goudy, “Hydrogen Storage in Modified LiBH4 Metal Hydride Materials” NOBCChE Southeast Regional Meeting, University of Maryland, November 2009.

8. Saidi T. Sabitu, George Gallo and Andrew J. Goudy, “Thermodynamic studies on the interactions of TiH2 and Mg2Ni with MgH4 for high capacity hydrogen storage” NOBCChE Southeast Regional Meeting, University of Maryland, November 2009.

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 engineering analyses to evaluate cost and efficiency of hydrogen storage materials and spent fuel regeneration processes.
- Develop life cycle analysis.
- Transfer chemical hydrogen storage systems information to the Hydrogen Storage Engineering Center of Excellence, and receive feedback from its analyses.

Technical Barriers

This project addresses the following technical barriers from Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

(A) System Weight & 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 have been addressed during the Center's activity, 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. 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 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 gH₂/s/kW, is the DOE 2010 target. A tabulation of all of the Center's interim targets are published in “2008 Overview - DOE Chemical Hydrogen Storage Center of Excellence”, 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 for 2010 from across the Center are organized into four main areas: 1) Hydrogen Release, 2) Spent Fuel Regeneration, 3) New Materials, and 4) Engineering Supporting Research and Development.
Hydrogen Release from Ammonia Borane (AB):
- Demonstrated increased rates at temperatures below 100°C for release from AB in ionic liquids using metal ion catalysts.
- Kinetics data for ionic liquid/AB mixtures delivered to Argonne National Laboratory (ANL) for preliminary onboard release system analysis.
- Development of new ionic liquid fuel compositions with greater than 10 wt% hydrogen.
- Demonstrated high rates at temperatures as low as 70°C with non-platinum group metal heterogeneous catalysts demonstrated.
- Deselected amine borane/AB liquid fuels for further consideration because of unresolved catalyst deactivation issues.
- Quantification of impurities and their rates of formation lead to demonstration that impurities may be mitigated by proper choice of process conditions.

Spent Fuel Regeneration, First-Fill Processes, and Boron Resources Studies:
- A complete one pot regeneration cycle has been proven with overall yield of spent fuel digestion through reduction steps exceeding 90%. This method works for multiple spent fuel forms including spent fuels from ionic liquids giving ammonia borane, and is chemically simple relative to previous regeneration schemes.
- Cost analysis on this new regeneration process is underway in collaboration with Dow Chemical Company. Preliminary analysis indicates substantially reduced costs as compared to Dow’s previous analysis of the thiocatechol route ($7-8/gasoline gallon equivalent, gge), but higher raw materials costs.
- AB first-fill reactor capable of 100 gram batch.
- 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:
- All metal amidoborane materials currently known show exothermic hydrogen release. It is not possible to regenerate these materials efficiently and thus they are not considered further for onboard applications, but these materials are useful for stationary near-term applications.
- University of Oregon demonstrated additional syntheses of endothermic/exothermic cyclo-carbon-boron-nitrogen (CBN) compounds, pathways for regeneration of spent fuel, first-fill syntheses, and measured thermodynamic parameters that have corroborated computational studies on these molecules.

Engineering-Supporting R&D
- First order estimation of U.S. and global borate reserves completed, taking into account consumption by competing applications through initial fill timeframe.
- Developed cost analyses of most promising first fill pathways to prepare sodium borohydride and AB.
- Parametric studies to understand engineering scale up of first-fill reactor; semi-continuous flow reactor being designed.
- Eliminated plasma-based process for NaBH₄ production due to irreproducibility.
- Identification of a scalable, solid-solid reactive milling technology has been met with challenges because of poor yields of NaBH₄.
- Identified alternative, scalable solution route to NaBH₄ that has implications for successful scale up of any boron hydride-based fuel.

<table>
<thead>
<tr>
<th>TABLE 1. Criteria for Materials Down-Selection</th>
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<tbody>
<tr>
<td><strong>Criterion</strong></td>
</tr>
<tr>
<td>Material Wt.%</td>
</tr>
<tr>
<td>Potential to Regenerate On-Board</td>
</tr>
<tr>
<td>Regenerable</td>
</tr>
<tr>
<td>Acceptable Phase Change</td>
</tr>
<tr>
<td>Acceptable H₂ Release Rate</td>
</tr>
<tr>
<td>Stable Material &lt; 50 °C</td>
</tr>
<tr>
<td>Temperature of Release</td>
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</tbody>
</table>
**Introduction**

Chemical hydrogen storage involves storing hydrogen in molecular chemical bonds where an onboard 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 five years of this project, CHS-SoE 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 boron-nitrogen (BN) 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 CHS-SoE 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. A recent hydrazine-based one pot regeneration scheme has been demonstrated in the lab, and has substantially reduced separations and processing costs relative to prior regeneration schemes. The major cost in this scheme is the cost of the hydrazine, indicating that research to reduce this cost could lead to a very cost-effective regeneration of spent fuel.

The Center is the team comprised of researchers at LANL, the University of Pennsylvania, Dow Chemical Company, Pacific Northwest National Laboratory (PNNL), Pennsylvania State University, the University of California, Davis, the University of Alabama, the University of Washington, the University of Oregon, U.S. Borax, and the University of Missouri. The Center has been supported in our work through analyses performed by ANL and TIAx, and our interactions with the Hydrogen Storage Engineering Center of Excellence.

**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 R&D in chemical hydrogen storage. The Center’s activities fall into four general areas of hydrogen release from AB or its mixtures, regeneration of spent fuel from AB, materials discovery, and engineering supporting R&D. The goals of these four parallel approaches is to increase the rates of hydrogen release from BN compounds at moderate temperatures, regenerating the spent fuel that results from dehydrogenation of boron-nitrogen-hydrogen (BNH) compounds, and discovering new release materials with more favorable thermodynamics that may enable direct rehydrogenation of the spent fuel. All of these activities are supported and guided by modeling and simulation of the related molecular processes and engineering-based analysis that provides direction to the experimental efforts that are focused on developing a practical hydrogen storage material that meets DOE’s 2010 technical targets.

**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 CHS-CoE 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. For example, AB in solid form, can readily release 13-15 wt% hydrogen. Because of the engineering issues surrounding the handling of solids onboard, the Center has focused significant effort at developing stable liquid fuels comprising AB in ionic liquids, or AB in liquid alkylamineboranes. The latter approach, while potentially realizing greater hydrogen capacity because of the contribution of the dehydrogenation of the liquid alkylamineborane, has run into difficulty because of catalyst deactivation for which the Center at present has no straightforward solution.

The Center this year has provided ANL with kinetics data for the dehydrogenation of AB/ionic liquid mixtures. With this data, ANL has provided a preliminary onboard hydrogen release system analysis. Their preliminary findings are that the exothermicity of hydrogen release drives adequately rapid release of hydrogen, but the heat released provides a challenge for onboard heat management. Several configurations of onboard release reactor are suggested to accommodate these features, but more work is necessary.

**New Materials**

By synthesizing metal-substituted derivatives of AB, a wide array of new metal amidoborane (M-AB) storage materials have been previously discovered...
and characterized by researchers at PNNL, LANL, and Missouri. As one example, PNNL has shown that Li-AB releases 5 wt% hydrogen in 2 minutes at 100°C. This year, additional thermodynamics data have been obtained on a subset of these compounds. The thermodynamics of release indicate that all of the mono metalamidoborane compounds studied to date are still too exothermic to enable direct rehydrogenation of spent fuel (Figure 1). Because of this, and the fact that there are no energy-efficient pathways to regenerate spent fuel from metal amidoboranes, that this line of research should be curtailed. There remains the possibility that multimetallic metalamidoboranes may have more favorable thermodynamics. Also, some of these metal amidoboranes may find use in small niche non-vehicular applications such as portable power.

Another line of research into new materials by our University of Oregon partner has shown that exothermic release of hydrogen from the BN segment of a cyclo-CBN compound coupled with the endothermic release of carbon-carbon (C-C) segments achieves more thermodynamically favorable release of hydrogen as compared to highly exothermic ammonia borane (Figure 2). The thermodynamics of release in these systems that was previously explored using theoretical techniques in collaboration with our University of Alabama partner have been corroborated experimentally. Because of the more favorable thermodynamics, regeneration of spent fuel using H₂ directly in concert with H⁺ and H⁻ reagents under mild conditions has been demonstrated.

**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. Last year, 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 that indicated that AB regeneration could cost as little as $7-8/gge. Based on our lessons learned from this process, the Center has discovered a very simple, one-pot regeneration of AB spent fuels using hydrazine in liquid ammonia that results in fast, high conversions back to AB (see Figure 3). Dow has performed a preliminary cost analysis of this hydrazine route, and has found that because of the simpler process that requires far fewer separations steps, that process energy and capital equipment costs are substantially reduced vs. the multistep thiocatechol route. They also find that the most significant cost is in the cost of hydrazine. An

**FIGURE 1.** Measured heat flow during hydrogen release for a series of metal amidoboranes M(NH₂BH₃)ₙ compounds. Hydrogen release temperature, rate of release, and heat released vary with the identity of the metal ion. All of the heat flow measurements indicate that these compounds release hydrogen exothermically.
FIGURE 2. Cyclo-CBN compounds such as shown in this figure may be interconverted using chemical approaches. The intermediates along the hydrogenation-dehydrogenation pathway have been structurally characterized using single crystal X-ray diffraction techniques, and are depicted at the bottom of the figure.

FIGURE 3. One-pot regeneration scheme using hydrazine as the digestion and reduction agent. Digestion of spent fuel in a mixture of hydrazine and ammonia results in near quantitative conversion to ammonia borane. This approach also works for regeneration of other forms of BNHx spent fuels that arise from ionic liquid/AB mixtures, and from the ‘pentamer’ that results from the release of one equivalent of hydrogen from AB using specific homogeneous transition element catalysts.
additional feature of the hydrazine route is that multiple spent fuel forms may be readily regenerated, such as the spent fuel from ionic liquid/AB liquid mixtures, or the 'pentamer' spent fuel that results from rapid room temperature release of one equivalent of hydrogen using certain homogeneous Co and Ir pincer ligand catalysts. This latter observation may be interesting for certain stationary applications, where rapid release at room temperature is required and where only the heat related to the release of one equivalent of hydrogen is generated.

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. Liquid fuels that have the potential to remain liquid during the dehydrogenation cycle may enable simplified reactor designs. Heat management of these exothermic processes will remain a challenge. Preliminary baseline costs for off board regeneration have been modeled, and may be reduced further, and energy efficiencies may still be improved.

Remaining issues include:

- Regeneration – develop inexpensive hydrazine synthesis routes, or develop alternative regeneration schemes.
- New materials – continue search for reversibility in covalent materials such as the cyclo-CBNs or multimetallic amidoboranes with goal of discovering on board regenerable materials, or materials that are less exothermic. Search for liquid hydrogen storage materials.
- Hydrogen release – measure and understand any catalyst deactivation or lifetime issues, develop and describe mitigation of any and all impurities and their impact on fuel cell operation if any, develop stable optimal liquid fuels, develop reactor schemes to handle the exothermicity of hydrogen release from this class of materials.

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.
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:
  - are structurally well-defined along the desorption/absorption processes
  - exhibit appropriate enthalpy of H₂ desorption
  - are liquids at operating temperatures
  - 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- System Weight and Volume
- Efficiency
- Charging/Discharging Rates
- Regeneration Processes

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 2015 hydrogen storage targets:

- Specific energy: 1.8 kWh/kg (5.5 wt%)
- Energy density: 1.3 kWh/L (4.0 vol%)

Accomplishments

- Selected two materials with favorable thermodynamics to move forward.
- Synthesized all intermediates along the proposed desorption pathway for Material (1).
- Developed a first-fill synthesis of fully charged fuel for Material (1).
- Demonstrated a pathway for regeneration of the spent fuel for Material (1).
- Performed preliminary thermodynamic measurements that corroborate computational predictions for Material (1).

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. This project is developing structurally well-defined liquid carbon-boron-nitrogen (CBN) hydrogen storage materials (i.e., heterocycles containing carbon, boron, and nitrogen) that 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., $\Delta G \approx 0$ 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 $\text{H}_2$ storage system. Indeed, high-level computational analysis indicates that the release of $\text{H}_2$ from CBN heterocycles such as (1) has favorable overall thermodynamics conducive to reversibility, (e.g., see eq. 3). 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, this project is investigating several CBN heterocycle materials for $\text{H}_2$ 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. The structurally well-defined nature of these CBN heterocycle materials will facilitate their characterization and mechanistic investigation of the proposed desorption/absorption processes.

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 $\text{H}_2$ desorption for seven proposed CBN materials. Theory predicts that Materials (1), (3), and (7) have the potential for reversibility ($\Delta G \approx 0$ kcal/mol). With the help of theory, and based on availability of synthetic methods, we conclude that our synthetic efforts should be initially directed toward Materials (1) and (7).

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 $\text{H}_2$ release and uptake properties of this particular storage system. We pursued the preparation of N-protected derivatives 2'-6' ($R = \text{t-Bu}$, Scheme 2, bottom) as models for 2-6 due to their ready availability. 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).
Scheme 3 illustrates the synthesis of 2'-6'. We previously reported the preparation of heterocycle 7, which ultimately serves as the universal precursor to 2'-6'. The yields described in Scheme 3 have not been optimized. Compounds 2'-6' are all liquids with melting points below –30°C.

We also developed a first-fill synthesis of the fully charged model fuel 1', thus making all the materials/intermediates along the proposed dehydrogenation pathway synthetically available for further experimental investigation. Scheme 4 describes our synthesis.

Reaction of homoallyl bromide 12' with t-butylamine produced homoallylamine 13'. Treatment of this amine with BH₃•THF furnished the amine-borane complex 14. Subsequent intramolecular hydroboration yielded the desired model charged fuel 1' (R = t-Bu) with a storage capacity of 4.3 wt%. Replacement of the t-butylamine with methylamine gave a material with 6.1 wt% storage capacity, an increase of 42%. The yields described in Scheme 4 have not been optimized.

Development of Conditions/Catalysts that will Recharge the Spent Fuel

We investigated the regeneration of spent-fuel material 2' using a combination of molecular H₂ and hydride/proton sources. We determined that the spent-fuel material 2' readily takes up two equivalents of molecular H₂ to furnish 3' under mild conditions (Scheme 5). We also established that addition of potassium hydride (KH) to 3' followed by protonation with hydrochloric acid in a single pot gave the desired product 1' in 71% isolated yield. The regeneration route illustrated in Scheme 5 represents a simple and atom economic way to regenerate our spent fuel, with potassium chloride salt being the only byproduct from the regeneration sequence. However, the use of KH needs to be avoided to improve the energy efficiency of the process. The yields described in Scheme 5 have not been optimized.
Preliminary Experimental Thermodynamic Measurements

The availability of 2', 4', and 6' allowed us to experimentally assess the thermodynamic properties of CBN material system (1). Scheme 6 shows the calculated hydrogenation enthalpies [in brackets] versus the experimentally determined values (in parenthesis). These hydrogenations were carried out using a homogeneous catalyst RuCl₂(PPh₃)₃. Thus, calorimetric measurements in general support the computationally determined reaction enthalpy values. We determined that compound 2' can be readily hydrogenated using Pd/C as a catalyst. However, we were unable to measure the hydrogenation enthalpy of this reaction due to the heterogeneous reaction conditions. RuCl₂(PPh₃)₃ did not promote the hydrogen uptake of 2'.

Conclusions and Future Directions

In summary, we developed a versatile synthetic toolbox for the preparation of novel CBN heterocycle H₂ storage materials, including a first-fill synthesis of the charged fuel, the synthesis of the spent fuel, and all proposed partially spent fuel along the desorption pathway. The synthetic availability of CBN heterocycle materials enabled us to 1) determine preliminary thermodynamic data and 2) demonstrate a pathway for regeneration of the spent fuel. In Fiscal Year 2011, we will:

- Optimize our current synthetic toolbox with regard to yields.
- Complete experimental thermodynamic properties for model CBN heterocycles using appropriate homogeneous catalysts.
- Improve energy efficiency for recharging the spent fuel.
- Develop conditions/catalysts for H₂ desorption for CBN materials.
- Formulate the charged fuels as liquids.

FY 2010 Publications/Presentations

IV.B.1c Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

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Start Date: March 1, 2005
End Date: September 30, 2010

Objectives

• Provide demonstrated spent fuel regeneration chemistries and physical properties to enable preliminary cost analyses by Dow.
• 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 (\(\Delta G^\circ\) ideally no less negative than ca. −0.8 kcal/mol).
• Develop analytical methods to quantify gas-phase impurities that may accompany hydrogen release, 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 Fuel Cell 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

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Description</th>
<th>Metric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Wt. %</td>
<td>Maximum calculated hydrogen weight fraction, potential to exceed 9 wt %</td>
<td>&gt; 7 wt. % H2</td>
</tr>
<tr>
<td>Potential to Regenerate On-Board</td>
<td>Potential to rehydrogenate spent fuel directly</td>
<td>yes/no/potential</td>
</tr>
<tr>
<td>Regenerable</td>
<td>Ability to chemically reprocess fuel offboard</td>
<td>yes/no/potential</td>
</tr>
<tr>
<td>Acceptable Phase Change</td>
<td>Problematic liquid to solid phase change</td>
<td>yes/no/potential</td>
</tr>
<tr>
<td>Acceptable H2 Release Rate</td>
<td>Maximum rate of hydrogen release</td>
<td>&gt; .02 g H2/s/kW</td>
</tr>
<tr>
<td>Stable Material &lt; 50 °C</td>
<td>Stable in fuel tank &lt; 50 °C to H2 release, or decomposition</td>
<td>yes/no/potential</td>
</tr>
<tr>
<td>Temperature of Release</td>
<td>Demonstrated, or potential for release at T &lt; 100 °C</td>
<td>&lt; 200 °C</td>
</tr>
</tbody>
</table>
Accomplishments

- Completed chemistry and demonstration of a one-pot simplified spent fuel regeneration scheme utilizing hydrazine and liquid ammonia.
- Demonstrated regeneration of spent fuel from ionic liquid AB mixtures indicating that properly designed ionic liquids will not interfere with regeneration chemistries.
- Prepared new storage materials that have lower exo-thermicity, higher rates to higher extents of release at lower temperatures compared to AB, with many compounds exceeding 2010 targets.
- Heterogeneous base metal catalysts for hydrogen release have been prepared and demonstrated to have high rates of release to >9 wt% H₂.
- Worked with University of Pennsylvania (Penn) partners to further develop promising ionic liquid AB fuels that remain liquid throughout the dehydrogenation cycle.
- Worked with Argonne National Laboratory (ANL) and Penn to provide data ANL required to develop preliminary onboard release system analysis of an ionic liquid AB fuel.
- De-selected liquid fuel systems comprised of alkylamineborane–AB because of catalyst lifetime issues.
- Using previously developed hydrogen purity test stand, examined numerous hydrogen release systems, quantifying evolution of impurities vs. time and temperature where impurities were observed.
- Worked with Hydrogen Storage Engineering Center of Excellence to define acceptable impurity mitigation strategies for onboard gas cleanup.

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, Pennsylvania State University, the University of Washington, Dow, U. S. Borax, and the Pacific Northwest National Laboratory (PNNL). These partners collectively work with LANL on four major areas of research and development (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. LANL 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 hydrogen release from AB, LANL’s approach is to develop liquid compositions containing AB.
and to develop mechanistic information to guide heterogeneous catalyst discovery for hydrogen release from AB and AB-like liquid systems. In the area of spent fuel regeneration, LANL’s approach is to optimize the routes to the digestion, reduction, and recycle of reagents to complete a spent fuel regeneration process, and work closely with Dow process engineers to develop preliminary baseline cost and efficiency analyses of spent fuel regeneration. This also involves collaborating closely 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 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 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


To enable low-temperature catalytic release of hydrogen over a heterogeneous catalyst, the fuel must be a liquid. Liquid systems are also more readily engineered into a system. Research has continued in working with Penn and ANL to work toward a preliminary onboard hydrogen release system analysis of the liquid fuel system of AB in ionic liquids. Work has continued to develop a complete set of kinetics from which ANL bases their onboard release analysis, and to optimize the liquid properties of the fuel and spent fuel. In addition, LANL has made progress in understanding some of the systematics of impurity formation in hydrogen release materials, and has worked closely with the Engineering Center to develop mitigation strategies to deal with any residual gas-phase impurities.

LANL has discontinued working on what was an initially promising liquid fuel formulation comprised of certain alkylamineboranes mixed with AB. While many of these compositions had useful liquid ranges, an additional requirement is that they must be compatible with catalytic release strategies to obtain the highest rates of hydrogen release possible at the lowest temperatures possible. Our work during this past year indicates that the alkylamineborane mixtures lead to rapid deactivation of the catalyst. The accompanying figure indicates that the rate of hydrogen release from mixtures of sec-butylamineborane/AB are low, and are similar with and without catalyst, indicating that the catalyst is deactivated (Figure 1). In a separate experiment, we observe that sec-butylamineborane by itself is unstable above 50°C, and also decomposes to yield free sec-butylamine, which is a potential catalyst poison (Figure 2). While there may be a solution to these two problems, LANL did not feel it was warranted to expend the effort to continue this line of research in the last year of the project.

2. Regeneration of Spent Fuel

LANL’s prior 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). 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

FIGURE 1. Dehydrogenation of a mixture of sec-butylamineborane and AB at 60°C is invariant in rate with or without a catalyst, indicating that the catalyst is deactivated.
Another potential improvement was to combine steps whenever possible. LANL successfully addressed these opportunities, and discovered and developed a new, simplified spent fuel regeneration scheme that is shown in Figure 3. This scheme involves the use of hydrazine, \(N_2H_4\), a lightweight reducing agent as digestion and reduction agent. During the past year, LANL has demonstrated that by optimizing the conditions, the generation of byproducts can be avoided, and by using liquid ammonia solvent, pure AB may be obtained directly from spent fuel in a single operation of dissolving spent fuel in a hydrazine/ammonia mixture that results in reduction of spent fuel directly to AB. Removing the volatile excess ammonia completes the cycle. Dow has begun a preliminary analysis of this process, and it appears that the process energy is substantially less than the thiocatechol route, and because of the significant reduction in unit operations and separations that the capital costs for the hydrazine route are very favorable. The largest cost appears to be in hydrazine, which is not a surprise to us, as hydrazine is not produced in an efficient process nor on a large scale that makes hydrazine expensive. Future research could be directed at significantly reducing the cost of hydrazine.

### 3. New Materials Discovery

Our previous effort in the discovery of new materials has focused on preparing metal amidoboranes. The driving force behind our research in this area was to explore whether replacing a hydrogen atom of AB with a metal atom would sufficiently alter the reaction pathways and thermodynamics of hydrogen release such that potentially reversible systems would result. We feel that to be practical that these compounds must be reversible, because we have no ideas that will result in an energy efficient regeneration of the resulting spent fuel. It appears to us that any regeneration will require the re-synthesis of the corresponding metal hydride (M-H), and react that with AB to prepare metal amidoborane (M-AB). Of course, if the regeneration requires synthesis of M-H, one might as well use M-H as the storage material, and consider hydrolysis. However, this approach has been determined by DOE to not have a path forward because of the too numerous issues with hydrolysis systems and the regeneration efficiencies involved.

Among the metal amidoborane compounds that LANL has examined to date (\(M = Na, Li, K, Ca, Mg, Al, Ti, Sc, Zn, Sr\)), the thermochemical properties and the hydrogen release temperatures show a good deal of diversity. However, the thermodynamics of hydrogen release for all of the mono metal amidoboranes are still too exothermic to enable direct rehydrogenation using \(H_2\) gas pressure, and so to date, no materials have...
been discovered that can be directly regenerated on board. LANL has discontinued work on mono metal amidoboranes, but we suggest that bimetallic M, M’-amidoboranes still should be surveyed to determined if there are any members of that series that offers the potential of direct rehydrogenation with hydrogen pressure.

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. This year our efforts in engineering support have been focused on working with Penn on their ionic liquid (IL)–AB system that is a potential liquid fuel. Two issues that influence engineering design decisions for these potentially liquid systems are 1) impurities that may arise during release, and 2) stability of the materials at 50-60°C. Impurities and stability are monitored using similar approaches. LANL monitored the stability of IL–AB mixtures as a function of time at three temperatures of 50 and 60°C for periods of 5 days. Fourier transform IR spectroscopy of the gas above the IL-AB mixture was monitored to detect potential impurities while the mass of the sample was simultaneously and continuously monitored to detect any weight loss due to decomposition resulting in gas phase products. To monitor impurities at higher temperatures during release, we use both gas-phase IR, TGA, and mass spectroscopy of the evolved gas stream to detect and quantify impurities. Among the impurities that may be detected this way are diborane, ammonia, borazine, and any impurities arising from potential decomposition of the ionic liquid. Figure 4 indicates that at 50°C, there is no detectable mass change, and we find no impurities in the gas phase over a period of 5 days. At 60°C, we detect no mass change after 5 days, but we do observe water in the gas phase. As the particular IL used is known to be hygroscopic, we assume for now that the water arises from water adsorbed on the IL starting material used to prepare the mixture. At 70°C (data not shown) where the onset of hydrogen evolution begins, we observe small quantities of ammonia being evolved initially. A small amount of borazine is also observed, but in quantities much less than from neat AB dehydrogenation.

Conclusions and Future Directions

Research at LANL in collaboration with Penn has demonstrated that the use of heterogeneous catalysts for the release of hydrogen from AB-IL fuels may begin to release hydrogen at high rates at low temperatures, and that these mixtures are quite stable up to at least 60°C. Impurities are released as well, and they include ammonia (an initial small pulse at low temperatures) and a small quantity of borazine at higher temperatures. The quantity of borazine released is relatively smaller than from pure AB. In the area of regeneration, we have discovered and demonstrated an entirely new regeneration scheme that involves digestion and reducing spent fuel to AB in a single process using hydrazine. This hydrazine process successfully regenerates a variety of spent fuel types, including the spent fuel from dehydrogenation of AB-IL 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 ammonia borane using hydrazine.

FY 2010 Publications/Presentations and Patents

Peer-Reviewed Publications


Invited Presentations

Invited presentations by K. Ott

4. “Recent results from DOE’s Chemical Hydrogen Storage Center of Excellence”; 2nd LANL-HU Workshop, Hiroshima, Japan, November 2009.

Invited presentations on chemical hydrogen storage by A.K. Burrell

1. Florida State University, May 2010.
2. IEA HHA Meeting Death Valley, CA April 2010.
6. 2nd LANL-HU Workshop, Hiroshima, Japan, November 2009.
7. AIST Osaka, Japan, November 2009.
8. 4th International Workshop on Sustainable Materials Science Hiroshima, Japan, November 2009.

Patents

Patents Issued:


Patent Applications Published:

1. 20090297423 Dec. 3, 2009, “Energy efficient synthesis of boranes” Thorn, Tumas, Schwarz
2. 20090274613 Nov. 5, 2009, Hydrogen Production Using Ammonia Borane” Hamilton, Baker, Semelsberger, Shrestha

DOE Hydrogen Program 452 FY 2010 Annual Progress Report
IV.B.1d Chemical Hydrogen Storage Research at PNNL

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Start Date: March 1, 2005
End Date: September 30, 2010

Objectives

- Quantify borazine release from ammonia borane (AB).
- Develop hydrogen release mechanism for metal amidoboranes.
- Demonstrate high efficiency methods for large-scale synthesis of chemical hydrogen storage materials.
- Develop high-efficiency off-board methods for chemical hydride regeneration to achieve DOE targets (60%):
  - Coordinate with Argonne National Laboratory (ANL) 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 Chemical Hydrogen Storage Center of Excellence (CHSCoE) 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 Fuel Cell 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, ammonia borane, 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.

**SCHEME 1.** Materials currently under study and provides both the gravimetric and volumetric density of hydrogen.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction Equation</th>
<th>Hydrogen Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄BH₄</td>
<td>NH₄⁺ + BH₄⁻ + H₂</td>
<td>240 g H₂/kg, 130 g H₂/l</td>
</tr>
<tr>
<td>NH₃BH₃</td>
<td>NH₃⁻ + BH₃⁻ + H₂</td>
<td>195 g H₂/kg, 140 g H₂/l</td>
</tr>
<tr>
<td>[NH₃BH₂(NH₃[BH₄])]⁺</td>
<td>[NH₃⁻][BH₄⁻]⁺ + H₂</td>
<td>195 g H₂/kg, 140 g H₂/l</td>
</tr>
<tr>
<td>LiNH₂BH₃</td>
<td>Li⁺ + NH₂⁻ + H₂</td>
<td>109 g H₂/kg, 52 g H₂/l</td>
</tr>
<tr>
<td>NaNH₂BH₃</td>
<td>Na⁺ + NH₂⁻ + H₂</td>
<td>76 g H₂/kg, 43 g H₂/l</td>
</tr>
</tbody>
</table>

Accomplishments

- Provided high-purity AB to CHSCoE partners and others from our scaled-up first fill reactor.
- Metal amidoborane (MAB) release mechanism identified as metal assisted hydride transfer
- Quantified H₂ impurities from AB and demonstrated approaches to mitigate and control them.
- AB+ metal hydride mixtures showed different features compared to AB: decreased impurities, less foaming, lower exothermic release.
- Demonstrated >99% boron recovery from digestion of real spent fuels.
- Identified potential new AB synthesis route which may be able to combine first-fill and regeneration lowering costs and increasing efficiency.
- Fully characterized spent AB.

IV.B.1d Chemical Hydrogen Storage Research at PNNL
**Introduction**

Fuel cell vehicles need improved hydrogen storage to meet the DOE driving range targets of 500+ kilometers. To meet this need, the DOE established three Centers of Excellence to develop materials for hydrogen storage. PNNL is part of the CHSCoE which is a partnership between national laboratories, universities and industrial partners. The CHSCoE is tasked with inventing, testing, and recommending chemical hydrides that may meet the DOE targets.

**Approach**

PNNL’s approach is consistent with the philosophy of the CHSCoE. A comprehensive understanding of reaction mechanisms 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 CHSCoE. Therefore, PNNL’s work within the CHSCoE is inherently multidisciplinary and highly collaborative with several of the CHSCoE 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 leads the engineering activities within the CHSCoE, 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 (FY) 2010 focused on five major tasks: (i) demonstration of scale up of the “first-fill” synthesis of AB, (ii) examining mixtures of AB and metal hydrides, (iii) International Partnership for the Hydrogen Economy (IPHE) materials including

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**Table 1.** Summary of the rates of hydrogen release, enthalpies of hydrogen release and impurities measured for various materials, temperatures and reaction conditions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gravimetric Rate g H2/kg</th>
<th>Volumetric Rate g H2/l</th>
<th>Additive</th>
<th>Enthalpy kJ/mol</th>
<th>Peak Rate g/s/kg</th>
<th>Temperature °C</th>
<th>NH3 ppm</th>
<th>Bz wt%</th>
<th>Notes</th>
<th>Continue?</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3BH3</td>
<td>194 (160)</td>
<td>146 (120)</td>
<td>none</td>
<td>-23</td>
<td>1.3</td>
<td>160</td>
<td>100-250</td>
<td>4-12+</td>
<td>foams</td>
<td>D</td>
</tr>
<tr>
<td>NH3BH3</td>
<td>“</td>
<td>“</td>
<td>none</td>
<td>-23</td>
<td>0.93</td>
<td>145</td>
<td>100-250</td>
<td>2-4</td>
<td>foams</td>
<td>D</td>
</tr>
<tr>
<td>NH3BH3</td>
<td>“</td>
<td>“</td>
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<td>100-250</td>
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<td>117 (102)</td>
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<td>-23</td>
<td>0.43</td>
<td>130</td>
<td>100-250</td>
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Summary of rates, enthalpies and purity of hydrogen. theoretical density (measured density). Bz = borazine. ? = not yet measured, will be determined in future work. All compositions tested are not shown. C = Continue, D = Discontinue for on or off board transportation systems, still may be applicable for stationary or portable applications.
identifying the hydrogen release mechanism from MAB, (iv) quantifying the concentration of impurities, NH$_3$, and borazine in the hydrogen released form AB, and (v) regeneration.

**First-Fill:** PNNL demonstrated the bench-scale reactor designed and built in FY 2009. The reactor scaled up PNNL's AB synthesis to 100 g quantities (factor 10x). It is a one-pot synthesis reactor which provides high yield (95-99%) and high purity (>99%) AB. Parametric studies were done using the reactor. The results indicate that a semi-continuous reactor scheme may be viable, and its design is underway. Dow's (formerly Rohm and Haas) analysis of our process indicated that the projected cost was $9.1/kg AB and the high purity and yield make our process superior to the state-of-the-art.

**AB/Metal Hydride Mixtures:** We investigated different combinations of AB mixed with metal hydrides (MH), i.e. MgH$_2$, CaH$_2$, TiH$_2$ and/or ZrH$_2$. We ball milled a series of different combinations of AB+MH powders to obtain tuned materials properties. The composite of ammonia borane+10 mol% TiH$_2$ shows a remarkable drop in impurity levels to <1%, as compared to neat AB, specifically borazine and ammonia which are released simultaneously with hydrogen. The mixture of AB+0.5 MgH$_2$ with addition of 10 mol% TiH$_2$, did not release any detectable amounts of borazine, ammonia or diborane and did not show any foaming. Moreover, the hydrogen release temperature was lowered by ca 20°C.

**IPHE Materials and MAB Hydrogen Release Mechanism:** A new series of substituted metal amidoboranes MNHRBH$_3$ (M = Li,Na,K; R = H, CH$_3$, C(CH$_3$)$_3$-) have been synthesized. A detailed study has indicated that hydrogen release takes place through a metal ion-assisted hydride transfer mechanism and the formation of a metal hydride intermediate. In these compounds the dihydrogen bonding of the parent AB has been replaced by a $M^+$...H$^+$B interaction and this, in agreement with our detailed studies of release from AB, may explain why there is no induction period observed. No ammonia (<10 ppm) was observed for the materials when the material is decomposed in a sealed reactor and the strong dependence of reaction rate on temperature suggests the materials will be unaffected by storage at even high ambient temperatures.

The reactivity trend of hydrogen release from metal amidoboranes is the opposite of the reactivity trend of hydrogen release from metal borohydrides. In the case of the MABs the metal cation performs a hydride transfer (or relay) from the neighboring borane to the protonic hydrogen of the amine. This is interesting from a mechanistic outlook as the formation of the nascent metal hydride is faster for the more stable hydrides, however the more stable the metal hydride the greater the barrier for hydride transfer to the amine – thus the rates for each step are opposite in reactivity the observed rates tend to be moderated. However, as the K > Na > Li the formation of the nascent MH appears to be rate limiting and therefore give the opposite reactivity of the corresponding borohydrides, that is Li > Na > K. As the ionization energy increases, the activation barrier for the M-step decreases, whereas the activation barrier for the H-step increases thereby explaining why the rate trend for release is K > Na > Li [1].

**Impurities from AB:** Hydrogen generated from AB decomposition was analyzed using various analysis tools such as nuclear magnetic resonance (NMR), Fourier transform infrared, and mass spectrometry to determine the ammonia and borazine levels. Quantitative amounts of borazine were found by bubbling AB-generated hydrogen with a sweep gas of 20 ccm nitrogen through a liquid trap (Tetrahydrofuran or glyme) which captured the borazine impurities. We then used solution NMR to measure the amount of borazine produced. Figure 1 contains a summary of the results. It was determined that the ramp rate and temperature impacted the amount of borazine produced, with the temperature being the dominant factor. At temperatures below 150°C, the borazine levels was <1 wt%, but increased by an order of magnitude when the temperature exceeded 150°C. High temperatures combined with fast temperature ramping (>5°C/min) increased the borazine levels to >12 wt%. As far as we can tell the ammonia produced (100-250 ppm) was independent of temperature and ramp rate within our experimental error of measuring ammonia with a Draiger tube. In addition, if the reactor was sealed during hydrogen generation, and the hydrogen released slowly much less ammonia was detected indicating that residence time impacted the ammonia production rate. This is especially true for the MABs. Additives impacted the impurities in different ways. For example, both AB on mesoporous silica scaffolds (1:1) and AB mixed with CoCl$_2$ (<5 wt%) were found to have decreased borazine (<1 wt%) produced even at temperatures >150°C and ramp rates >5°C/min; however, AB on a BN scaffolds resulted in no improvements in regards to borazine.

**FIGURE 1.** Summary of Borazine Release from AB and AB with Additives
production. Since high temperature and ramp rates will be required to generate hydrogen in sufficient quantity to meet the hydrogen generation targets, neat AB research should be discontinued. However, AB with additives such as CoCl₂ showed low borazine release, and CoCl₂ significantly reduced foaming making AB with additives a “Go” decision for future research. Metal amidoboranes did not produce any borazine since the release mechanism is different than that of AB; however, the ammonia release was higher (0.2 wt%) than that of AB.

**Regeneration of Spent Fuel:** Another key aspect of the PNNL project is chemical regeneration. A process was envisioned as shown in Scheme 2; where R is tert.-butanol; PhOH is phenol; M is a transition metal complex. PNNL has found precedent for and demonstrated all the steps individually.

Digestion chemistry had been demonstrated using model spent fuels in previous years: borazine and borazine-derived polyborazylene. However, information is needed to assess regeneration cost and efficiency of real spent fuel. In FY 2010 we worked on digestion of real spent fuels obtained from AB dehydrogenation. Monothiols do not digest spent fuel. We tried to transesterify alkyl borates with thiophenol, but those results were unsuccessful. Digestions with aliphatic alcohols produce borate esters and a white residue, to varying degree depending on the alcohol. We optimized reaction conditions to maximize total conversion and recovery of boron. Approximately 85% of the boron was recovered as B(OEt)₃. This ester as well as other alkyl borates can be transesterified with phenols to produce aryl borates [2]. The boron residue was recovered as boric acid by adding aqueous HCl. Boric acid converts to B(OEt)₃ under same conditions as used for transesterification [2]. Therefore it is envisioned that >99% B can be recovered. Digestion with ammonium tetrafluoroborate was tried since we have been able use BF₄⁻ in reactions analogous to Step 3 using HRh(dmpe)₂. Reacting NH₄BF₄ with spent fuel in effect combines Steps 1 and 4 to accomplish recycling of BF₄⁻ byproduct of Reaction 3.

All the steps of Scheme 2 have been demonstrated using Rh based catalysts. Due to the high cost of Rh, lower cost transition metals (Co and Ni) were examined. In FY 2009 PNNL synthesized complexes with dmpe and other bis phospine ligands and explored their properties and reactivities (for steps 2 and 3). 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(O(CF₂)₃)₃, which has greater H⁻ affinity compared to B(OPh)₃. On the basis of these observations and recent theoretical analyses, PNNL in FY 2010 examined the use of chlorophenols and fluorophenols in place of phenol in the above process with complexes of Co and Ni. We used theory to identify aromatic borate esters with hydride affinities greater than that of B(OPh)₃. Literature reports [3] suggested that halogenated phenyl borates would have greater Lewis acidity than phenyl borate. We calculated hydride affinities for several chloro and fluoro-substituted phenol borates and found indeed that hydride affinities could be significantly increased by halogen substitutions. In collaboration with US Borax scientists (Dave Schubert and Duane Wilson), several compounds were synthesized and characterized by NMR. Their relative Lewis acidities were determined as well based on the adduct with triethylphosphine oxide. We used this index to corroborate calculated hydride affinities and correlate with reactivity toward HRh(dmpe)₂ and HCo(dmpe)₂, and identified the most likely halogenated phenyl borates for Step 3. We found that Co hydrides de-chlorinate chlorophenyl borates. The reactions of HCo(dmpe)₂ with less than fully fluorinated phenyl borates are complex. Evidence for hydride transfer to 2-fluorophenyl borate was not observed, suggesting that esters of mono-fluorophenols do not have high enough hydride affinity. HCo(dmpe)₂ did react with the borate ester of 3,5-difluorophenol and evidence of hydride transfer was observed, but the reaction was complicated by side reactions that consumed B-H containing products and partially decomposed the Co(dmpe)₂⁺ complex.

Reactions of B(SPh)₃ with HCo(dmpe)₂ and HNi(dmpe)₂⁺ were investigated to assess the range of boron compounds that could be reduced with these hydrides. For the Co complex, facile reduction of all B-S bonds to B-H bonds occurs. Reactions run in the presence of triethylamine produced triethylamine borane as the sole boron containing product.

### Scheme 2. Process using Transition Metals Catalysts to Regenerate Spent AB Fuel

1) **Digestion**

\[
\text{BH}_3 + 3 \text{t-BuOH} \rightarrow \frac{9}{2} \text{H}_2 \uparrow + \text{NH}_3 \uparrow + \text{B(O-t-Bu)}_3
\]

\[
\text{B(O-t-Bu)}_3 + 3 \text{PhOH} \rightleftharpoons \frac{3}{2} \text{B(OPh)}_3 + 3 \text{t-BuOH}\uparrow
\]

2) **Transition Metal Hydride Formation**

\[
3 \text{M}^+ + 3 \text{H}_2 \rightarrow 3 \text{MH}^+_3 \ 	ext{[+ 3 base]} \rightarrow 3 \text{MH} + 3 \text{H}^+\text{base}
\]

3) **Hydride Transfer/Ligand Redistribution**

\[
3 \text{MH} + 4 \text{B(OPh)}_3 + \text{Et}_3\text{N} \rightarrow 3 \text{M}^+ + \text{B(OPh)}^-_3 + \text{Et}_3\text{NBH}_3
\]

4) **Recycle**

\[
3 \text{B(OPh)}^-_3 + 3 \text{H}^+\text{base} \rightleftharpoons 3 \text{PhOH}\uparrow + 3 \text{base} + 3 \text{B(OPh)}_3
\]

5) **Ammoniation**

\[
\text{Et}_3\text{NBH}_3 + \text{NH}_3 \rightarrow \text{BH}_3\text{NH}_2\downarrow + \text{Et}_3\text{N}
\]
For the Ni complex, two of the three B-S bonds were readily replaced to give PhSBH₂NEt₃. As mentioned, digestion of spent fuel to B(SPh)₃ has not been demonstrated. Also, these reactions produce metal complexes with SPh ligated to the metal. Digestion to B(SPh)₃ and recycle of these complexes remain to be worked out.

Finally, Dow’s cost analysis of AB synthesis revealed the most significant cost being NaBH₄ production from AlH₃-L (Scheme 3). Adding to the cost is the fact that 25% of the hydrogen in the NaBH₄ is lost in the conversion to AB. After looking at the process production route, we believe that AB could be produced directly from the AlH₃-L improving the hydrogen utilization and eliminating NaCl production potentially resulting lower cost (Scheme 4). A literature search revealed that all the steps of PNNL’s proposed process have been demonstrated except one. We successfully demonstrated that step this year. This process still requires Al³⁺, which is very expensive to produce. We believe there is a way to avoid the smelting process and potentially decrease the cost of AB synthesis. If the smelting process can be avoided, then this new synthesis process would also be applicable to regeneration of spent fuel. Therefore, a single facility could be used for fuel synthesis and spent fuel regeneration decreasing capital costs. This is a recommendation for future work.

Conclusions and Future Directions

Conclusions

- Bench-top scale AB synthesis reactor demonstrated a 10x increase in AB production capability showing

- AB + metal hydride mixtures showed different features compared to AB, with some mixtures showing no borazine production, less foaming, and lower exothermicity.

- Quantified impurities in H₂ from AB and demonstrated approaches to mitigate and control.

- In order to meet the hydrogen generation targets, the ramp rate and temperature needed for AB to generate hydrogen also result in high impurities, it is recommended that neat AB not be further developed for use in on-board hydrogen storage.

- AB with additives such as CoCl₂ can meet the hydrogen generation rates without producing excessively large amounts of borazine, further development of AB with additives is recommended.

- Identified potential new AB synthesis/regeneration route.

- Since the chlorinated phenyl borates undergo dechlorination in reactions with Co hydrides, work to develop AB regeneration via this system is not recommended.
Future Work

This project has ended. Therefore the future work is primarily working with the Engineering Center in the development of systems. Recommendations for future work based on this project include:

- Development of a flow reactor for AB synthesis.
- AB with additives to reduce borazine impurities.
- Investigation of the new AB synthesis/regeneration route.
- Metal amidoborane development to find an endothermic system that is regenerable on-board.
- Develop and assess routes for converting spent fuel to B(SPh)₃ and recycle of Co(dmpe)₂SPh and [Ni(dmpe)₂SPh]⁺.
- Develop better understanding of reactions of fluorinated phenyl borates with Co hydrides to assess feasibility of their use in regeneration scheme.
- Assess reactivity of fluorinated and chlorinated phenyl borates using Ni²⁺ hydrides.

FY 2010 Publications/Presentations

Publications


Presentations

1. JD Holladay, National Hydrogen Association, Long Beach, CA (May 2010).


4. TD Smurthwaite, American Chemical Society Joint Northwest/ Rocky Mountain Meeting, Pullman WA, (June 2010).

5. JD Holladay, Materials Challenges in Alternative & Renewable Energy 2010, Cocoa Beach FL (Feb 2010).
References


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), Vin Crespi, Michael Chung, Henry Foley, and Peter C. Eklund (deceased)
- Rice University, James Tour, Boris Yakobson, Carter Kittrell, Robert Hauge and Richard E. Smalley (deceased)
- 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: September 30, 2010

Objectives

The Hydrogen Sorption Center of Excellence (HSCoE) developed high-capacity sorbent materials that operate at cryogenic to ambient temperatures and are efficiently and quickly charged in the tank with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Work was directed at overcoming barriers to DOE system goals and identifying pathways to meet the hydrogen storage system targets. In particular, the HSCoE strove to:

- Develop high specific surface area (SSA) sorbents 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 were organized in focused groups to optimize development and avoid duplication of effort, with seamless integration of experiment/theory.
  - Quantitative down-select criteria were used prior to beginning significant development and at go/no-go points.

Technical Barriers

The HSCoE developed novel high SSA sorbents to be used in hydrogen storage systems for advanced fuel cell technologies. During the past year, the HSCoE had 15 active projects at 18 institutions. HSCoE partners conducted a wide range of applied research and engineering studies on currently available sorbents and developed design principles and synthetic methods with the goal of creating next-generation materials that have the potential to meet the critical DOE hydrogen storage system targets. The technical barriers addressed by these projects from the Fuel Cell Technologies (FCT) Program Multi-Year Research, Development and Demonstration Plan included:

General:

(A) System Weight and Volume  
(B) System Cost
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(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 developed sorption materials for hydrogen storage systems. In general, sorbents can be used in systems to meet most of the DOE hydrogen storage targets for light-duty vehicles. Thus, the HSCoE focused efforts to address the highest-risk targets for sorbents which are primarily 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 worked closely together to systematically accelerate the development of advanced hydrogen sorbents. For specific details, please review their individual contributions to this report. A summary of the major accomplishments for the HSCoE overall is listed in the following.

- Designed and developed reversible sorbents via ambient temperature hydrogenation techniques that have over 4 wt% storage capacities with isosteric heats of adsorption of 10-30 kJ/mol.
  - Pioneered the development of spillover that has been validated on numerous materials and that have relatively low chemical binding of hydrogen, potentially allowing efficient reversible on-vehicle refueling. This class of materials enables hydrogen storage system designs with more than 75% of the volumetric and gravimetric capacities of the materials and substantially reduces system costs and complexity.
- Developed new materials that increased the gravimetric (~40%, e.g. from ~5 to >7 wt% at 77 K) and volumetric (~150%, e.g. from ~15 to >35 g/L at 77 K) hydrogen storage by physisorption onto high SSA sorbents by optimizing pore sizes (0.7 to 1.5 nm) to increase specific surface area and packing density.
- It may be possible to meet DOE 2015 on-vehicle refueling hydrogen storage system capacity targets with physisorption-based optimized material at cryogenic temperatures and relatively low pressures (i.e. 10 to 50 bar). The decreased pressures, compared to high pressure 350 to 700 bar storage systems, enabled by relatively inexpensive carbon-based sorbents could substantially reduce tank and balance-of-plant costs.
- Synthesized new high SSA physisorption materials with optimized uniform pore size using a variety of scalable/inexpensive processes.
- Discovered and championed an entire class of viable materials that uses lightweight (e.g. 3d metals) metal centers to enhance H₂ isosteric heats of adsorption and enable multiple H₂ binding on each metal site.
- Initial theoretical work demonstrating multiple molecular hydrogen (H₂) binding to electronically unsaturated 3d metals (50 kJ/mol – H₂) was first performed by the HSCoE. These studies initiated hundreds of subsequent theoretical and experimental studies in the research area of strong/multiple H₂ binding. The original paper [1] has been cited nearly 200 times. This work paves the way to meet DOE’s ultimate storage targets at ambient temperatures.
- Designed and developed substitutional materials with enhanced dihydrogen binding energy to increase capacities at near ambient temperatures, on a per SSA basis.
- Substituted materials enhance hydrogen isosteric heats of adsorption (e.g. ~11 kJ/mol for B substituted carbon, compared to ~5 kJ/mol for pure carbon) sufficiently to increase capacities at near ambient (e.g. ~200 K) temperatures. Substituted materials have the potential to meet DOE’s 2015 hydrogen storage system capacity targets. Increasing storage temperatures to near ambient helps decrease system costs by reducing the amount of insulation, tank, and balance of plant costs.
- Confirmed that standard physisorption-based dihydrogen adsorption scales with SSA. To date, no validated experimental evidence exists that any substantial capacity enhancements occurs due to geometric configurations.
- At the outset of the Center, numerous publications had reported extraordinary results for high SSA materials where the enhanced capacities where potentially a result of novel geometries or structures within the material. In general, heats of adsorption can be increased
with multiple wall interactions in very small pores, but this ultimately reduces capacities. The Center did not validate any single element material or any materials with unexceptional electronic states that have substantially higher hydrogen storage capacities beyond what is expected based on the SSA and specific storage conditions.

- Developed unique measurement capabilities to accurately and reliably characterize hydrogen storage properties.
  - Neutron scattering.
  - High-pressure H₂ nuclear magnetic resonance that performs measurements from 77 K to ambient.
  - Hydrogen storage properties with small laboratory-scale (1-100 mg) samples:
    - Enables high throughput and rapid screening analysis:
      - Accurate hydrogen storage property measurements a major problem in the community for decades.
      - Partly due to only having small quantities of “laboratory-scale materials” to characterize.
      - Developed protocols and measurements capable of accurate results from small amounts of sample:
        - Substantially enhanced throughput by eliminating need to develop larger scale synthetic methods or repeating synthesis processes numerous times to make enough material.

Introduction

To realize the full energy efficiency, energy savings, and environmental improvements that fuel cells can provide, significant improvements over currently available high pressure-based gas storage technologies are required. The storage targets presented in DOE’s FCT Program Multi-year Research, Development and Demonstration Plan state the critical needs and goals. To improve the mass, volume, cost, safety, and efficiency requirements for vehicular or early market storage systems, DOE is investigating solid-state storage options such as metal hydrides, chemical hydrides, and sorbents. Nanostructured high surface area materials containing carbon, metals, oxygen, and other elements show tremendous promise for breakthrough performance in gas storage. Enough progress has been made by the HSCoE that it may be possible to use sorbents to construct a hydrogen storage system that meets DOE’s 2010 targets. The capabilities of these materials can be improved further 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 developed reversible sorbent materials for energy storage within this DOE Fuel Cells Technology Project. The HSCoE developed the science base and technology advances needed to identify and create nanostructured sorbents that have the potential meet DOE goals for on-board storage. A guiding principle in developing the required materials was 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 40 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 (10–40 kJ/mol) [2], 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 HSCoE discovered the limits of performance of high surface area adsorbents and synthesized and tested sorbents with the potential to meet the DOE system targets for reversible storage. This involved the design and synthesis of new 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 focused on determining binding mechanisms and energies, and the manner in which suitable sites could be organized in space to achieve a high-volumetric density using low-weight frameworks. This involved determining the affects of geometry, introduction of defects, adventitious dopants, and catalytic species, as well as elemental substitution. The HSCoE investigated a range of different lightweight nanomaterials and porous frameworks and championed the development of new sorbents for ambient temperature hydrogen storage.
Results

HSCoE members worked closely together to effectively leverage unique partner capabilities in a coordinated set of focused efforts to accelerate storage materials development. These close and actively coordinated interactions resulted in dozens of joint projects in the past year, in which the rapid materials development is illustrated by the more than 20 joint publications. In addition, the HSCoE works with more than 40 groups from around the world and directly with the chemical hydride, metal hydride, and engineering 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 100 presentations at conferences and more than 50 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 in the following.

Optimizing High SSA Materials: In general, storage capacities increase with higher SSAs 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. Within the last year, the HSCoE continued to increase specific surface areas and capacities of materials using coordinated framework and porous carbon materials (Figure 1). The HSCoE used 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. Material capacities of more than 7 wt% and 40 g/L have been demonstrated at 77 K. These capacities increase by ~30% if the sorbent system stored hydrogen at ~50 K, i.e. >8 wt% and >50 g/L. At this temperature, only ~20 bar pressures would be required and it may be possible to design a storage system that could meet the DOE 2015 hydrogen storage capacity targets. This increase in capacity would be traded against decreases in well-to-fuel cell efficiencies but could improve overall system cost compared to high pressure (i.e. 350 to 700 bar) storage by using much lower pressures (Figure 2).

Improving Site-Specific Dihydrogen Binding Energy: In addition to optimizing geometric structures to improve storage properties, the HSCoE pioneered the use of multiple-element materials to improve dihydrogen binding. In good agreement with theoretical models [3], B substituted with an sp2 structure in carbon enhances hydrogen binding to ~11 kJ/mol [4]. Over the past year, the HSCoE also demonstrated this enhanced hydrogen binding in B substituted carbons through the use of neutron scattering and diffuse reflective infrared fourier transform spectroscopy (DRIFT) (see PSU and NIST contributions to this report). The main issues...
remaining include the need to substantially increase the B concentration while maintaining a high SSA (see PSU and NREL contributions to this report). In this regard, the HSCoE investigated the use of several synthetic techniques to address these issues, including: pyrolysis of BC precursor materials, templating BC₃, and chemical replacement processes.

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. The HSCoE has championed the use of coordinated metal centers to increase dihydrogen binding and to also enable multiple dihydrogen binding at a single adsorption site. Work by TAMU and NIST have demonstrated the enhanced binding of metal centers in metal organic framework materials. Furthermore, the neutron scattering work confirm the theoretical prediction that the binding energy depends on the metal used. 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. Over the past year, the HSCoE has focused efforts in identifying materials and processes that are more synthetically possible (e.g. Figure 4, [6]) starting from existing materials. These types of materials provide a reasonable path for meeting DOE’s ultimate storage targets (i.e., 7.5 wt% and 70 g/L) with inexpensive sorbents.

**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 metal organic framework material, and calculations indicate that 7–8 wt% (50–60 g/L) should be achievable at ambient temperature. Over the past year, the HSCoE continued developing new spillover based materials including demonstrating the spillover is enhanced on pyrolized sucrose; a material often used to bridge between catalysts and high surface are receptors. In addition to improving catalyst processing, receptor materials, reproducibility, and rates, the HSCoE also identified potential mechanisms based on geometrical structures and electronic properties that substantially reduce the barrier to diffusion and thus could significantly increase the kinetic transport rate of atomic hydrogen on the receptor surfaces.

**Conclusions**

- The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent materials. This
Designed/developed substituted materials to enable higher hydrogen binding energies in porous materials. Confirmed the enhanced hydrogen binding of the B substituted materials with neutron scattering and DRIFTS measurements. BC$_x$ materials could increase the storage tank temperature and capacity, thus reducing overall system costs once sufficient B concentration and specific surface area are achieved. Substituted materials also enhance stabilization of metals and potentially improve weak chemisorption processes.

Developed new materials with stronger H$_2$ binding either through interactions with exposed metal centers or electrostatic effects. This work included the experimental validation by neutron scattering that the binding energy depends upon the specific metal used. The Center also identified materials that could be more easily synthesized. This work paves the way to meet DOE’s ultimate storage targets with ambient temperature storage densities greater than liquid H$_2$.

Improved spillover process understanding to help create sorbents with higher capacities and sorption rates that can meet DOE 2015 hydrogen storage targets at ambient temperatures. This included identification of electronic and structural dependencies for atomic hydrogen diffusion on the receptor materials, the thermodynamic processes of the catalysts, and improved spillover rates and capacities with functionalization.

HSCoE works with dozens of groups and provides leadership throughout the world.

resulted in the development of multiple new materials that may be able to be used to meet the 2010 and possibly the 2015 DOE storage system targets including cost and gravimetric/volumetric capacities.

**FIGURE 3.** Some coordinated metal center materials designed by the HSCoE maintain optimum hydrogen binding energies for their entire capacity range. This helps engineering and enhances the material capacity.

**FIGURE 4.** Covalent-organic framework with Ca atoms integrated on carbon linkers. This is an example where known materials where used to form sorbents with a potential for high hydrogen storage capacities.
Future Directions

The HSCoE will focus the remaining effort on completing a comprehensive final report. Provide DOE with a comprehensive review of all significant work done, results, lessons learned, and recommendations for future sorption materials development. 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, including:

- The Center recommends that development efforts for specific material classes be continued where viable routes exist for synthesizing sorbents that can be used to meet the appropriate set of targets:
  - The specific selection criteria for future efforts should focus on the DOE 2015 and the ultimate full-fleet hydrogen storage targets.
  - Numerous materials recommended for no further development.
- Develop materials for hydrogen storage by weak-chemisorption:
  - Ambient-temperature storage via catalytic hydrogen dissociation and transfer to high SSA receptor materials (e.g., spillover) demonstrate 10 to 30 kJ/mol reversible hydrogen binding energies, which enable ambient-temperature storage.
  - Minimizes thermal management and reduces overall storage system cost.
  - Need to improve understanding of atomic H transport to increase rates/capacities and enhance reproducibility and durability.
  - Weak chemisorption enables ambient temperature storage with systems having more than 75% of the material capacities at moderate (~100 bar) pressures.
- Develop materials for multiple hydrogen storage on designated sites:
  - Maybe only route that enables materials to be developed to meet DOE ultimate system targets; especially for on-vehicle refueling.
  - Inexpensive material systems identified to meet ultimate targets.
  - Meeting DOE’s ultimate targets will enable hydrogen to become a viable energy carrier for transportation and other important renewable energy applications.
- Develop substituted/heterogeneous materials that have demonstrated hydrogen binding energies in the range 10–25 kJ/mol:
  - Enables near-ambient-temperature (150–250 K) hydrogen storage.
  - These heterogeneous materials also demonstrate substantial stabilization of single-metal centers and other absorbed species that improve hydrogen storage.
- Limit development of materials in which the storage mechanism is physisorption to only those with optimized structures:
  - To meet the DOE 2015 targets, the only physisorption materials that should be considered for development are those that can have SSAs greater than ~3,000 m$^2$/g, optimized uniform pore sizes in the range of ~0.7 to ~1.5 nm, and excess material hydrogen storage capacities greater than 50 g/L and 7 wt% at cryogenic temperatures (~80–200 K) and moderate pressures (less than 100 bar).

Remaining Issues:

- Develop robust, reproducible, and scalable synthetic methods that create materials where all the adsorption sites are accessible to the hydrogen.
- Improve computational methods to more accurately predict the ability to synthesize designed materials and the hydrogen storage capacity as a function of temperature and pressure.
- Develop a better understanding of atomic hydrogen transport on receptor materials.
- Develop a better understanding of metal center coordination and it's effect on hydrogen adsorption.
- Develop materials in concert with designs for hydrogen storage systems.
- Develop sorbent material measurements standards and certifications.

Support the Hydrogen Storage Engineering Center of Excellence (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 HSCoE has developed several materials that may meet DOE’s 2010 on-board refueling targets.
References

3. e.g., Kim et. al., PRL 96, 016102 (2006).
4. e.g., Chung et al., JACS Comm. (2008), PSU & APCI AMR 2009.
Objectives

- Design, synthesize, and characterize 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 (3.3.4) of the Fuel Cell 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.
- 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).

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010</th>
<th>2015</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(0.045)</td>
<td>(0.055)</td>
<td>(0.075)</td>
</tr>
<tr>
<td>System Gravimetric Capacity: Usable energy density from H₂ (net useful energy/max system mass)</td>
<td>kWh/kg (kg H₂/kg system)</td>
<td>1.5</td>
<td>1.8</td>
<td>2.5</td>
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<tr>
<td></td>
<td></td>
<td>(0.028)</td>
<td>(0.040)</td>
<td>(0.070)</td>
</tr>
<tr>
<td>System Volumetric Capacity: Usable energy density from H₂ (net useful energy/max system volume)</td>
<td>kWh/L (kg H₂/L system)</td>
<td>0.9</td>
<td>1.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Accomplishments

- Crystal twins with two isomeric phases have been discovered, and gas sorption studies revealed that compared to the β-phase, the α-phase possesses a larger surface area leading to higher hydrogen capacity. This symmetry-preserving isomerization strategy can be applied to other MOFs.
- A MOF, which is based on a polyyne-coupled di-isophthalate linker formed in situ, was constructed. Compared to phenyl rings, the polyyne chains showed improved hydrogen affinity.
- An isoreticular series of MOFs with dendritic hexacarboxylate ligands tend to have high surface area and stability. PCN-68 has an excess gravimetric H₂ uptake of 7.2 wt% at 77 K and 50 bar.
- Porous organic frameworks (POFs) with high surface area and tunable pore size were designed and synthesized. They exhibit promising H₂ uptake.

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 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 desorption. 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 H₂ uptake was as follows: (1) Prepared the catenation isomer pair to evaluate the contribution from catenation to the hydrogen uptake of a MOF material. Catenation can be utilized to reduce pore sizes in porous MOFs and has also been explored as an efficient method to improve the hydrogen uptake of MOFs. (2) Synthesized porous MOFs with high hydrogen adsorption capacities based on different coordinatively UMCs. The implementation of coordinatively UMCs into porous MOFs has been considered one of the most attractive ways to improve their affinities to hydrogen. (3) Hydrogen storage studies in MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers. Those ligands containing phenyl rings in MOFs have been proved favorable for hydrogen adsorption. (4) Design and synthesis porous MOFs based on an anthracene derivative which can provide additional hydrogen binding sites to increase the hydrogen uptake. (5) Obtained stable MOFs with high surface areas by the incorporation of mesocavities with microwindows. (6) Constructed MOFs with “close-packing” alignment of open metal sites, which can increase the number of nearest neighboring open metal sites of each H₂-hosting void in a three-dimensional framework so that they can interact directly with the guests (H₂ molecules) inside the void. (7) Built up porous lanthanide MOFs and studied their potential application in gas adsorption. (8) Prepared symmetry-preserving isomer pair of MOFs and studied the impact of isomerization on H₂ storage capacity in MOFs. (9) Incorporated polyyne unit into MOFs, which exhibit H₂ affinity higher than that of MOFs containing phenyl rings. (10) Designed and synthesized POFs with chemical stability higher than that of MOFs.

Results

In the past year, we prepared a series of MOFs and POFs and explored their applications in hydrogen storage. Table 2 shows the comparison of hydrogen uptakes of selected MOFs and POFs. Next we will discuss in detail the results of H₂ uptakes of these materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>ΔH_ads (kJ/mol)</th>
<th>H₂ Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravimetric</td>
<td>Volumetric</td>
</tr>
<tr>
<td></td>
<td>H₂ uptake (Wt%)</td>
<td>H₂ uptake (g/L)</td>
</tr>
<tr>
<td>PCN-16</td>
<td>-</td>
<td>5.10</td>
</tr>
<tr>
<td>PCN-16'</td>
<td>-</td>
<td>2.90</td>
</tr>
<tr>
<td>PCN-46</td>
<td>7.20</td>
<td>5.31</td>
</tr>
<tr>
<td>PCN-61</td>
<td>6.36</td>
<td>5.87</td>
</tr>
<tr>
<td>PCN-68</td>
<td>6.22</td>
<td>6.23</td>
</tr>
<tr>
<td>PCN-69</td>
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<td>7.20</td>
</tr>
<tr>
<td>POF-1</td>
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<td>3.30</td>
</tr>
<tr>
<td>POF-2</td>
<td>6.89</td>
<td>3.76</td>
</tr>
<tr>
<td>POF-3</td>
<td>5.51</td>
<td>4.28</td>
</tr>
</tbody>
</table>

(a) Symmetry-Preserving Isomer Pair

A symmetry-preserving isomer pair (α phase and β phase NbO-type structures) of MOFs crystallized in the same R-3m space group but with different pore sizes have been discovered, allowing the direct study of the impact of pore size on gas storage capacity in MOFs for the first time (Figure 1a). The α phase MOF (PCN-16) is isostructural with previously reported NbO-type MOFs constructed from tetracarboxylate linkers and has two distinct types of cages. The first consists of 12 ebdc ligands connecting six paddlewheel secondary building units (SBUs) to form an octahedral cage, in which each ligand utilizes only two of its four carboxylate functionalities; half of the ligands join adjacent SBUs through carboxylate groups from the same phenyl ring and half use carboxylates at opposite ends of the ligand. The dimensions of the windows into the cage are about 10 × 10 Å and 8 × 8 Å (atom to atom distances). The second type of cages, which is elliptical, is formed from six edbc ligands connecting twelve paddlewheel SBUs. In this type, each ligand uses all of its four carboxylate groups. The dimensions of the windows into the elliptical cage are also 10 × 10 Å and 8 × 8 Å. These two
kinds of cages are connected to each other by sharing three paddlewheel SBUs to result in a three-dimensional framework with the NbO topology. The resulting dimensions of the -3m (in space group R-3m) channels are about 8 × 8 Å along the c-axis consistent with the size of the channels in the previously reported NbO-type MOFs. The solvent accessible volume in the dehydrated structure is 72.5% calculated from PLATON/SOLV. In PCN-16', however, the channels are larger than those in PCN-16, with the dimensions of 11 × 11 Å. The solvent accessible volume in the dehydrated structure is 70.1% calculated from PLATON/SOLV, which is slightly smaller than that of PCN-16.

To check the permanent porosities of the pair of isomers, N2 sorption isotherms at 77 K were collected for the dehydrated samples. As shown in Figure 1b, both PCN-16 and PCN-16' display typical Type-I sorption behavior. PCN-16 has a Brunauer-Emmett-Teller (BET) surface area of 2,273 m²/g (Langmuir surface area, 2,800 m²/g) and a total pore volume of 1.06 cm³/g while PCN-16' possesses a 1,760 m²/g BET surface area (Langmuir surface area, 2,200 m²/g) and a 0.84 cm³/g pore volume.

The differing pore structures as evidenced by the BET surface areas directly impact the adsorption capacities for hydrogen as indicated in Figures 1c. PCN-16 demonstrates significantly higher hydrogen adsorption capacity than PCN-16'. At 77 K and 760 torr, PCN-16 can adsorb 2.6 wt% hydrogen, comparable to the values observed in other α phase NbO-type copper MOFs. In contrast, PCN-16' can only adsorb 1.7 wt% hydrogen, much lower than that in PCN-16. This difference persists at higher pressures where the excess hydrogen uptake of PCN-16 saturates at 5.1 wt%, while the saturation for PCN-16' occurs with the value of only 2.9 wt% (Figure 1c).

Because PCN-16 and PCN-16' are isomers of each other and both crystallize in the same space group and contain similar nanoscopic cages, the superior gas adsorption properties of PCN-16 can mainly be attributed to the pore size, which is smaller than that of PCN-16'. The small pores lead to an increased effective surface area, offering more adsorption sites for hydrogen. Indeed, the saturation uptake of hydrogen at 77 K for each isomer is consistent with the different BET surface areas, as explained in a recent analysis. The results above also suggest that α phase NbO-type copper MOFs should be better for gas storage than their β phase counterparts.

The NbO-type MOFs, which consist of 4-connected di-isophthalate ligands and 4-connected secondary building units, have shown excellent framework stability, porosity, and gas adsorption capacity. On the other hand, their hydrogen adsorption capacity at room temperature is relatively low due to weak framework-hydrogen interactions. In our continuing exploration of MOFs as a hydrogen storage medium, double bonds and aromatic rings were studied as possible framework-hydrogen interacting sites. However, prior to this work, carbon-carbon triple bonds, especially polyyne chains, have not been systematically studied for gas adsorption purposes in MOFs. In this contribution, we report an NbO-type MOF (PCN-46) that is constructed based on a polyyne-coupled di-isophthalate ligand formed in situ (Figure 2). The ensuing MOF has permanent porosity after the removal of guest molecules, with a BET surface area of 2,500 m² g⁻¹ and a uniform pore size around 6.8 Å (Figure 2d). At 77 K and 760 Torr, PCN-46 can reversibly adsorb 1.95 wt% of H₂ (Figure 2e). Under high pressure range, the saturated excess gravimetric H₂ uptake is 5.31 wt% (56.1 mg g⁻¹) at 32 bar. Taking the gaseous H₂ compressed within the void pore at 77 K into consideration, the total gravimetric H₂ uptake can reach as high as 6.88 wt% (73.9 mg g⁻¹) at 97 bar. Calculated from the crystal density of the activated form (0.6185 g cm⁻³), PCN-46 has an excess volumetric...
H₂ uptake of 34.7 g L⁻¹ (32 bar) and a total volumetric uptake of 45.7 g L⁻¹ (97 bar).

Based on a variant of the Clausius-Clapeyron equation, the H₂ isosteric adsorption enthalpy of PCN-46 reaches 7.20 kJ mol⁻¹ at low coverage, and decreased to 4.06 kJ mol⁻¹ at medium coverage. The increased heat of hydrogen adsorption in PCN-46, compared to those of other NbO type MOFs, can be attributed to the interaction between dihydrogen molecules and the exposed and delocalized π electrons in the polyyne unit in bdi⁴⁻, which is evidently stronger than that for the phenyl rings in other ligands in the NbO-type MOFs. In addition, the replacement of phenyl rings by polyyne chain leads to a boost of pore volume and hydrogen uptake. Furthermore, in the absence of a catalyst, the hydrogen addition reaction on the polyyne unit has not been observed even at high pressure as shown by the reversible hydrogen sorption isotherms of PCN-46, validating the stability of the MOF under hydrogen storage conditions.

(c) An Isoreticular Series of MOFs with Dendritic Hexa-Carboxylate Ligands and Exceptionally High H₂ Uptake Capacity

It has been well established that the high-pressure gravimetric hydrogen adsorption capacity of a MOF is directly proportional to its surface area. However, MOFs of high surface areas tend to decompose upon activation. In previous work, we've described an approach toward stable MOFs with high surface areas by incorporating mesocavities with microwindows. To extend this work, herein we present an isoreticular series of (3,24)-connected MOFs made from dendritic hexa-carboxylate ligands (Figure 3). In order to test the framework stability, nitrogen sorption measurements were carried out in fully activated PCN-68 and PCN-610. In PCN-68, a dramatic increase of nitrogen sorption has been observed (Figure 3d). The BET surface area calculated based on the low-pressure region data can reach as high as 5,109 m² g⁻¹, with a Langmuir surface area of 6,033 m² g⁻¹. To the best of our knowledge, PCN-68 possesses the highest surface area reported to date for MOFs based on paddlewheel clusters.
The hydrogen uptake capacities of PCN-6X series are shown in Figure 3e. At a low-pressure region (<1 bar), the hydrogen uptake capacity is mainly controlled by the hydrogen affinity towards the framework, which can be quantified by the isosteric heat of adsorption. PCN-61, which has the smallest pore size, also has the highest heat of adsorption and highest capacity (2.25 wt% at 77 K, 1 bar). PCN-66 and PCN-68 have heats of adsorption and adsorption capacities similar to each other (1.79 wt% in PCN-66 vs. 1.87 wt% in PCN-68). This trend is consistent with the nature of physisorption, in which narrower pores would have stronger interactions with guest gas molecules due to increased interaction between the guests and the opposite potential walls within small pores. Unlike low-pressure hydrogen sorption capacity, which is dominated by hydrogen affinity, the maximum excess hydrogen uptake capacity in MOFs, which typically can only be reached at high pressure range, is controlled mainly by the surface area and pore volume. This is consistent with observations in the PCN-6X series. As can be seen from Figure 3e, PCN-68, which has the highest surface area, also has the highest maximum excess hydrogen uptake capacity (7.2 wt%, Table 2), which makes it one of the best adsorbents with the highest gravimetric hydrogen uptake capacity. It is worth noting that the maximum adsorption pressure increases from PCN-61 (33 bar) to PCN-66 (45 bar) and PCN-68 (50 bar), indicating higher pressure is needed to reach maximum adsorption in sorbents with higher pore volumes.

Using the crystal density data, volumetric hydrogen uptake capacities were also calculated. Unlike the trend in gravimetric capacity, where material with the highest surface area has the highest capacity, volumetric capacity follows the opposite trend, which is dominated by the densities of the sorbents. The gravimetric capacity has been emphasized in the past hydrogen storage research, and rightfully so. However, volumetric capacity is particularly relevant in volume-limited fuel cell applications. Both of these criteria should be emphasized equally in the search for ideal hydrogen storage materials.

(d) POFs

In the last decade, the chemistry of porous materials has witnessed a renaissance in design and synthesis of porous polymers. Compared to MOFs, porous polymers have higher chemical and thermal stability, which is suitable for further decoration. Three POFs have been synthesized by homocoupling reactions (Figure 4). The polymeric frameworks have high stabilities and surface areas of up to 5,523 m² g⁻¹. Their hydrogen uptake capacity at 1 bar is directly proportional to the surface area. This trend is more obvious at higher pressure ranges, with the highest uptake capacity obtained for POF-3 (4.28 wt%, 42 bar), which compares favorably with the highest ones of carbon materials. This trend is the same for other adsorbents, indicating the importance of a high surface area for maximal hydrogen uptake capacity. Based on a variant of the Clausius-Clapeyron equation, the hydrogen isosteric heat of adsorption can be calculated. Compared with POF-2 and POF-3, the heat of adsorption in POF-1 is surprisingly high (7.59 kJ mol⁻¹) and, most importantly, it remains almost constant over the whole gas loading range. This value is higher than those for other porous polymer analogs, such as PAF-1 (4.6 kJ mol⁻¹) and covalent-organic frameworks (6.0-7.0 kJ mol⁻¹). The high heat of adsorption may stem from the narrower pores, which allow stronger overall interactions of the guest gas molecules because of additional interactions with the opposite walls. In addition, the polyyne motifs may help to increase the gas affinity as well. This hydrogen affinity difference is reflected in the hydrogen sorption isotherms at a lower pressure range (less than 0.5 bar), where the hydrogen uptake in POF-1 rises most steeply. In the higher pressure range, where the surface area and pore volume become dominant, POF-3 has the highest uptake capacity.
Conclusions and Future Directions

Conclusions:

• α Phase NbO-type copper MOFs should be better for gas storage than their β phase counterparts.
• Small pores (5 to 10 Å) in MOFs lead to an increased effective surface area, offering more adsorption sites for hydrogen.
• The polyene chains showed improved hydrogen affinity compared to phenyl rings.
• Constructing MOFs containing mesocavities with microwindows is proven as a general approach towards stable MOFs with high surface areas and high hydrogen uptake.
• Porous organic frameworks with tunable pore size and surface area can be prepared with high chemical and thermal stability, which are good candidate for hydrogen storage.

Future Directions:

• Further enhancement of H₂-MOF interaction by doping coordinatively unsaturated metal centers (heat of adsorption 15 kJ/mol). Based on theoretical calculations, main group metals such as Mg and Ca will be tested.
• Working with partners, test H₂ uptake at temperatures higher than 77 K.
• Preparation of MOFs with high surface area and optimized cage size with newly designed ligands based on theoretical calculations.
• Incorporation of entatic-state metals based on theoretical guidance.
• Preparation of POFs containing active metals.

FY 2010 Publications/Presentations

IV.C.1c 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 Fuel Cell 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 corn cob 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

- Validated H₂ performance of University of Missouri carbons (University of Missouri; National Renewable Energy Laboratory; “blind laboratory”) to within ~ 5%.
- Manufactured B-substituted carbon by thermolysis of B₁₀H₁₄, with B:C = 1-7 wt% without compromising high surface areas.
- Observed significant changes of hydrogen adsorption on B-substituted samples subjected to neutron irradiation (fission tracks in carbon matrix from boron neutron capture). Irradiation shifted excess adsorption peak and slope at 80 K to lower pressures, consistent with an increase in binding energy and decrease in density of the saturated film. Irradiation did not change surface area or pore-size distribution. Estimated saturated film densities at 80 K and 50 bar were 3-8 times the density of unadsorbed hydrogen gas.
- Developed method to determine isosteric heats of adsorption at high coverage from Clausius-Clapeyron equation in a thermodynamically consistent way.
- Developed sub-nm pore structure characterization methods based on small-angle X-ray scattering (SAXS) [1], and incoherent inelastic neutron scattering [2].
Built a large “library” of B-substituted and B-free carbon materials, generating a systematic study of the structure and performance of activated carbons under various processing conditions (KOH concentration, activation temperature, pyrolysis of B-carrying polymers). Demonstrates a wide spectrum of different behaviors, with excess adsorption peaks ranging from 20 bar to pressures way above 100 bar, including record excess storage capacity of 1.3wt% at room temperature.

Found evidence from library that B-substitution and irradiation raises average binding energy to 9-11 kJ/mol (B:C = 1.4 wt%) and alters entire shape of adsorption isotherm (B:C = 1.7 wt%). Ab initio calculations of H2-(B,C) interactions and Grand Canonical Monte Carlo (GCMC) simulations gave $E_B = 10-14$ kJ/mol at B:C = 10 wt% [3].

**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 m$^2$/g to ~5,000 m$^2$/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, $^{10}$B + n $\rightarrow ^{11}$B $\rightarrow ^7$Li + $^4$He + $\gamma$ + 2.4 MeV, traversing stacks of graphene sheets, will add as much as another 3,000 m$^2$/g. Thus boron serves in two functions: (i) raise the binding energy by electron donation from H$_2$ 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 (80 K, 303 K) for a selected group of seven samples with different sorption characteristics: (i) commercial reference sample MSC-30 (Maxsorb, Kansai Coke and Chemicals Co., Ltd); (ii) boron-free biocarbon, 3K-20100217; (iii) boron-doped unirradiated and irradiated biocarbons 3K-H6 (II, A), 3K-H6 (II,
A) Irr., and 3K*-H6 (II, A) Irr; and (iv) polyvinylidene chloride (PVDC)-based carbons HS;0B (0% B:C) and HS;2B (1.7 B:C). Sample 3K-20100217 is a member 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”). Samples 3K and 3K* differ in that the two were fabricated in a stainless-steel vessel, resulting in a ~1 wt% Fe and Cr content, and alumina, resulting in ~1 wt% Al. Boron doping was performed by vapor deposition followed by pyrolysis of decaborane (B10H14). Samples reported here were exposed to air. Irradiated samples were produced at the University of Missouri Research Reactor, with irradiation times between 1 minute and 2 hours, and result in the production of fission tracks from boron neutron capture, 10B + n → 7Li + 4He + γ + 2.4 MeV. PVDC-based samples were formed by thermal decomposition of PVDC or PVDC co-polymerized with n-hexyl-orthocarborane (samples were not further activated, all pores result from pyrolysis) [4]. Adsorption isotherm for sample 3K-20100217 at 77 K was validated at the National Renewable Energy Laboratory and a “blind laboratory,” resulting in an agreement in the excess adsorption to within a ~5% average relative error. Pore-size distributions (PSD) determined from N2 adsorption at 77 K (Figure 2) show that samples 3K-20100217 and MSC-30 contain a comparable number of sub-nm pores, but MSC-30 contains a significantly larger number of supra-nm pores. In contrast, PVDC samples, HS;0B and HS;2B, are essentially free of supra-nm pores. PSDs are consistent with SAXS analyses (Table 1, [1]). The existence of very narrow pores in HS;0B and HS;2B result in large binding energies [5] and explains the high room temperature excess adsorption of HS;0B (Figure 1), despite their low surface areas (Table 1). At low pressures HS;2B excess adsorption grows faster than HS;0B, indicating a number of high binding energy sites, as expected from our ab initio calculations of boron-containing carbons [3].

For irradiated samples, no significant differences in surface area or pore-size distribution between irradiated and unirradiated materials were found (Table 1, Figure 2). But significant differences in hydrogen adsorption isotherms at 80 K were observed (Figure 1). Irradiation shifted the maximum in excess adsorption from ~40 bar to ~20 bar, and made the slope at high pressures steeper (Figures 1, 3). The maxima, $p_{\text{max}}(T)$,
and intercepts with the pressure axis, $p_0(T)$ (Figure 3), were related to the average binding energy, $E_{B,av}$, and mass density of the saturated film, $\rho_{film}(T)$ using:

$$
\rho_{film}(T) = m_{H_2} \frac{N_A}{\nu} \frac{h}{(kT)}
$$

($1$)

$$
E_{B,av} = \frac{m_{H_2} N_A k}{\nu} \ln \left[ \frac{p_0(T) - 2 p_{film}(T)}{p_{film}(T)} \right] \left\{ (1 - \frac{2 m_{H_2}}{N_A}) \frac{h}{(kT)} \right\}^2
$$

($2$)

where $m_{H_2}, N_A, k, \nu,$ and $h$ are the mass of a hydrogen molecule, Avogadro’s number, Boltzmann’s constant, the vibrational frequency of an adsorbed hydrogen molecule relative to the substrate, and Planck’s constant, respectively, and we have assumed the ideal gas law, Eq. (1), and Langmuir adsorption, Eq. (2) [5]. Results are shown in Table 2. The increase in binding energy and decrease in film density as a result of irradiation were attributed to the creation of surface defects, perhaps free radicals, created by fission products, and film discontinuities at edges of fission tracks. Film densities at 80 K and 50 bar were 3-8 times the density of unadsorbed hydrogen gas (Table 2). The binding energies for B-substituted carbons inferred in Table 2, brackets, show that B-substitution raises the average binding energy to ~11 kJ/mol (B:C = 1.4 wt%) and alters entire shape of adsorption isotherm (B:C = 1.7 wt%; Figure 1). 

Ab initio calculations of $H_2-(B,C)$ interactions and GCMC simulations gave $E_B = 10–14$ kJ/mol [3].

### Table 2. Experimental density of the saturated $H_2$ film at 80 K and average binding energy from Figures 1 and 3 and Eqs. (1, 2), with $\nu$ for $H_2$-graphite potential and $\nu$ estimated for $H_2$-B/C potential (in brackets).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$p_0$ (bar)</th>
<th>$p_{film}$ (bar)</th>
<th>$\rho_{film}$ (g/cm$^3$)</th>
<th>B:C (wt%)</th>
<th>$E_{B,av}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSC-30</td>
<td>360</td>
<td>~40</td>
<td>0.11</td>
<td>0.0%</td>
<td>6.4</td>
</tr>
<tr>
<td>3K-H6 (II,A)</td>
<td>300</td>
<td>~40</td>
<td>0.09</td>
<td>1.4%</td>
<td>6.2 (10.9)</td>
</tr>
<tr>
<td>3K-H6 (II,A)</td>
<td>160</td>
<td>23</td>
<td>0.05</td>
<td>1.4%</td>
<td>6.5 (11.2)</td>
</tr>
<tr>
<td>3K*-H6 (II,A)</td>
<td>190</td>
<td>24</td>
<td>0.06</td>
<td>1.9%</td>
<td>6.6 (11.3)</td>
</tr>
<tr>
<td>HS-2B</td>
<td>190</td>
<td>21</td>
<td>0.06</td>
<td>1.7%</td>
<td>6.9 (11.5)</td>
</tr>
<tr>
<td>H2 gas, 80 K &amp; 50 bar</td>
<td>N/A</td>
<td>N/A</td>
<td>0.016</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A – not available

The isosteric heat of adsorption, $\Delta H$, equals the heat released when a molecule is adsorbed at constant coverage (number of adsorbed molecules, absolute adsorption), and an according temperature change [6]. It is related to the binding energy through the relation $\Delta H = E_{B,av} +$ zero-point/thermal energies $= E_{B,av} + (3-5$ kJ/mol), depending on the details of how $H_2$ is adsorbed on the surface [7]. The isosteric heat can be computed from two adsorption isotherms via the Clausius-Clapeyron equation,

$$
\Delta H = \frac{RT}{T_2 - T_1} \ln \left( \frac{p_2}{p_1} \right)
$$

($3$)

where $p_1, T_1$ are two pressures and temperatures corresponding to the same absolute adsorption. This requires conversion of experimental excess adsorption isotherm, $G_{ex}$, into absolute adsorption, $G_{abs}$ (both in mass of $H_2$ per mass of adsorbent),

$$
G_{abs} = G_{ex} + \Sigma \cdot t_{film} \cdot \rho_{gas}
$$

($4$)

where $\Sigma, t_{film},$ and $\rho_{gas}$ are the specific surface area of the adsorbent (Table 1), thickness of the adsorbed film,
and density of bulk gas, respectively. In much of the literature, no distinction is made between absolute and excess adsorption, i.e., the conversion (4) is carried out with a film thickness of zero, and Eq. (3) is evaluated at constant excess adsorption instead of constant absolute adsorption. This leads to an incorrect behavior of isosteric heats at high coverage, where the film thickness is far from negligible. Whenever the excess adsorption isotherm has a local maximum in the pressure range analyzed (Figure 4a), the isosteric heat calculated from excess adsorption rises at high coverage (Figure 5a), which is unphysical. No such unphysical behavior occurs when isosteric heats are calculated from the absolute adsorption isotherm, which has no local maximum (Figure 4b). Figure 5a shows isosteric heats calculated for various hypothetical film thicknesses, \( t_{\text{film}} = 0 \) (“\( G_{\text{abs}} = G_{\text{ex}} \)”), \( t_{\text{film}} = 2.3 \) Å (van der Waals diameter), ..., \( t_{\text{film}} = 4.1 \) Å (best estimate from GCMC simulations of adsorbed \( \text{H}_2 \) on carbon surfaces). Significant differences in isosteric heats, due to incorrect values for \( t_{\text{film}} \), are observed already at pressures as low as 2 bar (Figure 5a). The smallest film thickness at which the calculated isosteric heat curve no longer rises is a lower bound for the actual film thickness.

Figure 5b displays the effect of different choices of the pressure interval.

**FIGURE 4.** Determination of isosteric heats of adsorption from excess (a) and absolute (b) adsorption isotherms, from Eq. (4) with \( t_{\text{film}} = 4.1 \) Å. The maximum in the excess adsorption result in an unphysical rise of the isosteric heat (Figure 5).

**FIGURE 5.** Isosteric heats of adsorption calculated from Eqs. (3, 4) for four different film thicknesses. (a) The increase in isosteric heat at high coverage is unphysical because high-energy adsorption sites are expected to fill at low coverage. The isosteric heat curves for \( t_{\text{film}} = 0 \) and \( t_{\text{film}} = 2.3 \) Å end at \( G_{\text{abs}} \approx 50 \) and \( 60 \) g H\(_2\)/kg °C, respectively, because the 80 K “absolute adsorption” isotherm for these film thicknesses has its maximum at \( -50 \) and \( -60 \) g H\(_2\)/kg °C. (b) Effect of different choices of the pressure interval over which absolute adsorption was fitted for interpolation (determination of \( p_1 \) and \( p_2 \) at constant coverage).
pressure interval over which absolute adsorption was fitted for interpolation (determination of $p_1$ and $p_2$ at constant coverage).

For the case study, MSC-30, isosteric heats drop from $-6$ kJ/mol to $-3.5$ kJ/mol as absolute adsorption increases from $-2$ to $-70$ g H$_2$/kg °C. This is consistent with the expectation that sub-nm pores host binding energies as large as 10 kJ/mol, with larger pores hosting binding energies $\sim 5$ kJ/mol. The analysis also shows that isosteric heats from excess instead of absolute adsorption yield reliable values only at pressures below $\sim 1$ bar (Figure 5a). At the same time, isosteric heats at low pressures may differ by as much as 1 kJ/mol, depending on the pressure interval over which adsorption isotherms are fitted for interpolation (Figure 5b). Work is underway to determine isosteric heats on B-doped samples under oxygen-free conditions.

**Conclusions and Future Directions**

- Observed an unexpected increase in binding energy and decrease in adsorbed film density/thickness in neutron-irradiated boron-containing carbons.
- Developed pore characterization methods using SAXS.
- Developed thermodynamically consistent method to determine isosteric heats at high coverage.
- Future work: (i) Construction of decaborane deposition and decomposition instrument to automate production of samples which will allow optimization of boron doping methods (time, temperature, decaborane concentration). (ii) Characterization of boron-free and boron-containing carbons under exclusion of oxygen and humidity. (iii) Etching of fission tracks to increase surface area and comparison of performance of etched/non-etched materials. (iv) Continue to investigate whether hydrogen and nitrogen see the same surface area. (v) Investigate pressure/temperature/pore shape dependence of new variable $\rho_{\text{sat}}(T)$ (density of saturated film) experimentally and by GCMC simulations. (vi) Design materials with high $\rho_{\text{sat}}(T)$, as a concurrent strategy with increased binding energy. (vii) Improve theoretical models for analysis of excess adsorption isotherms ($p_{\text{max}}$, $\rho_{\text{sat}}$, $\partial G_s / \partial p$) in terms of the binding energies and surface areas. (viii) Develop understanding of correlations between hydrogen storage at 80 K and 303 K. (ix) Expand experimental library of high $E_b$ from boron doping (with extreme care to avoid exposure to oxidizing agents). (x) Attempt synthesis of bulk BC$_3$ and test for predicted H$_2$ intercalation.

**FY 2010 Publications/Presentations**


References


4. Work performed under a different project.


IV.C.1d Neutron Characterization in Support of the Hydrogen Sorption Center of Excellence

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Project Start Date: October 2005
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 of the Fuel Cell 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 Hydrogen Sorption Center of Excellence (HSCoE) 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

- Characterized the hydrogen environment upon adsorption in graphite intercalation materials despite lack of periodic crystal structure.
- Characterized the hydrogen diffusion mechanism and geometry.
- Determined multiple binding sites for H₂ in one of an isostructural series of benzene tris-tetrazole (BTT) compounds. Partial understanding of the local adsorption potential is obtained from the current inelastic neutron scattering data.
- For the first time we have observed a significant perturbation of the hydrogen rotational levels in a high surface area B-doped carbon.
- Further understood the surface chemistry and hydrogen adsorption capacities in zeolite-templated carbons loaded with Pt nanoparticles. Failed to observe any spillover in these materials.

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**

**MOFs**

MOFs have recently come under intense investigation for gas storage and separation applications, owing to their high internal surface areas, convenient modular synthesis, and chemical tenability. Previously, we have reported a number of MOFs in which removal of a solvent molecule from the coordination sphere of the framework metal cations yields strong adsorption sites for H₂. One possibility for improving the isosteric heat of adsorption within this structure type would be through constructing the structure with M²⁺ cations having a smaller radius. The greater charge density of the exposed metal cations on the framework surface should then be more effective at inducing a dipole in H₂, leading to stronger binding.

The synthesis of a new framework structure with open Fe²⁺ coordination sites, Fe-BTT [1], has confirmed that the large isosteric heat of adsorption for H₂ in Fe-BTT is associated with the presence of open Fe²⁺ coordination sites associated with the [FeCl]⁷⁺ clusters of the framework. The initial isosteric heats are larger than those in isostructural Mn²⁺ and Cu²⁺ derivatives (Figure 1) and much greater than the prototypical MOF-5. Combined with neutron diffraction data and inelastic neutron scattering spectroscopy we have shown that these exposed Fe²⁺ sites provide a strong interaction with H₂, drawing it close to the surface. There is a correlation between the higher initial enthalpies in this series and how close the D₂ molecules can approach the metal ion. The relative distance increase from 2.17(5) Å, 2.27 Å and 2.47 Å, for Fe³⁺, Mn²⁺ and Cu²⁺ ions, respectively. Increasing the adsorbed amount of D₂ reveals a progression of site fillings away from the cation with 10 sites identified at saturation (Figure 2).

The H₂ loading characteristics of Fe-BTT have been further probed by inelastic neutron scattering. In the lowest loading data (< 0.5 wt%), there is an absence of a rotational line at 14.7 meV that would correspond to the first rotational transition of free hydrogen. This is indicative of a strong rotational hindering potential of the binding sites occupied at these levels, consistent with the large initial isosteric heat of H₂ adsorption. At this low loading the strongest adsorption sites are populated, giving rise to two transitions observed at ≈13.2 and ≈19.7 meV. These peaks gain intensity upon increasing the loading to 0.5 wt% of H₂, and can be assigned as rotational lines that correspond to a rotational barrier of approximately 15 meV. Upon increasing the loading, weaker sites become occupied and features closer to the expected ‘free hydrogen’ energy are seen.

The low pressure (1 bar) adsorption of 2.3 wt% at 77 K, and 1.6 wt% at 87 K, is completely reversible, and the steep initial portion of each isotherm is also indicative of the presence of strongly-polarizing binding sites with a high affinity for H₂. The strongly polarizing Fe³⁺ affords an enhanced storage capacity at 298 K 1.1 wt% and 8.4 g/L; the total uptake in Fe-BTT at 95 bar constitutes a 16% increase in volumetric density compared to that of pure H₂ gas at the same pressure. This work was performed in collaboration with J.R. Long (University of California, Berkeley) and A. Dailly (General Motors).

**Neutron Imaging of Adsorption**

The development of new tools that may be of potential beneficial to enabling the engineering of storage tanks is presented. Briquettes of compressed activated carbon (Pfeifer, Missouri), were cut into cylindrical slugs and placed in a thick walled aluminum cell with a gas loading apparatus attached via a capillary.
Illuminating the cell, and recording the image on a neutron sensitive charge-coupled device camera, gives an image as shown in Figure 3; darker pixels indicate more neutrons have been scattered away from the camera at that pixel. Subtracting the ‘noise’ through the darkfield image, and normalizing a hydrogen-loaded image to that of the bare material highlights only the adsorbed hydrogen. Images can be captured using this technique at specific loadings and with relative good statistics in under a second (instrumentation limit is much faster); we averaged 5 seconds to generate the images in Figure 3. As expected, this room temperature adsorption showed little time dependence at room temperature within the measurement timescale. A false color image of the hydrogen adsorbed in the system on increasing pressure form 2 bar to 5 bar is shown in the right panel of Figure 3. The shape of the briquettes are easily observable at 5 bar. While this data has not been taken to the point where we can be quantitative about the amount of hydrogen adsorbed, it would be a relatively simple exercise to complete that and compare to traditional adsorption isotherms. Of some note is that this technique could distinguish the amount of gas in the free space away from the briquettes and that in the briquette itself.

Conclusions and Future Directions

We have continued our primary task of performing various neutron characterization measurements in support of other HSCoE members focusing on optimizing our knowledge of hydrogen interactions for current and future materials development. Specifically we achieved the following results this year:

- Characterized the hydrogen environment upon adsorption in graphite intercalation materials despite lack of periodic crystal structure.
- Characterized the hydrogen diffusion mechanism and geometry.
- Determined multiple binding sites for H\textsubscript{2} in one of an isostructural series of BTT compounds. Partial
understanding of the local adsorption potential is obtained from the current inelastic neutron scattering data.

- For the first time we have observed a significant perturbation of the hydrogen rotational levels in a high surface area B-doped carbon.
- Further understood the surface chemistry and hydrogen adsorption capacities in zeolite-templated carbons loaded with Pt nanoparticles. Failed to observe any spillover in these materials.
- Performed preliminary test-bed work on a macroscopic imaging of hydrogen adsorption in a high surface area carbon.

This work can be extended in the future. In particular there are issues pertaining to: limits for the enthalpy of adsorption of hydrogen in MOFs; understanding electrostatic/morphological control of hydrogen diffusion rates; chemistry of the nanoparticle and substrates used to obtain significant amounts of hydrogen spillover; clearly distinguishing physisorbed hydrogen form a spin-off hydrogen; obtaining quantitative interpretation of imaging adsorption in storage beds; and extending imaging facilities to include cryogenic sample environment.

Special Recognitions & Awards/Patents Issued

1. Craig Brown, Department of Commerce Silver Medal.
3. Craig Brown, Presidential Early Career Award for Scientists and Engineers (PECASE).
4. Dan Neumann, Fellow of the APS.
5. Dan Neumann, Fellow of the Neutron Scattering Society of America.
6. Jae-Hyuk Her, Young Scientist Travel award July 2009, American Crystallographic association, Toronto, ON, Canada.

FY 2010 Publications/Presentations


Presentations

7. Craig Brown, From metal hydrides to physisorbed H₂-systems: what we are learning with neutrons, Metal Hydrogen-Metal Systems Gordon Conference, July 2009, Lucca, Italy.
8. Jae-Hyuk Her, Crystal structures of MnB₁₂H₁₁₂ (n=1,2) compounds – possible intermediate species in the decomposition of Mn(BH₄)₂, July 2009, ACA Toronto, Canada.
References

Objectives

NREL’s research in the Hydrogen Sorption Center of Excellence (HSCoE) is targeted at addressing key technical barriers in DOE’s sub-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 storage system 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 hydrogen binding energy in the range of 10–50 kJ/mol (for room temperature operation).
  - Decrease heat-transfer requirements to increase on-vehicle 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 at ~$1/kg with carbon costs being only a small fraction. Thus, material costs for a system could be ~$15/kg-H₂ (i.e. >$0.5/kWh, 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.

Technical Barriers

This project addressed 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 sorbents for hydrogen storage systems. In general, the effort focuses on creating hydrogen adsorption materials with optimized binding energy (10–30 kJ/mol) such that the system may operate at near-ambient temperatures and moderate pressures. 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 optimal pore structure and composition for H₂ storage.
- Developed materials with ~5% sp² coordinated boron substitution in carbon (BCₓ) and demonstrated that this increases capacity and binding energy. Also developed nitrogen (N) substituted in C and demonstrated that BCₓ improves spillover processes.
- 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.
- Identified new inexpensive hydrogen sorbents with viable synthetic routes. These included materials like titanium (Ti)-graphite oxide that was experimentally synthesized and demonstrated enhanced dihydrogen adsorption.
- Identified that some oxygen groups are needed for spillover. Spillover does not occur when oxygen groups are missing, spillover rates and capacities are substantially increased when the correct oxygen groups are present, and secondary reactions with the H occur when other oxygen groups are present. These results provide development paths to create higher-capacity, higher-rate H storage spillover materials that meet DOE targets.
- Developed new catalyst processing that improved spillover capacity and charging rates. The decreased processing time, scalability, and improved performance helps spillover materials' development.
- Worked with groups around the world to improve measurement capabilities to provide more accurate and unique hydrogen storage materials characterization at high throughput. This included helping to improve measurement calibrations at other laboratories that have clear issues with irreproducibility and data that are not consistent with standard sorption materials.
- Held workshops and Center partner meetings to develop a comprehensive set of accomplishments and recommendations for the HSCoE. In addition, NREL organized numerous conferences/conference sessions on hydrogen storage to ensure optimal dissemination of results that helps accelerate sorbent development.

Introduction

NREL led the HSCoE to develop reversible sorbent materials for hydrogen storage within the U.S. DOE National Fuel Cell Technologies Project focused on vehicular applications. The HSCoE developed the science base and technology advances required to meet DOE storage goals by investigating a range of hydrogen sorbents. NREL performed 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 of interest for sorbents. The DOE goals can be met with sorbents 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 development of sorption materials, we 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. Provides 11 kJ/mol H₂ binding energy from B-substitution to enable 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. Greater than 2,500 m²/g specific surface area (SSA) with 0.7 to 1.2 nm pore sizes may provide >6 wt% cryocompression.

- **Form Multiple H₂ 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 H₂ adsorbed at each binding site and material densities >1g/ml.
  - Develop materials with multiple dihydrogen molecules per binding site.
  - Use inexpensive chemical and gas phase syntheses of organometallics.
  - Combine theory and experiment to optimize development effort.
  - Identify new dihydrogen storage materials based on slight modifications to existing materials.

- **Develop Near-Ambient T 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. Improve processes and measurements to make stable reproducible materials.

**Results**

**Increasing Hydrogen Binding Energy with Substituted Elements:** We used templating to make high-SSA materials, but more importantly, we used this technique to make boron substituted carbon materials with higher binding energy sites (experimental demonstration of ~11 kJ/mol agrees well with calculations). 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 [1].

The main challenges for creating highly loaded boron substituted carbon include:

- As the boron composition increases, the SSA tends to decrease.
- The boron must be sp2 coordinated in the carbon structure to enhance binding properties.

NREL developed processes to form B-substituted C materials with high B composition and high specific surface area. For example, the use of vapor phase boron trichloride with benzene at ~1,100 K is a well-known process that forms BCₓ films [2]. 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 quantitatively determined the amount of B and the binding environment (Figure 1). These XPS data indicate that the B in the BCₓ 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. The boron 1s and carbon 1s spectra are useful in determining the exact state of boron binding, Figure 1a shows the high-resolution B1s spectrum and the associated boron binding energies. The four main peaks are attributable to boron carbide, elemental boron, sp2 boron, and boron oxide. Based on the entire four binding energy peaks, a total atomic B composition value was determined to be 12.6% in this sample. The sp2 coordinated boron was ~4.5%. Another indication of the incorporation of boron into the graphitic carbon lattice is in the carbon 1s spectrum shown in Figure 1b. In this spectrum, the carbon base peak is shifted from 284.5 eV, the recognized value for graphitic carbon, to 283 eV with an associated shoulder at 282 eV. The shift to lower binding energies and the shoulder in the spectrum is attributed to the boron-carbon binding sites.

Through the use of temperature-programmed desorption (TPD) measurements, NREL also demonstrated that BCx 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. The effects of enhanced hydrogen binding and perhaps smaller pore structures associated with BCx materials is also observed with TPD (Figure 2). In general, as the B content of the BCx materials is increased, the hydrogen takes a much longer time to desorb under vacuum conditions. This is consistent with a higher binding energy and/or a more tortuous path associated with the potential formation of smaller porous structures. That said, similar effects are not observed with nitrogen substituted templated carbon materials, suggesting that the higher binding energies associated with boron substitution is playing a major role.

FIGURE 2. Representative example of hydrogen TPD for a templated BCx sorbent. The hydrogen desorption from templated BCx materials with higher B concentration is much slower than from materials with less B.

Coordinated Metal Centers to Enhance Hydrogen Sorption: NREL investigated 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 [3]. Theorists and experimentalists worked closely at NREL to iteratively design and synthesize new materials with coordinated metal centers. We 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. The calculations used to identify these novel materials were validated with all known 3d metal-H2 experimental results. There is good agreement for both the binding energy and the number of dihydrogens being stored between the theory and the known experimental results.

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. A specific example of this issue was demonstrated by NREL investigating Li integration with carbon materials. While all attempts to date have not observed enhanced hydrogen interaction effects using Li integrated with pure carbon supports, substantial interactions were observed when Li was integrated with BCx materials. This is in good agreement with theoretical calculations [3]. We used a boron-substituted carbon (BCx) and successfully lithiated it in a tetrahydrofuran solution of Li naphthalide. As shown in Figure 3, TPD measurements demonstrate the reversible desorption of hydrogen at <50°C following room temperature hydrogen exposure. Hydrogen desorption temperatures increased from -120°C to ~50°C by the addition of Li. These TPD measurements are consistent with NREL theoretical predictions that boron sites appear to provide well-defined Li metal binding sites. In addition, high-pressure hydrogen adsorption measurements on the lithiated BCx material at 100 bar and 30°C were ~1.5 times greater than the parent BCx material. Interestingly, the Brunauer-Emmett-Teller SSA of the Li-BCx material was only ~5 m²/g. Surprisingly, the H₂ adsorption sites in the lithiated BCx were stable in O₂ and H₂O.

Work by Hamaed et al. [4] demonstrated that Ti dispersed on amorphous-silica internal surfaces are coordinated via strong Ti-silanol bonds (i.e., ~400 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 kJ/mol>) and models (2.4 H$_2$ at <31 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 two dihydrogen molecules with energies appropriate for reversible hydrogen storage at ambient temperatures. In a similar approach, we identified that graphene oxide (GO) can be a potential substrate to covalently anchor transition metal atoms that are undercoordinated and well-exposed to accommodate multiple H$_2$ [5]. Zhang et al. reported that Ti atoms grafted on GO could bind multiple H$_2$ ligands with the desired binding energies (Figure 4, 14-41 kJ/mol-H$_2$). The gravimetric and volumetric densities for this system are predicted to be 4.9 wt% and 64 g/L, respectively. NREL developed a successful reaction pathway to synthesize Ti-GO by employing the theoretical calculations [5] to guide experimental investigations. The Ti-GO materials were isolated in an inert atmosphere and then exposed to 500 Torr of H$_2$. TPD measurements demonstrated enhanced H$_2$ binding sites with one benzyl fragment removed. Additional work is being performed to remove the other benzyl fragment to enable multiple dihydrogen adsorption.

**Weak Chemisorption of Hydrogen:** The HSCoE developed spillover materials with the potential for ambient-temperature hydrogen storage. We improved material processing, demonstrating enhanced spillover performance with boron substituted materials, and identified specific surface functional groups that affect spillover.

Improved spillover material processing: The objective was to reproducibly make materials with higher kinetics and hydrogen storage capacities. In general, improved catalyst processing increases hydrogen storage rates and capacities. Thus, we developed processes that reproducibly integrated catalysts (e.g., Pt, Pd, Ru) with controlled particle size (e.g. 1 to 2 nm) and structure, uniformly with different types of receptor materials (e.g., activated carbon, BC$_x$).

**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, CO$_2$, CO, CH$_4$, 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 content of some oxygen species in the receptor material results in higher secondary-reaction products such as water, we recommend that careful analysis be performed whenever oxygen is present in the spillover materials. That said, NREL performed experiments using carbon black (a well known commercial product with no oxygen species on the surface) with Ru catalysts and observed no substantial increase in hydrogen uptake. This suggests that the complete absence of oxygen functional groups prevents spillover. In addition, we synthesized Pt/ carbon from pyrolyzed sucrose templated on silica.
sphere templates, which contains substantial oxygen containing functional groups. This is partly due to the fact that to remove the silica template, the powder after pyrolysis was soaked in 6 M potassium hydroxide solution for four days, filtered, washed with deionized water and dried in at 120°C. The resultant material is highly functionalized. As shown in Figure 5, an enhancement of well over 30% is observed from the base material, and on a per specific surface area basis, the material has well over a 100% enhancement. All these results demonstrate that appropriately functionalized receptor materials can dramatically enhance hydrogen storage capacities at ambient temperature. In general, these materials have excellent kinetics (<5 min to saturation), are the first Pt catalyst based carbon substrate with spillover enhancement of hydrogen adsorption that has been observed at NREL, the adsorption of hydrogen was still increasing approximately linearly at 150 bar, and had minimal irreversibility (multiple cycles were conducted with no loss of sorption capacity or water/methane formation).

Calculations predict that the use of boron-substituted materials may enhance spillover. At the very least, boron substitution may help stabilize catalyst particles for use in weak chemisorption hydrogen storage. While SSA and boron concentration issues must be resolved for boron-substituted carbons, initial evaluations indicate that BCx materials with Ru catalyst provide highly reproducible and reversible spillover that is 20 to 30% above the base material (Figure 6). In general, the capacities of even the non-Ru containing materials are substantially higher on a per specific surface area (i.e. 750 m²/g) bases compared to activated carbons. The higher capacity observed with Ru catalysts while modest is well above detection limits, and unlike other materials used for spillover, this Ru/BCx material is extremely durable providing identical repeated performance even after multiple air exposures. The BCx material substantial enhances kinetics. The spillover binding energies for these materials were measured to be ~20 kJ/mol, and the higher-pressure loading improved to ~83% of maximum in ~5 minutes, which is a substantial improvement from <60% for spillover on pure carbon materials.

Overall, NREL demonstrated that substantial increases in hydrogen storage capacity can be achieved at ambient temperatures with weak chemisorption processes like spillover. While a significant amount of work is still required to develop highly reproducible and robust materials that have the high capacities demonstrated by the HSCoE with less durable materials, the clear indication is that weak chemisorption is a viable path for on-vehicle refuelable hydrogen storage.

**NREL Collaborations and Partnerships:** As the 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 Analysis Group. These interactions have led to
several joint publications, and NREL performed ~200 sample measurements this year to assist partners and collaborators in characterizing their hydrogen storage materials.

Conclusions

- Developed novel scalable synthetic processes using templating techniques to form high surface area lightweight materials with optimal pore structure and composition for H₂ storage.
- Demonstrated that B substitution in C increases capacity and binding energy when in the correct sp² coordination. 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. NREL demonstrated that only a small amount of B in most of the BCₓ materials is in the correct coordination state with carbon.
- Identified and synthesized coordinated metal center materials for improved ambient storage of hydrogen. Materials with binding energies between 15 and 25 kJ/mol and/or multiple dihydrogen adsorption have been demonstrated. Ultimately, it should be possible to use these sorbents to meet DOE ultimate storage targets.
- Identified processes and surface functionalizations that helped to synthesize more robust, reproducible spillover materials. Improvements in catalysts and receptors including boron substitution and appropriate oxygen species led to enhanced hydrogen storage performance via weak chemisorption (spillover).
- Improved measurement capabilities and worked with Center partners and other groups around the world to provide more accurate H₂ storage materials characterization at high throughput. This included working with DOE to assemble and publish the best practices document on how to perform and interpret hydrogen storage measurements correctly.

Future Direction

- Establish relationships to improve hydrogen storage measurements techniques.
- Establish hydrogen sorbents working group for continued materials development independent of the HSCoE.

Special Recognitions and Awards/Patents Issued


FY 2010 Publications

FY 2010 Presentations


References


IV.C.1f Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

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Project Start Date:  July 1, 2007
Project End Date:  June 30, 2012

Objectives

- To design, synthesize, and evaluate porous organic polymers (POPs) as hydrogen storage adsorbents for transportation applications.
- To support POP development with in-depth understanding of hydrogen–adsorbent interactions through modeling/simulation and advanced characterization.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cells 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 new POPs as hydrogen adsorbents with improved storage capacity and heat of adsorption through rational design, guided by computational modeling and advanced characterization. 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 DOE 2015 targets:

- Gravimetric density: 1.8 kWh/kg
- Volumetric density: 1.3 kWh/L
- Cost: $2/kWh net

Accomplishments

- Successfully designed and synthesized a coproporphyrin-based POP with high Brunauer-Emmett-Teller (BET) specific surface area (SSA) and narrow pore size distribution. Gravimetric capacities of 5.0% at 77 K and 0.6% at ambient temperature were achieved. Iron was successfully exchanged into the new POP which improved hydrogen heat of adsorption.
- A series of aromatic POPs with similar BET SSA but variable pore sizes were prepared through facile ethynyl trimerization reaction. An H$_2$ isosteric heat of adsorption up to ~10 kJ/mol was achieved.
- New synthetic schemes were developed to integrate various non-C elements (B, N, etc.) into POPs while maintaining high surface areas and narrow pore diameters. Preliminary experiments demonstrated improvement in H$_2$ heat of adsorption.

Introduction

The capacity of on-board hydrogen storage is critical to H$_2$-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. We plan to address these challenges by exploring a new class of hydrogen adsorbent, POPs. Compared with other adsorbents, POPs have excellent thermal stability and tolerance to contaminants such as moisture. POPs also have low skeleton density and high intrinsic porosity generated by 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 the polymeric adsorbent research [1-3]. Our approach focuses on improving hydrogen uptake capacity and the heat of adsorption by enhancing SSA, porosity, and surface-adsorbate interactions through rational design at the molecular level.
**Approach**

Our design principles aim at improving the following POP attributes: (a) high SSA to provide sufficient interface with \( \text{H}_2 \) (b) narrow pore diameter to enhance van der Waals interactions in the confined space, and (c) “metallic” characters, either through \( \pi \)-conjugation or metal doping, to promote electronic orbital interactions with hydrogen. During Fiscal Year (FY) 2010, we focused our effort on improving \( \text{H}_2 \) isosteric heat of adsorption over POPs by controlling adsorbents’ surface chemical and physical properties. Several series of POPs were systematically designed and synthesized. One example is a polyporphyrin POP with relatively high SSA and narrow pore size distribution. The N4 macrocycle within the POP serves as a coordination site where transition metal (TM) ions can be exchanged in the center of the square-planar ring to bind with \( \text{H}_2 \). Another example is a series of aromatic POPs prepared by facile trimerization reaction with nearly identical SSA but variable pore sizes. Such system can be used to investigate the dependence of adsorption enthalpy on the pore dimension. The surface property, hydrogen uptake capacity, and isosteric heat of adsorption were measured through N\(_2\)-BET and Sievert isotherm methods. In addition, \textit{ab initio} and density functional theory calculations were conducted to compare with the experimental results for a better understanding of the hydrogen-POP interaction.

**Results**

Isosteric heat of adsorption, \( \Delta H_{\text{ads}} \), is an important property for hydrogen adsorbents. To anchor \( \text{H}_2 \) at ambient temperature without consuming excessive energy for extraction, the preferred \( \Delta H_{\text{ads}} \) is from 15 to 20 kJ/mol. Unsaturated metal ligated in a high surface area organic support could promote the interaction with molecular hydrogen through \( d-s \) orbital interaction. For example, theory suggested an enhanced \( \text{H}_2 \) adsorption energy over porphyrin when a selective group of TMs are exchanged into N4-macroyclic ring [4]. We designed and prepared a polyporphyrin POP, poly-tetrakis(3,5-dithiophen-2-ylphenyl)-porphyrin (PTTPP) in FY 2010 and studied the improvement in \( \Delta H_{\text{ads}} \) by comparing \( \text{H}_2 \) adsorption over the metal doped and undoped versions. Figure 1 shows a three-dimensional structure of iron-exchanged polyporphyrin Fe(PTTPP), where Fe is coordinated by four nitrogens in the porphyrin ring. The surface properties of PTTPP and Fe(PTTPP) were investigated by N\(_2\) adsorption isotherm and their hydrogen uptake capacities were measured by a Sievert isotherm apparatus. The results are listed in Table 1. We also investigated the \( \text{H}_2 \) adsorption isotherms at 77 K, 87K, 197 K, 273 K and 297 K. From which we extracted \( \Delta H_{\text{ads}} \) at different hydrogen loadings, as are shown in Figure 2. The isosteric heat of adsorptions was indeed increased when Fe was exchanged into the porphyrin center. However, the enhancement is limited and still falls below the targeted value. We plan to use PTTPP system as a new platform for studying the impact of different metals on \( \Delta H_{\text{ads}} \), taking advantage of versatility of metal exchange through ligation chemistry with the porphyrin.

It has been postulated that the adsorbent pore size influences \( \Delta H_{\text{ads}} \) and the preferred dimension should be slightly higher than the adsorbate’s van der Waals diamater in the range of 0.6 nm to 0.9 nm [5]. In FY 2010, we designed and prepared a series of aromatic POPs through trimerization reaction using monomers

**TABLE 1.** Surface Properties and Hydrogen Adsorption Capacities of PTTPP and Fe(PTTPP)

<table>
<thead>
<tr>
<th></th>
<th>BET SSA (m(^2)/g)</th>
<th>Langmuir SSA (m(^2)/g)</th>
<th>Total Pore Volume (cm(^3)/g)</th>
<th>Micropore Volume (cm(^3)/g)</th>
<th>Pore Diameter (nm)</th>
<th>Excess H(_2) Ads. @ 65 bar &amp; 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTTPP</td>
<td>1,522</td>
<td>2,030</td>
<td>0.85</td>
<td>0.67</td>
<td>0.85</td>
<td>5.0%</td>
</tr>
<tr>
<td>Fe(PTTPP)</td>
<td>1,248</td>
<td>1,665</td>
<td>0.68</td>
<td>0.54</td>
<td>0.82</td>
<td>4.6%</td>
</tr>
</tbody>
</table>
substituted with ethynyl groups at different position, shown as M1 to M4 in Figure 3a. The trimerization reaction led to the formation of four POPs (POP-1 to POP-4) with nearly identical SSAs but variable pore diameters ranging from 8 to 9 Å, as shown in Figure 3b. Hydrogen adsorption was subsequently performed at four temperatures from liquid nitrogen to ambient. Isosteric heats of adsorption, together with the uptake capacities, were obtained. Figure 4 shows $\Delta H_{\text{ads}}$ as the functions of hydrogen loading for all four POPs. Interestingly, no direct correlation between pore diameter and the heats of adsorptions was observed. Instead, we found a correlation between $\Delta H_{\text{ads}}$ and $N_p$ where $N_p$ represents the average number of phenyl groups connected to a benzene after trimerization. The $N_p$ values for POP-2 (2.3) and POP-1 (2.5) are considerably lower than those for POP-3 (3) and POP-4 (3.5), leading to lower $\Delta H_{\text{ads}}$ values. We also performed a quantum mechanical calculation on the interaction between hydrogen and monomers in both open and confined configurations and found the results were consistent with our experimental observation.

**Conclusions and Future Directions**

In summary, we investigated several functionalized POP systems during FY 2010 in an effort to increase...
hydrogen adsorption enthalpy. The two examples we included in this report demonstrate that enhancement of $\Delta H_{ads}$ can be achieved through doping TM or altering chemical environment although further improvement is necessary to reach the preferred value. Our future study will focus on the following areas:

- Continue to incorporate metal and non-C elements to POPs for better hydrogen uptake and heat of adsorption.
- Explore non-conventional activation and doping methods for major improvement in storage capacity and temperature.
- Identify new pathway for next generation POP-adsorbent through rational design and advanced characterization.

### Special Recognitions & Awards/Patents Issued

1. The POP-based adsorbent development was cited as one of the highlights of technical accomplishment by FreedomCAR and Fuel Partnership.
2. Member of Hydrogen Sorption Center of Excellence received 2010 DOE Hydrogen Program Team Award.

### FY 2010 Publications/Presentations


### References

IV.C.1g Hydrogen Storage by Spillover

Accomplishments

We have developed two metal-doped zeolites that showed 20 and 21 g/L volumetric capacity at 298 K and 100 atm. Unlike metal organic frameworks (MOFs), zeolites are highly stable and low-cost. The Ni-doped zeolites, in particular, are most promising for practical applications after further development [1].

Introduction

Because of the high bulk densities of zeolites which are substantially higher (2-3 times higher) than that of carbons and metal organic frameworks, plus the high densities of cation sites on a variety of zeolites, zeolites are promising sorbents for achieving high volumetric storage capacities.

Approach and Results

Hydrogen adsorption properties of low-silica type-X zeolites (LSX, Si/Al = 1) [1,2] containing alkali or alkali-earth metal cations (Li+, Ca2+, and Mg2+) have been studied in this project. Li-LSX is commercially used for air separation. It was found that the hydrogen adsorption capacities of LSX zeolites at 77 K were determined mainly by the porosity of the zeolite, while at 298 K, the storage capacities depended on both the H2–cation interactions and the porosity. Among the three exchanged zeolites, Li-LSX had the highest H2 capacity of 1.5 wt% at 77 K and 1 atm, and Ca-LSX had the highest capacity of 0.50 wt% at 298 K and 10 MPa.

Hydrogen storage in LSX zeolites via spillover was also investigated [1]. Three methods including bridge building with a catalyst, metal doping via incipient wetness impregnation and metal doping via chemical vapor deposition (CVD) were employed to induce hydrogen spillover and enhance the storage capacities. Thus, the storage capacities were increased to 0.96-1.2 wt% on the Pt-doped zeolites at 298 K and 10 MPa. The differences between the three methods were compared and discussed [1]. Furthermore, 5 and 10 wt% Ni were doped on Ca-LSX zeolite. The 10 wt% Ni-doped Ca-LSX zeolite showed a storage capacity of 1.15 wt% at 100 atm and 298 K. The important volumetric storage capacities of these zeolites were also estimated based on the densities of the densified zeolites. 21 g/L was obtained for Pt-doped Ca-LSX and 20 g/L was obtained for Ni-doped Ca-LSX, both at 298 K and 10 MPa. The high volumetric capacities were obtained because of the high densities of zeolites which are substantially higher (2-3 times higher) than that of carbons and MOFs.
CVD-Pt/Ca-LSX

In the present study, 5 wt% Pt was doped on Ca-LSX zeolite by CVD of the platinum precursor (Trimethyl methylcyclopentadienyl platinum (IV) and subsequent reduction in a hydrogen atmosphere. The transmission electron microscope (TEM) image of CVD-Pt/Ca-LSX showed nanosized Pt (∼1-3 nm) were well dispersed on the particles of LSX. The hydrogen adsorption isotherm at 298 K (Figure 1) showed that CVD-Pt/Ca-LSX had a storage capacity of 1.20 wt% at 10 MPa, enhanced by a factor of 2.4 compared with that of plain Ca-LSX (0.5 wt%). Reversibility was evaluated by measuring the desorption branch down to 1 atm. The desorption branch nearly followed the adsorption branch although there appeared to be a slight hysteresis. The second adsorption isotherm was in agreement with the first adsorption isotherm. These results indicated that hydrogen adsorption in the CVD-Pt/Ca-LSX was reversible at 298 K.

Ni/Ca-LSX

5 wt% Ni was doped on Ca-LSX by incipient wetness impregnation of an aqueous solution of Ni(NO₃)₂·6H₂O and subsequent reduction in a hydrogen atmosphere at 723 K. The TEM image showed that black Ni particles were dispersed on the LSX zeolites with sizes around 4-10 nm. The loading amount of Ni on Ca-LSX was further increased from 5 to 10 wt% to increase the dissociation sites. As shown in Figure 2, the 10 wt% Ni/Ca-LSX had a storage capacity of 1.15 wt%. Although the loading amount of Ni was doubled, the storage capacity was not increased much.

The volumetric storage capacity of Ni/Ca-LSX was estimated to be 20 g/L (Figure 2), based on the pellet density of 1.7 g/cm³. This indicates Ni/Ca-LSX is a promising sorbent for onboard hydrogen storage.

Conclusion

The updated DOE volumetric target for onboard storage is 28 g/L at near ambient temperature and 100 atm. The two metal-doped zeolites reported here showed 20 and 21 g/L. Unlike MOFs, zeolites are highly stable and low-cost. The Ni-doped zeolites, in particular, are most promising for practical applications after further development.

References


Highlights of 2005-2010

- Developed a bridge-building technique for spillover storage, and obtained up to 4 wt% storage with MOFs at 298 K and 100 atm (U.S. and foreign patents pending).
- Achieved 1.2 wt% hydrogen storage on a Pt-doped superactivated carbon (AX-21) at 100 atm and 298K. Capacities of 1.6 wt% was obtained on Ru/carbon, and 1.1 wt% on Ni/carbon.
- The spillover storage process is reversible at 298 K, i.e., full storage capacity is obtained after degassing at 298 K.
- Developed a simple isotherm equation that is applicable to all spillover sorbents.
- For all spillover sorbents, the rates of discharge at 298 K exceeded the DOE target of 0.02 g/s/kW.
- Developed catalysts that could increase the rates of both charge and discharge for spillover storage.
Increased spillover storage capacities on carbon by 10-40% by each of the following techniques: introducing surface oxygen groups, doping nitrogen and/or boron, plasma treatments, and dosing $\text{H}_2$ with hydrocarbon impurities.

Using deuterium isotope tracer, direct evidence for dissociation/spillover and reverse spillover was obtained.

**FY 2010 Publications**


## IV.C.1h Carbon Aerogels for Hydrogen Storage

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**Technical Advisor:** David Thorn  
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E-mail: dthorn@lanl.gov

**Project Start Date:** February 2005  
**Project End Date:** June 2010

### Objectives

- Demonstrate high-capacity hydrogen storage in high surface area carbon aerogels (CAs).
- Develop carbon-based sorbent materials that can store hydrogen at ambient temperature and reasonable operating pressures.
- Fabricate porous carbons as scaffolds for complex hydride systems to improve the kinetic performance of the hydride.

### Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume  
(B) System Cost  
(C) Efficiency  
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption  
(Q) Reproducibility of Performance

### Technical Targets

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 of 6 percent hydrogen by weight and 45 grams of hydrogen per liter.

### Accomplishments

- New monolithic carbon aerogels derived from sugars (i.e. sucrose, glucose) have been synthesized for use as spillover substrates. These materials possess surface areas up to 600 m²/g and can readily be doped with hydrogen dissociation catalysts, such as platinum or nickel.
- Novel CA-carbon nanotube (CNT) scaffolds have been prepared through catalyzed chemical vapor deposition (CVD) growth of CNTs on the inner pore surfaces of high surface area CA substrates. These substrates promote intimate contact between the surfaces of the CNTs and the incorporated complex hydride, thus influencing the kinetics of hydrogen exchange in the hydride.
- LiBH₄ nanocomposites prepared with the CA-CNT scaffolds showed significant decreases in the temperature of hydrogen desorption relative to that of bulk LiBH₄. These scaffolds also appear to outperform CA scaffolds prepared without CNT. Work performed in collaboration with Metal Hydride Center of Excellence (MHCoE) members at HRL Laboratories.

### Introduction

Porous carbon materials are promising candidates for hydrogen sorption due to their lightweight frameworks and high accessible surface areas. The low hydrogen binding energies, however, that are typical of carbonaceous sorbents (~6 kJ/mol H₂), require that cryogenic temperatures (77 K) be utilized for storage of hydrogen in these materials. In general, the amount of surface excess hydrogen adsorbed on porous carbons at 77 K and ~3.5 MPa varies linearly with Brunauer-Emmett-Teller surface area; gravimetric uptake is ~1 wt% H₂ per 500 m²/g of surface area. Our overall goal in this effort is the design of novel carbon nanostructures that exhibit enhanced binding energies for hydrogen and thus allows for reversible hydrogen storage at ambient temperature and reasonable operating pressures.

### Approach

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
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. Our previous efforts were focused on determining the extent to which the different structural aspects of the CA scaffold (pore diameter, interconnectivity, microporosity, surface chemistry) influence the kinetics of hydrogen exchange in LiBH$_4$. This research is a joint effort with HRL Laboratories, a member of the MHCoE. Our efforts were 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 was performed at HRL.

Results

Design of New Spillover Receptors Derived from Carbon Aerogels

Over the last review period, our work as part of the Hydrogen Sorption Center of Excellence (HSCoE) has been focused on the design of novel spillover receptor materials that can potentially improve both capacity and uptake kinetics in spillover materials. Specifically, we have synthesized novel CAs derived from sugars as spillover receptors. This approach builds on the concept developed by Yang et al. of using partially carbonized sugars as “bridges” to facilitate hydrogen diffusion from the catalyst to the receptor. Our material, however, is comprised entirely of “bridge” material and, therefore, these materials should provide sufficiently favorable surfaces for hydrogen spillover. The carbonized sugar aerogels are prepared through the sol-gel polymerization of simple sugars, such as glucose or sucrose, affording highly cross-linked sugar gels. These gels are then supercritically dried and subsequently pyrolyzed under an inert atmosphere to afford the sugar-derived carbon aerogels. These materials are monolithic and possess surface areas up to 600 m$^2$/g. In addition, these porous carbon structures can be readily doped with hydrogen dissociation catalysts, such as platinum, ruthenium or nickel, by either solution- or vapor-phase techniques. Room temperature hydrogen uptake in the metal-loaded sugar-derived CAs has not yet been evaluated within the HSCoE.

Carbon Aerogel as Scaffolds for Complex Hydrides

For our work with the MHCoE, we fabricated a new class of CA scaffolds that contain dispersions of CNTs within the scaffold framework. Incorporation of CNTs into the scaffold has the potential to not only improve the thermal conductivity of the scaffold, but may also affect the kinetics of dehydrogenation for...
certain metal hydrides. Recent work by other groups have indicated that the interaction of the hydride with an electronegative surface, such as that of a carbon fullerene or nanotube, can disrupt the bonding structure of the hydride and, as a result, provide lower energy pathways for hydrogen exchange. These novel CA-CNT scaffolds (Figure 1) were been prepared through the growth of CNTs by CVD on the inner porosity of high surface area carbon aerogel substrates. Because the CNTs populate the surfaces of the CA support, these scaffolds promote intimate contact between the surfaces of the CNTs and the incorporated metal hydride. To evaluate the influence of the CNTs on the kinetics of hydrogen exchange in LiBH₄, the hydride was incorporated into the free pore volume of these scaffolds using melt infusion techniques and the temperature of dehydrogenation was determined using thermogravimetric analysis. As shown in Figure 2, LiBH₄ nanocomposites prepared with the CA-CNT scaffolds showed significant decreases in the temperature of hydrogen desorption relative to that for bulk LiBH₄ and also out-perform earlier generation CA scaffolds prepared without CNT. This approach to scaffold design appears promising and we expect further improvements in performance as the structure of these composite scaffolds are optimized.

**Conclusions and Future Directions**

While this project finished at the end of this review period, we believe there are a number of aspects of this work that warrant future investigation based on the promising results from Fiscal Year (FY) 2010, including:

- Evaluation of room temperature hydrogen uptake (both capacity and kinetics) in the metal-loaded sugar-derived CAs. These results should provide guidance for further optimization of the surface chemistry and texture of the spillover receptors.
- Further investigation of the influence of CNTs and other graphitic nanostructures on the kinetics of hydrogen exchange in complex hydride systems. Initial results for our CA-CNT composites indicate improved kinetic performance of LiBH₄ in these scaffolds.
- Incorporation of other destabilizing agents and catalysts, such as Mg, Ni or Ti, into these CA-CNT scaffolds to facilitate the hydriding and dehydriding processes.

**FY 2010 Publications/Presentations**


IV.C.2 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 (no-cost extension to December 31, 2010)

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 (2007, section 3.3.4) outlined in the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(E) Charging/Discharging Rate

(P) Lack of Understanding of Hydrogen Physiosorption 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. The Hydrogen Program aims to address the critical need that has been recognized by DOE, which has established a national effort to develop new and advanced high-capacity hydrogen storage materials and technologies. 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>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2015 System Target</th>
<th>SUNY-Syracuse **</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>kWh/kg (wt% H2)</td>
<td>1.8 (5.5)</td>
<td>2.4 (7.2)</td>
</tr>
<tr>
<td>System Volumetric Capacity</td>
<td>kWh/L (gH2/L system)</td>
<td>1.3 (40)</td>
<td>1.2 (40)</td>
</tr>
<tr>
<td>Min/Max Delivery Temperature</td>
<td>K</td>
<td>233–358</td>
<td>77</td>
</tr>
<tr>
<td>Max Delivery Pressure</td>
<td>bar</td>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>

Accomplishments

- Demonstrated synthesis of a modified polymer-based carbon with high surface area (up to 4,000 m²/g) and low average pore width (down to 8.5 Å). Accomplished gravimetric storage capacity of ~6.7-7.0 wt%, and volumetric capacity of ~43-45 g/L at 77 K, 5-6 MPa.
- Achieve a high reproducibly on production in laboratory scale.
- Introduction of a carbon alloy with organocyclic-(CNH)n macromolecules rich with unsaturated bonds that should be available for room temperature (RT) application at moderate pressures for H2 storage systems. The melamine derivative carbonized or incorporating to the activated carbon
without the metal predicated at 77 K and 1 bar is 4-5 wt% with surface area ~2,000 m²/g.

- Using theoretical simulations (Monte Carlo computation) to obtain configurations of Melon (and g-C₃N₄) with d-transition metals (Mg, Ti, V, Ni, Fe) indicating that the complex structures with these metals can increase the hydrogen adsorption and with desirable binding energy.

Introduction

The 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 (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 to produce carbon with the designed morphology for activation to high surface area and controlled micropores. Thus, polymer precursors (modified poly(phenylene oxide), modified poly(ether ether ketone [PEEK]), polyetherimide [PEI]) are spun at high melt shear rates further to control 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 to control the carbons texture. Interaction of carbon with hydrogen is relatively low and may reach up to 6-7 kJ/mol. Since organocyclic-CNHN macromolecules with unsaturated bonds that exhibit rigid planar configuration and are abound in electronegative nitrogen atoms, can complex metal-salt and are enabled for RT application for H₂ storage systems at moderate pressure. Thus the synthetic methods are expanded to incorporate reactive sites into the carbon nanostructures by doping polymerized unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ni-Melem). Also, melamine derivatives have been synthesized and carbonized for adsorption of hydrogen. Alloying activated carbon with unsaturated functionalized polycyclic complex(ed) with Melem, F-Melem, and/or traces of Ni, Ti, Fe-Melem have been accomplished. Finding the proper compositions, and the ratio of carbon/alloy and other components, is needed. Also, surface modifications of the nanostructures of polymer based carbons (by blending different polymer precursors) and control of hydrogen’s binding energy with the carbon/alloys have been part of this study. Extensive physisorption and chemisorption (H₂ adsorption) characterizations have been performed to verify the synthetic effort.

Results

In Fiscal Year (FY) 2010, the main focus still 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. The hydrogen storage measurement has been tested at several laboratories. Figure 1 shows hydrogen uptake isotherms (excessive uptake) of polymer-based carbons measured gravimetrically (pressure up to 20 bar), and volumetrically high throughput (instrument pressure up to 60 bar) (measurement by Hiden Isochema Co. U.K).

The hydrogen uptake reaches 6.6 wt% for APKI-S6 at 50 bar, and for carbon 5.5 wt% 20 bar (as measured with both techniques). The APKI polymer-carbons are PEEK/PEI, and poly(2,6-dimethyl-1,4-phonylene oxide)-based carbon (APPO) is derivative of phenyl phosphine oxide. Surface areas for APKI6S2-N4, APPO-R8, APKI-S6 and APKI6S2-N20 are recorded as 3,070, 2,550, 3,034, 5,160 m²/g, respectively.

Figure 2 shows excessive hydrogen uptake of polymer-based carbons (PEEK, PEEK/PEI and APPO) at higher pressures evaluated at different testing laboratories.

The hydrogen binding energy for all carbons shown here are ~5-6 kJ/mol. A strategy for increasing hydrogen binding energy has been executed by introducing a large number of certain metal sites to polymer framework. In the past year, a set of Melon configurations, and Melon with Mg, Fe, Ti, V, Ni single metal atoms were first modeled by Monte Carlo computational method at 300 K. These models indicate that Ti and Mg do not only interact with the melon units but also “open” the spacing for hydrogen (up to four for Ti and two for Mg) which were situated here at the local
minimum potential (energy) configuration; where in the case of Ni the metal was found to be competing on the position and “close” the space for hydrogen molecules, which were found the minimum out of the melon units. Metal clusters M(n) (not shown here) are used to model “real” possible events. The Melon with different metal catalysts was carbonized at 700°C from C-N nano tubing with diameter ~12 nm traces of large cluster aggregation of Fe (Figure 3A). Figure 3B shows lattice structure formed on wall of this carbon. The electro diffraction gives a distance of 3.4 Å hydrogen adsorption of carbonized Melon carbon nano-tubing before complex with metal at 87 K and 1 bar is shown in Figure 4. All the samples have surface areas below 650 m²/g. The hydrogen adsorption increases linearly with the surface area. (Uptake about ~3 wt% hydrogen can be obtained by extrapolating to the surface area ~1,000 m²/g).

**Conclusion**

- Accomplished synthesis of a modified polymer based carbons with high surface area (up to 4,000 m²/g) and low average pore width (down to 8.5 Å). The gravimetric storage capacity of these carbons achieved ~6.7-7.0 wt%, and volumetric capacity of ~43-45 g/L at 77 K, 5-6 MPa!!
- Achieve a high reproducibly on production of these carbons in laboratory scale!!
- Organocyclic-(CNH)_n macromolecules rich with unsaturated bonds that should be available for RT
application at moderate pressures for H₂ storage systems has been established. The hydrogen storage of the melamine derivative carbonized or incorporating to the activated carbon without the metal predicated at 77 K and 1 bar is 4-5 wt% with surface area ~2,000 m²/g.

- Using theoretical simulations (Monte Carlo computation) to obtain configurations of Melon (and g-C3N4) with d-transition metals (Mg, Ti, V, Ni, Fe) indicating that the complex structures with these metals can increase the hydrogen adsorption and with desirable binding energy.

**FY 2010 Publications and Presentations**

IV.C.3  Electron Charged Graphite-Based Hydrogen Storage Material

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. Progress Toward Meeting DOE On-Board Hydrogen Storage Targets

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010 System Target</th>
<th>Fiscal Year 2009 System*</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>kg H₂/kg system</td>
<td>0.045</td>
<td>0.028</td>
</tr>
<tr>
<td>System Volumetric Capacity</td>
<td>kg H₂/L system</td>
<td>0.028</td>
<td>0.101</td>
</tr>
<tr>
<td>Storage System Cost</td>
<td>$/kg H₂</td>
<td>133</td>
<td>&gt;1,200</td>
</tr>
<tr>
<td>Adsorption/Desorption Temperature</td>
<td>°C</td>
<td>-30/50</td>
<td>-20/120</td>
</tr>
</tbody>
</table>

*GTI metal hydride-based material (3 wt% hydrogen storage) with tank at 1,000 psi

Accomplishments

- Tested a water cooling/heating system for hydrogen storage and release.
- Repeated the electron charge effect experiments on the hydrogen storage capacity of materials under water cooling and heating.
- Tested the in situ regeneration of borane-nitride materials.

Introduction

Hydrogen adsorption/desorption of metal-based materials with storage gravimetric capacity of 3.3 wt% of base material have slow kinetics with chemisorption. For comparison, 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 weak van der Waals force. The non-polar hydrogen molecules adsorbed on a polar (metal) substrate generate an electron spillover effect on hydrogen adsorption. Whether the substrate is polar or non-polar, the external electrical force could polarize the substrate surface to change the hydrogen adsorption capacity and kinetics. In the last annual report, it was concluded that positive charge increases hydrogen storage on metal based material and negative charge increases hydrogen storage non-metal hydrogen storage materials. This year, we focus on the substrate and regeneration of hydrogen storage materials.

**Approach**

- Test and evaluate the hydrogen storage system with cooling/heating:
  - 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%?
- Build a system with water cooling and heating to enhance hydrogen storage and release rate.
- 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

   External electron-charge has been demonstrated to affect hydrogen storage kinetics and capacities. Figure 1 shows the design of our electron-charged hydrogen storage system with cooling/heating feature. In this system, a stainless steel coil with polymer coating as insulation is inserted into the tank. The stainless steel coil conducts electron-charge and cools/heats the hydrogen storage materials. A similar system with 10 ml capacity is used for material screening and hydrogen storage tests.

2. Hydrogen Storage Tests

   The electron-charge hydrogen storage system was checked for any internal short under hydrogen storage pressure. It was determined that even if the voltage goes to 1,000 volts, the leak current is very small and would not affect experimental results. Therefore all the tests using this system show the electro-static non-Faradaic effect on the hydrogen storage due to low Faradaic current.

   Figure 2 is a pressure-composition-isotherm (PCI) curve of a metal-based hydrogen storage material during cooling and heating modes. Hydrogen is adsorbed during cooling and released during heating as expected. The system was verified for use in external charge experimental tests.

   The hydrogen storage system with cooling/heating was connected to an external electrical charge device to determine the effect of external charges on hydrogen storage. Figure 3 shows the PCI curves of the metal-based hydrogen storage material under positive charge (a) and negative charge (b) during cooling and heating. PCI curves with electrical charges shift and shows increased hydrogen storage. However the shift seems to be independent to the charge polarities. It could be due to activation of storage material by external charges. The key is to look for a hydrogen storage material that
3. Regeneration of Borane-Ammonia

The electrochemical activity of BH$_3$NH$_3$ was tested in diglyme because of its high boiling point of 162°C and capability to chelate small cations. For all supporting electrolyte used, when heated near 100°C, the BH$_3$NH$_3$ expanded greatly. This also had an effect on cyclic voltammograms (CVs). Figure 4 shows the CV for BH$_3$NH$_3$ in diglyme.

### Table 2. Borane-Ammonia Regeneration under Different Catalysts by TGA

<table>
<thead>
<tr>
<th>Sample content</th>
<th>Weight loss after 150°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_3$NH$_3$:Ni (1:1)</td>
<td>13.828</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:SAPO (1:1)</td>
<td>15.292</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:BiPbSnCd (1:1)</td>
<td>10.26</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:BZSM5 (1:1)</td>
<td>10.663</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:BZSM5 with Rh (1:1)</td>
<td>9.742</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:KA (1:1)</td>
<td>13.555</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:BiSn (1:1)</td>
<td>9.008</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:LaNi$_5$ (1:1)</td>
<td>8.583</td>
</tr>
<tr>
<td>BH$_3$FeTiO$_3$SAPO (2:1:1)</td>
<td>10.92</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:Fe,N:SAPO (2:1:1)</td>
<td>12.362</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:SiC:Rh (15:10:5)</td>
<td>8.662</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:hydroquinone:Rh (15:10:5)</td>
<td>7.773</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:Polyaniline emeraldine (1:1)</td>
<td>10.556</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:BZSM5:Ag/C (15:10:5)</td>
<td>11.273</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:TiC:BZSM5 (2:1:1)</td>
<td>8.826</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:Pyrene:PdCl(Ph)$_3$ (15:15:2)</td>
<td>8.266</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:CoPY/C:RhCl(Ph)$_3$ (15:15:2)</td>
<td>12.546</td>
</tr>
<tr>
<td>BH$_3$NH$_3$:CoPY/C:V:RhCl(Ph)$_3$ (15:8:7:2)</td>
<td>12.059</td>
</tr>
</tbody>
</table>

B. High Surface Carbon for Hydrogen Storage

The hydrogen storage electron-charge system is being developed under cooperation with the State University of New York (SUNY) at Syracuse. GTI tested eight samples provided by SUNY and the results are summarized in Table 3. The best hydrogen storage gravimetric capacity (Sample APKI-S6) is 7.0 wt% at 77 K.
TABLE 3. Summary of SUNY samples at 6,300 kPa

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>0°C (wt%)</th>
<th>77 K (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APKI-S6</td>
<td>0.58</td>
<td>6.38</td>
</tr>
<tr>
<td>APK25-N2</td>
<td>0.463</td>
<td>5.94</td>
</tr>
<tr>
<td>Ma015580-2</td>
<td>0</td>
<td>3.45</td>
</tr>
<tr>
<td>PZTAPK</td>
<td>0.39</td>
<td>5.47</td>
</tr>
</tbody>
</table>

Conclusions and Future Directions

- The electron charge experiments showed 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 also improves hydrogen charge/discharge kinetics. In situ regeneration of borane-nitride showed 75% increase in rate at 600 psig.

FY 2010 Publications/Presentations

1. A poster presentation on the overall project status was presented at the June 9, 2010 DOE Annual Merit Review Meeting in Washington D.C.

References

IV.D.1a Hydrogen Storage Engineering Center of Excellence

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Subcontractors:
• Pacific Northwest National Laboratory, Richland, WA
• United Technologies Research Center, E. Hartford, CT
• General Motors, Warren, MI
• Ford Motor, Dearborn, MI
• The National Renewable Energy Laboratory, Golden, CO
• Los Alamos National Laboratory, Los Alamos, NM
• Jet Propulsion Laboratory, Pasadena, CA
• University of Michigan, Ann Arbor, MI
• California Institute of Technology, Pasadena, CA
• Oregon State University, Corvallis, OR
• Lincoln Composites LLC, Lincoln, NE
• BASF GmbH, Ludwigshafen, Germany
• Université du Québec à Trois-Rivières, Canada

Project Start Date: February 1, 2009
Project End Date: Project continuation and direction determined annually by DOE

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 Fuel Cell 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 modeling, design, build and demonstration of prototype hydrogen storage systems for each metal hydride, chemical hydride and hydrogen sorption materials meeting as many of the DOE technical targets for light-duty vehicular hydrogen storage. The current status of these systems vs. the onboard hydrogen storage system technical targets are given in Table 1.

Introduction

The Hydrogen Storage Engineering Center of Excellence (HSECoE) brings together all of the materials and hydrogen storage technology efforts to address onboard hydrogen storage in light-duty vehicle applications. The effort will begin with a heavy emphasis on modeling and data gathering to determine the state-of-the-art in hydrogen storage systems. This effort will span the design space of vehicle requirements, power plant and balance of plant requirements, storage system components, and materials engineering efforts. These data and models will then be used to design components and sub-scale prototypes of hydrogen storage systems which will be evaluated and tested to
determine the status of potential system against the DOE 2010 and 2015 technical targets for hydrogen storage systems for light-duty vehicles.

**Approach**

A team of leading national laboratories, universities, and industrial laboratories, each with a high degree of hydrogen storage engineering expertise cultivated through prior DOE, international, and privately sponsored programs has been assembled to study and analyze the engineering aspects of condensed phase hydrogen storage as applied to automotive applications. This diverse group will bring creativity and originality to the HSECoE, where innovative concepts must be identified to develop hydrogen storage systems capable of meeting the stringent DOE goals. The technical activities of the HSECoE are divided into three system architectures: adsorbent, chemical hydride and metal hydride matrixed with six technologies areas: Performance Analysis, Integrated Powerplant/Storage System Analysis, Materials Operating Requirements, Transport Phenomena, Enabling Technologies and Subscale Prototype Construction, Testing and Evaluation.

**Results**

The following technical accomplishments were achieved by the partners in the HSECoE during the course of the past year. These accomplishments were the result of intense inter-organizational communication and interfacing through the existing technology area lead organization for the Center. These accomplishments are:

- The positions of system architects were formulated to give prime responsibility to individuals for driving technical solutions to identified technology gaps in storage system development.
- Completed programming of the Hydrogen Storage SIMulator to aid in prediction of impact of technical targets.
- Completed baseline fuel cell power plant models with physical storage fuel sources.
- Completed finite element models on metal hydrides and adsorbent system.
- Completed initial metal hydride hydrogen storage system models with various configurations of pressure vessels, buffer tanks, hybridization schemes, pumps and heat exchangers.

<table>
<thead>
<tr>
<th>TABLE 1. System Status vs. Technical Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Gravimetric Density</td>
</tr>
<tr>
<td>Volumetric Density</td>
</tr>
<tr>
<td>Minimum Operating Temperature</td>
</tr>
<tr>
<td>Maximum Operating Temperature</td>
</tr>
<tr>
<td>Min. Delivery Temperature</td>
</tr>
<tr>
<td>Max Delivery Temperature</td>
</tr>
<tr>
<td>Cycle Life (1/4 - full)</td>
</tr>
<tr>
<td>Cycle Life (% mean)</td>
</tr>
<tr>
<td>Min. Delivery Pressure (PEMFC)</td>
</tr>
<tr>
<td>Max. Delivery Pressure</td>
</tr>
<tr>
<td>On Board Efficiency (%)</td>
</tr>
<tr>
<td>Fill Time (5Kg H₂)</td>
</tr>
<tr>
<td>Minimum Full Flow Rate</td>
</tr>
<tr>
<td>Start Time to Full Flow (20°C)</td>
</tr>
<tr>
<td>Start Time to Full Flow (-20°C)</td>
</tr>
<tr>
<td>Transient Response</td>
</tr>
<tr>
<td>Fuel Purity (%)</td>
</tr>
<tr>
<td>Permiation &amp; Leakage*</td>
</tr>
<tr>
<td>Toxicity*</td>
</tr>
<tr>
<td>Safety*</td>
</tr>
<tr>
<td>Loss of Useable H₂</td>
</tr>
</tbody>
</table>

* indicates qualitative assessment
Anton – SRNL

IV.D Hydrogen Storage / Hydrogen Storage Engineering CoE

- Completed initial chemical hydride hydrogen storage system models with various configurations of mass transport mechanisms, spent fuel reservoirs and reactors.
- Completed initial adsorbent hydrogen storage system models with various configurations of heat exchangers, pressure vessels, buffer tanks and pumps.
- Completed coupling of vehicle modeling, fuel cell modeling and storage system modeling in a MATLAB/Comsol/Simulink environment.
- Identified acceptability criteria and UP/DOWN select methodology for metal hydrides, chemical hydrides and adsorbent materials.
- Completed identification of parametric models to be used for metal hydride, chemical hydride and adsorbent system thermal models.

\[
\frac{dC}{dt} = \mathcal{A} \exp\left(-\frac{E}{RT}\right) \left(C - C^0\right)
\]

Chemical Hydrides:

\[
\frac{dC}{dt} = \mathcal{A} \exp\left(-\frac{E}{RT}\right) \left(P - \frac{P}{\alpha}\right) \left(C - C^0\right)
\]

Metal Hydrides:

\[
n_{ex} = n_{max} \exp\left[-\frac{RT}{\alpha + RT}\right] \ln\left(\frac{P}{P_0}\right) - \rho_n V_a
\]

Adsorbents:

- Compiled a data base for each of the materials to be modeled and identified technical data gaps in the data with plans to fill these gaps as shown in Table 2.

<table>
<thead>
<tr>
<th>Tier 1 Developed Materials</th>
<th>Tier 2 Developing Materials</th>
<th>Down-selected Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX-21</td>
<td>Pr/AC-IRMOF 8</td>
<td>MOF 177</td>
</tr>
<tr>
<td>MOF 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH3BH3H</td>
<td>NH3BH4</td>
<td></td>
</tr>
<tr>
<td>AlH3</td>
<td>LiAlH4</td>
<td></td>
</tr>
<tr>
<td>NaAlH4</td>
<td>Mg(NH2)2 + MgH2 + 2LiH</td>
<td>MgH2</td>
</tr>
<tr>
<td>2LiNH2 + MgH2</td>
<td>TiCr(Mn)H2</td>
<td>Mg2NH4</td>
</tr>
</tbody>
</table>

- Completed an acceptability envelope for metal hydrides to aid in determination of the critical thermochemical characteristics required for storage system consideration:

\[
\left(\frac{1}{L^2}\right) \left(\frac{k M_{Hyd}}{\Delta H_{overall}} \cdot \frac{\Delta T}{\rho_{Hydride}}\right) = \frac{1}{mM_{H2}} \frac{\Delta m_{H2}}{\Delta t}
\]

- Identified critical technologies for pressure vessels, sensing, insulation, thermal generation and fuel purity required to enable use of various storage system materials.
- Determined the current system technical target status of metal hydrides based on NaAlH4 and technology gaps (gravimetric density, cycle life, safety and toxicity) needing to be addressed to meet the 2010 and 2015 technical targets (see Figure 1).

**FIGURE 1.** Spider chart against DOE 2010 targets for sodium aluminum hydride metal hydride system showing technical gaps in gravimetric density, cycle life, safety and toxicity.
• Determined the current system technical target status of chemical hydrides based on solid NH$_3$BH$_3$ and technology gaps (fuel purity, fill time, minimum full flow rate and loss of useable hydrogen) needing to be addressed to meet the 2010 and 2015 technical targets (see Figure 2).

• Determined the current system technical target status of adsorbents based on super-activated carbon and technology gaps (volumetric density, minimum delivery pressure and loss of useable hydrogen) needing to be addressed to meet the 2010 and 2015 technical targets (see Figure 3).

**FIGURE 2.** Spider chart against DOE 2010 targets for solid ammonia borane chemical hydride system showing technical gaps in fuel purity, fill time, minimum full flow rate and loss of useable hydrogen.

**FIGURE 3.** Spider chart against DOE 2010 targets for super activated carbon (ax-21) adsorbent system showing technical gaps in volumetric density, loss of useable hydrogen and minimum delivery pressure.
Conclusion and Future Directions

For each of the storage system types, many of the technical targets have been fully met with a number more met to at least the 40% level. The technical directions to achieve the Phase 2 Go/No-Go decision are set by the technical gaps noted in the spider charts. Furthermore, the technical targets will be prioritized in the coming year give guidance as to the technical gaps requiring further work.

For metal hydride systems, approaches must be proposed which have been shown minimally through modeling that:

- Gravimetric targets can be met through characterization of LiMgN materials systems.
- Cycle life of materials can be estimated through accelerated testing.
- Acceptable toxicity and safety risk levels can be achieved through mitigation strategies.

For chemical hydride systems, approaches must be proposed which have been shown minimally through modeling that:

- Fuel purity can be achieved through impurity trapping and materials development.
- Fill time can be achieved through solid mass flow concepts and novel system designs.
- Minimum full flow rate can be achieved through solid mass flow and solid reactor designs.
- Loss of useable hydrogen can be minimized through materials characterization.

For adsorbent systems, approaches must be proposed which have been shown minimally through modeling that:

- Volumetric densities can be achieved through compaction methods with minimal loss of gravimetric density.
- Minimum delivery pressures can be achieved through novel thermal designs.
- Loss of useable hydrogen can be minimized through utilization of novel low-cost insulation schemes.

As Phase 2 is entered, experimental validation of modeling will take precedence. Heat and mass flow experiments will be detailed constructed and performed to validate modeled performance. The modeling and empirical validation cycle will be used to obtain enhanced performance.

FY 2010 Publications/Presentations

Presentations

IV.D.1b Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

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Contract Number: DE-AC05-76RL01830  
Project Start Date: February 1, 2009  
Project End Date: January 31, 2014

Objectives

The Pacific Northwest National Laboratory (PNNL) 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 analysis, design and engineering for chemical hydride storage, pressure/containment vessel construction for metal hydride and cryogenic adsorbent systems, and component miniaturization to achieve PNNL, Hydrogen Storage Engineering Center of Excellence (HSECoE), and DOE goals.

- 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, thus advancing the hydrogen market sector and production of future hydrogen-powered vehicles.

Technical Barriers

Specific work scope at PNNL is addressing most of the technical barriers, as described by the Fuel Cell Technologies multi-year program plan, in system weight, volume, cost and efficiency, as well as operational constraints in hydrogen delivery and refueling rates, durability and operating temperatures bounds, and materials of construction. This project addresses the following needs in the Fuel Cell Technologies multi-year program 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  
(I) Dispensing Technology  
(J) Thermal Management  
(K) System Life-Cycle Assessments  
(O) Hydrogen Boil-Off  
(H) Balance of Plant (BOP) Components

Off-board Regenerable Specific:
(S) By-Product/Spent Material Removal
Technical Targets

The Center activities being conducted at PNNL range from process and reactor modeling and component design/engineering to technology application and prototype fabrication for demonstration. The final ultimate goal of the PNNL scope is to demonstrate, with Los Alamos National Laboratory (LANL) partners, a (100-g) scaled chemical hydrogen storage system that meets all the DOE storage performance targets. As a snapshot of progress to date, the spider chart in Figure 1 represents the principal DOE performance targets and status toward achieving those targets as a percentage. The DOE has established an initial in-process review gate of 40% for each of the targets; the dashed line represents this 40% threshold.

Accomplishments

Progress toward meeting formal Fiscal Year (FY) 2010 milestones is on track. Accomplishments achieved to date against these milestones include:

- 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.
- Determine functional criteria and design rules based on modeling performance predictions and hydride system needs.
- Complete a conceptual design for a solid chemical hydride reactor that will provide input to the HSECoE’s Phase 1 Go/No-Go decision making process, and insight into the ability of such a system to meet the 2015 volumetric capacity target of 1.5 kWh/L.
- Complete COMSOL modeling of configurations.
- Down-select systems to be modeled for transient response.
- Complete preliminary design for fuel element transfer system (solids handling coupled to reactor).
- Complete test station for monolithic fuel element and hydrogen release measurement.
- Provide Rev.0 cost model, structure details and spreadsheet to Center partners for their evaluation.
- Determine bulk kinetics measurements and impact on performance.
- Complete modeling and establish pressure vessel design rules for use with prototypes.

FIGURE 1. Progress toward achieving DOE performance targets for solid ammonia-borane (AB) hydrogen storage. Seventeen targets are above the 40% threshold set as an initial gate target in March 2011.
• Complete identification of known materials compatibility issues and establish corrective action plan for component designs.

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 sub-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 leading efforts as part of the HSECoE led by SRNL, to design and fabricate a 100 g of hydrogen scaled system based on solid or slurry chemical hydride storage media. This system is intended to be demonstrated at LANL during FY 2014 as the HSECoE concludes.

Approach

The PNNL will actively contribute to the five technology areas established as part of the HSECoE led by SRNL. The goal of this 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 or “viability” studies.

PNNL will also serve multiple leadership roles within the HSECoE technology area structure to help facilitate collaboration across the center partnership and to feed technical results back through and disseminate to other center partners. 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 original equipment manufacturers, thus advancing the hydrogen market sector and production of future hydrogen-powered vehicles.

Results

During FY 2010 the basis of a solid chemical hydride reactor design model and system construct was created. Further, system flow sheets were established for a solid monolithic system, which provides preliminary insight into component configurations for chemical hydrides. Flow sheets and design information from component and system models were used to identify knowledge gaps that would be addressed in an experimental program later in FY 2010 and FY 2011. This modeling and experimental data will be used as the basis for down-selection of flow sheets at the end of Phase 1.

To date multiple monolithic fuel element conceptual forms have been considered:

• Disks
  – Five-inch disks, 1/8” thick sequentially inserted into 60-120 3/16” slots.
  – Slots loaded every 2-4 seconds.
  – 170°C oil channels between each slot for preheat/cooling.

• Beads
  – Beads loaded into 60-120 1-1/4” diameter, 5-inch long chambers.
  – Chambers loaded every 3-6 seconds.
  – 170°C oil channels surround each chamber.

• Tape
  – Two-inch wide, 1/8” thick tape runs through reactor at 20 ft/min.
  – Eighteen passes in 3 ft long reactor.
  – 170°C oil channels surround each pass.

Models that represent these physical formats have been drafted, and for FY 2010 are being used to analyze hydrogen mass and heat transfer throughout the dehydrogenization reaction zone and within the fuel storage container. Furthermore, a fourth fuel element type is in the process of being added to the physical domain model that describes the fuel element in a gel or slurry form that may have the added advantage of easier loading on- and off-board the vehicle.

Additionally, a series of models that captures the physiochemical nature of a solid chemical hydride system was drafted that will be use to simulate hydrogen release in monolithic fuels in order to guide system design and determination potential for achieving hydrogen release rate target of 1.6 g H₂/s for an 80 kW fuel cell. This model also incorporates the fuel element engineered form models (e.g. disks, beads, tape) and takes into consideration two different reactor designs and processes routes – batch versus continuous.

The model is built upon a three-tier hierarchy, with the lowest level being a kinetics model that describes
the mass/heat phenomena of the systems; second tier describes the reactor function and physical design, while the highest tier is a BOP component model that follows the process flow diagram configuration. Basic inputs to the model are: reaction rate, reactor design, DOE targets (80 kWe), while outputs are: reactor size, fuel usage, hydrogen loss, and impurity level.

This three-tier series of models are built using a combination of COMSOL, MATLAB and Microsoft Excel, which input/output files are readily transferable between other Center partners. The models once refined and validated experimentally, will be used for sensitivity analyses, understanding reaction residence times, determining reactor size and complexity versus extent of reaction (fuel usage). The modeling effort will also focus on defining fuel element void space (e.g. slot gap size, packing density), ultimate reactor operating pressure, hydrogen loss, and level of impurities.

This initial baseline model utilizes AB in an engineered form, known (or predefined) reactor design dimensions, heat transfer, and diffusion resistance. Figure 2 shows this baseline reactor and storage system. The model is currently being adapted to also include provisions to simulate the functions of a gel or slurry fuel.

To address weight and volume constraints design consideration was given to combining function and components into single units, as well as integrating multiple functionality into the reactor and on-board mass transfer components. As an example, the AB thermohydrolysis reaction and control of kinetics exclusively in the auger rather than ballast tank with the baseline design show in Figure 2. Additionally, the fuel element feed and product tanks are combined into a single unit that works by displacing and refilling the tank volume with fresh and spent fuel, hence minimizing overall system volume. As a result, estimated system volume and weight appears to be within achievable
means relative of the DOE 2010 performance targets. Estimates weights and volumes for the primary systems components are given in Table 1.

Beyond process and kinetics modeling, PNNL has established the modeling approach, assumptions, and basic structure to simulate various pressure vessel geometries and layered structures, including model parameters that account for basic cost and performance. This effort and model is being used to conduct assessments of materials and design options between Type I-IV pressure vessels, which include a first-order approximation of cost from a materials-of-construction perspective. It was concluded that carbon fiber-wrapped Type-IV tanks is the closest known option to meet 2015 weight targets. However, the trade-off is higher cost of the carbon fiber, which may be a contrite to implementation at this point in time unless options for lower cost carbon fiber and/or tank designs can be developed. Based on this study further analysis will emphasize options for aluminum tanks and liners, as well as modeling lower cost and strength carbon fibers for use in Type-IV tanks.

Additionally in FY 2010 PNNL developed the selection criteria for storage materials to aid in down selecting materials systems for further focus on system modeling and design. These selection criteria are used as a screening tool for subsequent material considerations, and to identify gaps in the property data which will need to be addressed by HSECoE partners or other independent projects. As part of this effort, materials property data collection from the existing materials centers of excellence has been completed.

**TABLE 1. System Weight and Volume Estimates – Baseline solid AB Bead Reactor with Heated Auger System**

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB Storage</td>
<td>30.8kg</td>
<td>0L</td>
</tr>
<tr>
<td>Feed/Product Tanks</td>
<td>14kg</td>
<td>140L</td>
</tr>
<tr>
<td>Ballast Tank (carbon fiber)</td>
<td>29.7kg</td>
<td>9L</td>
</tr>
<tr>
<td>Hot Auger (steel)</td>
<td>10.8kg</td>
<td>3.2L</td>
</tr>
<tr>
<td>Cold Auger (steel)</td>
<td>20.2kg</td>
<td>6.3L</td>
</tr>
<tr>
<td>Burner/Blower</td>
<td>6.3kg</td>
<td>5.7L</td>
</tr>
<tr>
<td>Radiator</td>
<td>1kg</td>
<td>1.8L</td>
</tr>
<tr>
<td>NH₃ Filter</td>
<td>2.2kg</td>
<td>2.7L</td>
</tr>
<tr>
<td>Oil Piping/Pump/Tank</td>
<td>4.7kg</td>
<td>3.5L</td>
</tr>
<tr>
<td>Valves/Actuators</td>
<td>5kg</td>
<td>3.5L</td>
</tr>
<tr>
<td>Total</td>
<td>125kg</td>
<td>176L</td>
</tr>
</tbody>
</table>

* Total 2010 targets: mass 111 kg; volume 178 liters based on 5 kg of usable hydrogen stored

**Conclusions and Future Directions**

- A representative systems model of an AB-based bead reactor system was developed and successfully simulated in MATLAB/Simulink environment.
- A COMSOL transport model was developed for a bead and a block system. The heat and mass transfer model used a simple reaction rate expression: (1) Bead reaction can occur within the auger that has been designed assuming a 200°C wall. (2) Heating the outside surface of a block can light off the reaction for the entire block.
- An improved kinetic model has been developed and implemented into the system model.
- Hydrogen loss and impurities assessed for solid AB as material is moved into and out of the pressurized reaction system.
- Materials properties database established for HSECoE partners.
- Screening criteria/questionnaire created.
- Engineering cost model structure established.
- Studies and analysis of pressure vessels performed:
  - Metal hydride hybrid
  - Vessel material of construction sensitivity analysis
  - Liner material assessment
- Materials compatibility and reactivity studies started.

Future planned scope for FY 2011 will predominately include implementation of the new reactor designs in MATLAB/Simulink and corresponding simulation analysis for assessing impact on: improve hydrogen delivery temperature; increase volumetric/gravimetric density; include variable transport properties (ρ, Cp, k, zH₂); and address impurities and hydrogen losses in design. Investigation of alternate materials of chemical hydride options, such as alane, will also occur. Additionally, implementation of the new kinetic model in MATLAB/Simulink and corresponding simulation analysis is planned, including the additional of temperature dependent transport properties into models as they become available. This effort will be supported by experimental efforts to determine needed property and kinetics data for each storage material system, as well as for model validation and calibration purposes.
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 heat exchange configurations.
- Assess the viability of on-board purification for various storage material classes and purification approaches.

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 Fuel Cell 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 Phase I (March, 2011) seeks 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

Accomplishments of the current project comprise:

- Demonstrated that powder compaction with a uniaxial press can simultaneously increase the density of sodium alanate materials by 63% (39% reduction in volume) and the thermal conductivity by a factor of seven in comparison to the properties of loose powder while maintaining comparable hydrogen absorption and desorption rates.
- Developed a biaxial flexure screening test for determining the strength of compressed pellets and changes in the pellet strength due to hydrogen absorption and desorption cycles.
• Designed and optimized a heat exchanger for a sodium alanate-based hydrogen storage system with a fast refueling time and developed a lumped parameter model of such a system for inclusion in vehicle level modeling.
• Demonstrated viability of an onboard hydrogen purification cartridge for ammonia, which addresses concerns about the presence of ammonia in hydrogen from chemical hydride (e.g. ammonia borane) and metal hydrides (e.g. LiNH2/MgH2 mixtures).
• Designed and implemented an integrated power plant storage system modeling framework in Simulink.

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

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. A graphical representation of our approach to conduct the research is shown in Figure 1. It shows material-related tasks at the base of the pyramid, component design tasks in the center, and system-related tasks near the top, which all tie in with the overall structure of the HSECoE. The results will be used by the HSECoE to determine the viability of materials-based hydrogen storage systems. The project is divided into three phases with the first covering two years. A Go/No-Go decision at the end of Phase 1 (March 31, 2011) will guide activities and concepts for deeper evaluation in Phase 2.

Results

DOE’s 2010 target for the volumetric capacity of a hydrogen storage system is 28 grams hydrogen per liter on a system basis. At the time of this study sodium alanate was a Tier 1 material in the HSECoE, and it was therefore selected as a model material for evaluating the impact of compaction on the density and thermal conductivity of a prototypical hydrogen storage material. Reaching the targeted volumetric capacity with sodium alanate requires powder compaction. For this purpose UTRC installed a heated platen uniaxial press inside a glovebox with an inert atmosphere. The density of the pressed pellets as a function of the compaction pressure is shown in Figure 2. The thermal conductivity of the compacted material was measured with a Hot Disk® Thermal Constants Analyzer and is shown in Figure 3 as a function of density. The results show that compaction of sodium alanate enables an increase in density of about 63% in comparison to loose powder (59% reduction in volume) which results in a seven fold increase of the thermal conductivity. Compacted sodium alanate appeared to have a slightly slower hydrogen absorption rate and this is subject of future research.

Sodium alanate pellets need to be strong for this automotive application. A biaxial flexure screening test was developed in order to measure the strength and determine any strength change after hydrogen absorption and desorption cycles. Initial results show a small volumetric expansion (~2%) of the pellets due to repeated cycling and the pellets maintained their strength (1.4 kpsi), but experiments will need to be repeated and performed over a larger number of cycles in order to better determine the significance of those results.

DOE’s 2010 target of 4.2 minutes for system fill time (for 5 kg hydrogen) is challenging for a hydrogen storage system based on sodium alanate due to the relative high heat of hydrogen absorption (~40 kJ/mol hydrogen) and kinetic limitations. A COMSOL Multiphysics™
A thermochemical simulation approach was co-developed with Savannah River National Laboratory and used to engineer a sodium alanate-based hydrogen storage system with such a short fill time, while maximizing gravimetric and volumetric capacities. It required an enhancement of the reaction kinetics beyond what is currently observed. The allowable temperature rise in the sodium alanate bed during refueling was restricted to 170°C. This constraint was imposed as a decrease of the hydrogen absorption rate was observed when holding the material at 180°C for an extended period of time (15-75 hrs), which is undesirable. The heat exchanger tubing diameter, aluminum content in the bed and the tube spacing were optimized with this model and the results are shown in Figure 4. It clearly shows the improvement of the volumetric capacity due to compaction and how a relative high volumetric capacity can be achieved even at a short fill time by using tightly spaced small diameter tubing (1/8”) in the heat exchanger and improvement of the reaction rate beyond what is currently observed. However, compaction only reduces the volume of the hydrogen storage material and therefore the gravimetric capacity of the sodium alanate bed still remains low (<18 g H2/kg) in comparison to DOE’s 2010 target (45 g H2/kg system).

UTRC is leading the Integrated Power Plant Storage System Modeling technical area of the HSECoE and with other partners has developed a simulation framework that was implemented in Simulink™. The framework is shown in Figure 5 in a graphical form. The team developed an interface matrix between the different simulation modules under guidance of Ford. The framework created a strong focus for the team members. Each member contributed models such as the lumped parameter model of a sodium alanate system by UTRC, the sodium alanate system with a different design by General Motors (GM), the cryo-adsorption system by GM, the chemical hydride system based on ammonia borane by the Pacific Northwest National Laboratory, the proton exchange membrane (PEM) fuel cell system by Ford and the vehicle level model by the National Renewable Energy Laboratory (NREL). The integrated framework enables a dynamic evaluation of the performance of a vehicle with a materials-based hydrogen storage system and a seamless comparison of various hydrogen storage systems on a common and quantitative basis, which is critical for the Go/No-Go decision in the end of Phase 1.
Hydrogen from the hydrogen storage system needs to have a sufficient purity in order to enable high performance and long life of the PEM fuel cell system. The SAE J2719 guideline [1] was adopted as the hydrogen purity standard. This guideline not only specifies the total hydrogen content but also sets limits on the concentration of specific impurities such as ammonia. Ammonia was shown to be an impurity of concern by Keith Wipke from NREL [2] as part of the Hydrogen Fuel Cell Vehicle and Infrastructure Learning Demonstration project as some of the hydrogen that was tested contained 1 ppm ammonia, which exceeds the SAE guideline of 0.1 ppm. Ammonia is not only introduced on-board the vehicle by the hydrogen filling station but two candidate materials for hydrogen storage (ammonia borane and LiNH₂·Mg H₂ mixtures) have also been reported to release hydrogen that is contaminated with ammonia. Therefore, ammonia abatement was selected as an initial focus for the hydrogen purity task. A chemical adsorption cartridge was selected for an experimental evaluation as it has distinct benefits in terms of cost and low hydrogen loss in comparison to the two alternative purification approaches (palladium membrane and on-board regenerable physical adsorption). An experimental setup was designed and built to determine the dynamic sorption capacity of various sorbents. It uses a photo-acoustic analyzer to monitor the ammonia content in the effluent of the sorbent bed as a function of time. The breakthrough time was defined as the time at which the ammonia content would exceed 0.6 ppm, which is the detection limit of this analyzer. It was determined experimentally that a commercially available sorbent had a dynamic sorption capacity for ammonia of about 2-2.5 wt% as a result of both physical and chemical adsorption under dry conditions (no humidification). A cartridge with about 4 kg of this sorbent would last about 3 months when processing 5 kg of hydrogen per week if the hydrogen would contain 200 ppm ammonia. This appears to be a viable approach and improving the capacity of the sorbent to reduce weight and volume is part of our future work. It is realized that abating hydrogen impurities with purification methods is only one approach and that it would be desirable to have an improved understanding and control over the hydrogen release mechanism to avoid the formation of impurities all together.

Qualitative risk analysis was performed on a chemical hydride system (based on ammonia borane) and on a cryo-adsorption system (based on AX21) and fault trees were developed for both.

**Conclusions and Future Directions**

Conclusions derived from the work in Fiscal Year 2010 are:

- Compaction of hydrogen storage materials, with sodium alanate as an example, is a valuable engineering tool for improving thermal conductivity and volumetric capacity of a hydrogen storage system but there is a trade-off between how much one can compact and when the decrease in permeability starts to become an issue. Also,
verifying that strength and compact integrity is maintained, is important.

- Sodium alanate is a good model material for developing engineering tools (compaction method, multiphysics model) though it is recognized it cannot fulfill the DOE targets.

- Evaluating different hydrogen storage systems on a common basis, by establishing a common simulation framework, is important for down-selecting hydrogen storage systems for Phase 2 consistently across the center.

- On-board hydrogen purification with commercially available sorbents to remove ammonia is feasible as long as the ammonia content is low (e.g. <200 ppm).

Future work will comprise:

- Determine hydrogen permeability of compacted sodium alanate pellets and use results in COMSOL Multiphysics™ model to quantify impact of pressure gradients on hydrogen absorption and desorption rate.

- Develop a small test article of compacted sodium alanate to determine thermal performance with aspects of heat exchanger integration.

- Expand the compaction effort, thermal conductivity and permeability measurements, to other materials that are of interest to the HSECoE.

- Use the Simulink framework to compare performance of various hydrogen storage system designs on a common basis and evaluate against DOE targets in close cooperation with the HSECoE partners.

- Improve ammonia dynamic sorption capacity of sorbent material and expand hydrogen purification approach from ammonia to other impurities of concern.

- Qualitative risk assessment of hydrogen storage systems of interest to the HSECoE.

**FY 2010 Publications/Presentations**


**References**


IV.D.1d Chemical Hydride Rate Modeling, Validation, and System Demonstration

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Project End Date:  February 2014

Technical Objectives

- 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).

Management Objectives

- DOE Program Liaison: Coordinate/collaborate with the Chemical Hydrogen Storage Center of Excellence (CHSCoE).
- Chemical Hydride System Architect: Monitor and guide progress on chemical hydride systems.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Efficiency
- (A) System Weight and Volume
- (D) Durability/Operability

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 novel acoustic fuel-gauge sensor with metal hydrides:
  - Patent submitted
- Developed and updated testing protocols for accurate shelf-life data acquisition.
- Collected shelf-life data for neat ammonia borane (AB) and liquid AB formulation.
- Screened approximately 20 catalysts for room temperature dehydrogenation of liquid-phase AB.
- Developed dual-catalyst bed reactor model to investigate start-up and transient operation.
- Quantified borazine and diborane impurities generated from neat AB.
- Demonstrated that borazine and diborane can be scrubbed to produce fuel-cell quality hydrogen.
- Developed preliminary system designs for liquid-phase chemical hydrides.

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 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 CHSCoE 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.

**Technical Tasks**

**Technical Task 1: Design and Develop Fuel Gauge Sensors for Solid-State Hydrogen Storage Media**

Approach: LANL will employ an inexpensive, simple, and robust method of using the natural properties of the hydrogen storage media to develop novel fuel gauge sensors.

**Technical Task 2: Develop Models of the Aging Characteristics of Hydrogen Storage Materials**

Approach: 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).

**Technical Task 3: Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides**

Approach: LANL’s approach will be to collaborate with the CHSCoE 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.

**Technical Task 4: Develop Novel Strategies for Start-Up and Transient Operation with Candidate Chemical Hydrides**

Approach: 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.

**Technical Task 5: Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies**

Approach: As materials are down selected and available, we will produce hydrogen from
candidate materials and operate small, 5 cm$^2$ 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, 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 AB were unknown.

Results

Fuel Gauge Sensor Development (Task 1)

Experiments were performed to determine the viability of employing acoustic sensor technology on metal hydrides as a fuel gauge sensor. Data were collected on commercial and non-commercial steel cylindrical pressure vessels containing metal hydride storage materials. In each case, the mass of metal hydride was small compared to the total mass of the system. However, large differences in the swept frequency response were evident (Figure 1), thus establishing a proof-of-principle that a hydrogen level sensor based on acoustic principles is feasible.

Figure 2 shows changes in the measured acoustic response spectra of the fully charged, large Solid H™ cylinder as it was removed and replaced. A small amount of water-based gel couplant was added in between each measurement and the exact placement of the cylinder on the transducers (including rotation component) was subject to small variability. While there are differences in the recorded spectra, several resonance peaks (e.g. at 45, 87, 136, 191, 248 kHz, etc.) are present in each scan albeit with slightly different amplitudes.

These data strongly indicated the need for an improved method of controlling the charge state of the hydride without disturbing the position of the hydride cylinder or the acoustic couplant in between measurements. Moreover, the variability introduced into the measurement via the previous method would preclude tracking the acoustic response at intermediate levels of charge or discharge. Demonstration of this ability will be very important for the purposes of level gauge development. Furthermore, during initial reversibility experiments where the hydride was charged and discharged repeated, it found that the properties of the water-based gel couplant would change due to the large exotherms associated with incorporation of H into the crystalline lattice of the metal hydride. The gel became more viscous and overtime eventually became very tacky due to dehydration of the gel. It is known that this stiffening of the couplant would introduce changes

![Acoustic Responses for (a) Fully-Discharged Metal Hydride and (b) Fully-Charged Metal Hydride](image-url)
in the resonance spectra and in particular, change which modes of vibration within the system were excited.

Mathematically Model the Aging Characteristics of Candidate Hydrogen Storage Materials (Task 2)

Shelf-life models were obtained for neat AB under non-isothermal reacting conditions. Differential scanning calorimetry (DSC) heat flow data were used to correlate dehydrogenation activity (or reaction progress) as a function of temperature. Models were generated using the Freidman analysis (or differential isoconversional technique). A shelf-life mode for neat AB was generated and is shown in Figure 3. Figure 3 shows the modeled reaction progress (i.e., extent of dehydrogenation) as a function of time and temperature. According to the model, AB will be stable

FIGURE 2. Four measurements of the Solid-H™ BL-30 storage cylinder, charged state, from 5 to 300 kHz conducted in succession with minor changes in placement of cylinder on top of the transducers, the possibility for slight rotation of cylinder, and variation in amount of water-based gel acoustic couplant.

FIGURE 3. Shelf-Life Model for Neat AB
at 40°C for approximately 15 days before significant dehydrogenation occurs. This model, however, under predicts the shelf-life model of neat AB. Consequently, this model does not agree with experiment and therefore has been down-selected (or given a "no-go"). Disagreement between the experiment results and the current model can be attributed to the movement of the DSC pan upon dehydrogenation, giving rise to inaccurate heat flow results which translated into the model. Additional experiments are being performed that address this issue. Updated models will be generated and compared to the data to ensure agreement between them.

**Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides (Task 3)**

Rate models for the dehydrogenation of liquid phase AB have been generated using a limited data set. The data set primarily includes hydrogen production as a function of temperature. In addition, the data were collected in a batch reactor with hydrogen being the only measurable quantity. A complete set of kinetics data would include hydrogen production as a function of temperature, concentration, flow rate, and catalyst. In addition, mass balances resulting in selectivities and yields are necessary for an accurate and complete description of the reaction kinetics. We are working with the CHSCoE in obtaining these results for rate model regression.

**Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies (Task 4)**

Observed impurities generated from AB are ammonia, borazine and diborane. Impurities from the thermal decomposition of AB have been shown to be catastrophic to fuel cell operation and durability. We have quantified (via calibrations) borazine and diborane that are generated from neat AB, AB/methyl cellulose and AB dissolved in ionic liquids. The amount of borazine and diborane generated is strongly dependent upon temperature, catalyst, purity, additives, and physical phase (i.e., solid phase or liquid phase). Shown in Figure 4 are the gas phase infrared spectra of (a) neat borazine, (b) gas phase products observed from neat AB thermal decomposition, and (c) neat diborane. In contrast to neat AB, AB dissolved in ionic liquids only generates ammonia as the impurity. Borazine and diborane were successfully scrubbed using activated carbon (as shown in Figure 5) producing fuel cell grade hydrogen.

**Develop Novel Strategies for Start-Up and Transient Operation with Candidate Chemical Hydrides (Task 5)**

Start-up and transient operation are critical features that need to be addressed for all viable on-board hydrogen delivery systems. Our approach is to design and implement novel strategies that address these two DOE targets. We looked at a design where a room temperature dehydrogenation catalyst was homogeneously mixed with a high temperature catalyst (~70°C); refer to Figure 6. The room temperature catalyst provides a means to accommodate both the startup and transient operation of the fuel cell. The short coming of the room temperature catalyst is that it promotes the release of only one equivalent of hydrogen. This is in contrast to the high-temperature catalyst that allows for multiple equivalents of hydrogen to be released. In other words, there are two reaction pathways that are catalyzed by the different catalysts. Competing reaction pathways result in a trade-off scenario between hydrogen production efficiency, heat generation and transient response. The homogeneous dual catalyst bed design results in a hydrogen production efficiency that is below the DOE gravimetric targets.
Consequently, this approach will not work and has been discarded as a viable design. We have also screened approximately 20 different catalysts for room temperature activity. None of the dehydrogenation catalysts proved to be viable room temperature catalysts. Results are shown in Figure 7. Because of the poor room temperature dehydrogenation activity observed with all of the catalysts tested, research on these catalysts has been discontinued.

**Design, Build, and Demonstrate a Subscale Prototype Reactor Using Liquid or Slurry Phase Chemical Hydrides (Task 6)**

In order to address the DOE targets we must first assess the current status via preliminary system designs. Shown in Figure 8 are two preliminary on-board system designs for liquid/slurry-phase AB. The preliminary system designs will be translated into a spider chart that compares the system to the DOE targets as a whole. We have identified areas that need to be addressed. These areas include impurity mitigation, startup and transient operation, and heat management. Preliminary costs and overall system efficiencies will also be calculated from the system designs.

**Summary**

- Level gauge milestones for Fiscal Year (FY) 2010 are on track and will be met by end of the fourth quarter.
- The change in swept acoustic frequency response with metal hydride hydrogenation/dehydrogenation observed in commercially prepared metal hydride
cylinders has been reproduced in simple stainless steel vessels:
- Characteristic response observed for two different metal hydride alloys.
- Ergenics™ 208 and LaNi alloy obtained from Aldrich in different cylinder masses/volumes show same effect.
- Experiments confirm that sound waves are coupling with, and interacting with, the metal hydride within the stainless steel pressure vessels and not due to secondary effects.
- Patent submitted.
- Acoustic sensor may be useful for metal hydride and adsorbent cycling studies.
- Developed and updated testing protocols for accurate shelf-life data acquisition.
- Collected shelf-life data for neat AB:
  - Shelf-life model for neat AB under predicts stability because of foaming issues, resulting in inaccurate data.
  - Preliminary shelf-life data collected for a liquid AB formulation:
    - Liquid-AB formulations stable for 100 hrs @ 60°C; need to measure shelf-life for extended time periods (>1,000 hrs).
  - The homogeneous dual catalyst bed design for handling the startup and transient operation of the fuel cell has been discontinued because the low temperature catalyst is too fast resulting in hydrogen production efficiencies equal to 0.4 (max is 1.0).
  - Screened approximately 20 heterogeneous catalysts for room temperature activity:
    - Reactor tested catalysts cannot meet the startup requirement needed for an on-board hydrogen delivery system.
• Novel reactor designs (without auxiliary heating sources) addressing start-up and transient operation require the development of novel heterogeneous catalysts that are active at room temperature.
• Preliminary system designs for both liquid phase and solid phase chemical hydrides have been generated.

Future Directions

Acoustic Fuel Gauge Sensor
• Investigate the effects hydrogen head pressure on acoustic response.
• Investigate the effects valve positioning and supply lines on acoustic response.
• Perform compaction test to determine if acoustic coupling effects.
• Demonstrate tracking intermediate states of hydrogen charge of the commercial hydride cylinder and look at effects of temperature on the resonance spectra.
• Begin work with other H₂ storage media.

Shelf-Life Modeling
• Collect shelf-life data on solid AB with anti-foaming agent.
• Collect a complete set of shelf-life data on liquid-AB formulations.
• Update experimental setup and protocols as needed to ensure accurate data for model development.
• Verify model accurately predicts shelf-life models for extended time periods.

Reaction Rate Models for Hydrogen Release on Candidate Chemical Hydrides
• Acquire complete set of kinetics data:
  – Low-temperature catalyst route
  – High-temperature catalyst route
• Focus on segregated dual catalyst bed design.

Low Temperature Catalyst Development for Startup and Transient Operation
• Continued efforts will focus on converting the room temperature homogeneous catalysts into heterogeneous form while maintaining room temperature activity.

Hydrogen Impurities and Mitigation
• In collaboration with the CHSCoE, quantify impurities from liquid AB formulations as a function of temperature ramp.
• In collaboration with the CHSCoE, quantify impurities from solid AB formulations as a function of temperature ramp.
• In collaboration with MHSCoE, quantify impurities from candidate metal hydrides formulations as a function of temperature ramp.
• In collaboration with United Technologies Research Center, explore and test possible alternative scrubbing technologies for ammonia, diborane and borazine.

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Objectives
- Perform vehicle simulations of various systems configurations.
- Provide support in defining the fuel interface and forecourt requirements.
- Lead the storage system energy analysis and provide results.
- Compile and obtain media engineering properties through collaboration with the Hydrogen Storage Material Center of Excellence (HSMCoE).

Technical Barriers
This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan:
(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(E) Charging/Discharging Rates
(I) Dispensing Technology
(K) Systems Life-Cycle Assessments

Technical Targets
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: to be determined
- Specific energy: 0.055 kg H₂/kg system
- Energy density: 0.040 kg H₂/L system
- Charging/discharging rates: 3.3 min

Accomplishments
- Developed a vehicle model framework to aid in the development and understanding of hydrogen storage system requirements for light-duty vehicles.
- Devised a methodology to assess onboard hydrogen storage technical target sensitivity in a light-duty vehicle context.
- Obtained preliminary greenhouse gas emissions and well-to-wheels (WTW) efficiency figures for baseline physical storage systems.
- Identified potential materials for analysis and provided storage system design guidance to help meet DOE storage targets with sorption materials.

Introduction
Overcoming challenges associated with onboard hydrogen storage is critical for the widespread adoption of hydrogen-fueled vehicles to occur. The overarching challenge is identifying a means to store enough hydrogen onboard to enable a driving range greater than 300 miles within vehicle-related packaging, cost, safety, and performance constraints. By means of systems analysis and modeling, hydrogen storage system requirements for light-duty vehicles can be assessed. With these findings and through collaboration with our Hydrogen Storage Engineering Center of Excellence (HSECoE) partners pathways for successful hydrogen storage system technology can be identified thus enabling future commercialization of hydrogen-fueled vehicles.

Approach
An array of tools and experience at NREL is being used to meet the objectives of the HSECoE. Specifically, extensive knowledge of multiple vehicle simulation, WTW analysis, and vehicle performance tools are being employed and integrated with fuel cell and material-based hydrogen storage system models developed by our
HSECoE partners. This integrated model framework allows for the evaluation of various hydrogen storage options. Engineering requirements are defined from these studies thus enabling the design of hydrogen storage vessels that could potentially meet DOE performance and cost targets in a vehicle system context.

In the area of media engineering, attaining the objectives of the HSECoE relies on NREL’s leadership in developing custom analytical instrumentation for hydrogen sorption analysis. These tools are used to thoroughly characterize hydrogen storage sorbents so that an optimized storage vessel specific to the sorption material may be efficiently engineered. NREL will use these methods to analyze sorption materials identified by the HSECoE as holding promise for application in commercial on-vehicle refuelable hydrogen storage systems capable of meeting DOE targets.

Results

An approach to evaluate hydrogen storage system characteristic trade-offs across several vehicle configurations was demonstrated. Evaluating trade-offs between storage system characteristics – including gravimetric capacity, transient response time, cost, and full flow rate – and understanding their sensitivity to overall vehicle system viability can assist in prioritizing research areas of onboard hydrogen storage.

Initial analysis involved two parts. In Part 1, a fuel cell vehicle (FCV) configuration was assumed. Each of the four hydrogen storage system characteristics considered was swept in a parametric study and the vehicle viability, a normalized measure of the vehicle cost and performance, was recorded. Holding all other vehicle components – including the fuel cell, motor, and energy storage system (ESS) – constant through this exercise helped identify vehicle viability sensitivity to varying levels of certain hydrogen storage characteristics as shown in Figure 1.

In Part 2 of the analysis, each of the hydrogen storage characteristics was swept while allowing specific vehicle component power and energy levels to vary. These components included the fuel cell, motor, and ESS. By allowing the vehicle components to vary with changes in the hydrogen storage system, the “Most Viable” FCV configuration could be identified for a particular system.

The results in Figure 2 suggest that allowing the fuel cell, motor, and ESS power and energy levels to vary as

![FIGURE 1. Onboard Hydrogen Storage Technical Target Sensitivity in a Light-Duty Vehicle Context - Part 1 Results](image-url)
the transient response of the hydrogen storage system increases assists in maintaining a higher viability index than if the vehicle component sizing remained fixed.

In the area of media engineering, NREL worked with our HSECoE partners to compile engineering properties for selected sorbents. Initially, the commercially viable sorbents AX-21 (i.e. MSC-30) and MOF-5 were selected as model sorbents to provide the basic information needed to construct accurate hydrogen storage system models. However, the materials will probably not be sufficient to meet the HSECoE goals or the DOE 2015 targets. Thus, NREL led the sorption materials team to develop detailed sorbent selection criteria and to identify potential sorbent materials that may improve the hydrogen storage system designs. As part of this work, additional metal-organic framework, high specific surface area carbon, and weak-chemisorption sorbents were identified. With most of these novel sorbents, most of the engineering properties are unknown and thus need to be measured to feed into the storage system designs. As part of this work, the Engineering Center specifically removed from further consideration MOF-177, but identified four other materials to more fully characterize.

With NREL's unique sorption materials perspective, our initial assessment of the state of sorbent materials for hydrogen storage was refined based on recent modeling results from the Storage System Working Analysis Group (SSWAG) led by Argonne National Laboratory (ANL), and TIAx. The initial conclusion by NREL is that while confirmation of many of the specifics still needs to be made, sorbents should meet the vast majority of DOE targets. The main issues are cost, volumetric and gravimetric capacities, and depending upon the hydrogen storage conditions used, the well to fuel cell efficiency. Based on an initial assessment of the SSWAG using MOF-177, an optimized adiabatic storage system filled with liquid hydrogen would operate at ~250 bar and 80 K with a gravimetric capacity of >5 wt% and a volumetric capacity of ~35 g/L. However, this hydrogen storage system will be almost an order of magnitude higher than DOE present 2015 targets. Based on these results, NREL developed several recommendations for improving the hydrogen storage system including increasing the overall capacity of the system to ~13 Kg, decrease the storage maximum pressure to ~40 bar, and enable larger temperature swings to increase the amount of delivered hydrogen. With these changes, it may be possible to meet DOE 2010 capacity targets, and be within a factor of 2 or DOE 2010 cost targets (Figure 3).
NREL also recommended using improved and less expensive optimized pore size sorbents that more than double the volumetric capacities, and that enable lower operating pressures and operating at lower storage temperatures with larger temperature swings. This would enable sorbents to be used to potentially meet the HSECoE Phase II and perhaps the DOE 2015 targets, including cost and capacities. However, recent emphasis by DOE on overall well to fuel cell hydrogen efficiencies still need to be fully evaluated for this scenario.

Conclusions and Future Direction

- FCV viability sensitivity to onboard hydrogen storage system improvements can be estimated.
- Improved volumetric capacity by way of optimized materials is needed as well as the inclusion of system cost and efficiency for sorbent based system analysis.
- In collaboration with our HSECoE partners, sub-system models will be refined and fully integrated into the vehicle model framework.
- Working with our vehicle manufacturer partners, the Hydrogen Storage Simulation model vehicle viability index estimation methodology will be further reviewed and validated and sensitivity analysis repeated as necessary.
- NREL will investigate data and WTW model integration requirements.
- Systematic compaction measurements to determine maximum attainable sorbent material densities while maintaining the inherent capacities will take place.

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IV.D.1f 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

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.
- 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 Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan (MYPP):

- System Weight and Volume
- Efficiency
- Charging/Discharging Rates
- 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, the system design is to be optimized with emphasis on meeting following DOE 2010 targets.

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>System gravimetric capacity</td>
<td>(kg H₂/kg system)</td>
<td>0.045</td>
<td>0.055</td>
</tr>
<tr>
<td>System volumetric capacity</td>
<td>(kg H₂/L system)</td>
<td>0.028</td>
<td>0.040</td>
</tr>
<tr>
<td>System fill time (for 5 kg H₂)</td>
<td>min</td>
<td>4.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Minimum full flow rate (g/s)/kW</td>
<td></td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Min-max delivery temperature</td>
<td>°C</td>
<td>-40/85</td>
<td>-40/85</td>
</tr>
</tbody>
</table>

Approach

As part of the Hydrogen Storage Engineering Center of Excellence (HSECoE) team, the GM team is building system models for on-board hydrogen storage systems using metal hydrides and adsorbent materials, storage media structuring and enhancement studies, and building a cryo-adsorption vessel for validation of cryo-adsorption models.

**System Modeling:** Over the past year, we have concentrated our efforts on both metal hydride and adsorbent system simulation modeling. The system simulation models have been developed in a MATLAB/Simulink framework using lumped parameter representation for these systems. However, the lumped model development has been guided by estimation of necessary heat transfer parameters based on development of two-dimensional (2-D) models that include thermal transport and hydrogen absorption/adsorption kinetics. The HSECoE coordinating council decided to focus the Center efforts on sodium alanate and AX-21 as the representative metal hydride and adsorbent materials respectively. We have employed the system models for hydrogen discharge during the driving cycles and 2-D thermal transport and kinetic models for refueling the hydrogen storage system.

**Storage Media Structuring and Enhancement:**
To enable fast refueling, it is extremely important to employ storage media with good thermal transport 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. 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, and to improve cycling stability and durability of the metal hydride materials. Similarly for adsorbent materials, forming mechanically stable composite pellets out of a powderous material is very useful. 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 and to improve cycling stability and durability of adsorbent materials.

Accomplishments

1. System Modeling of Metal Hydride Systems

   We have developed system simulation models for two metal hydrides - Ti\textsubscript{1.1}CrMn and NaAlH\textsubscript{4}.

   On-board hydrogen storage systems employing high-pressure metal hydrides like TiCrMn promise advantages including high volumetric capacities and cold-start capability. We have developed a simulation model for this system in a MATLAB/Simulink platform. Transient equations for mass balance and energy balance are used and appropriate kinetic expressions are used for the absorption/desorption reactions for the Ti1.1CrMn metal hydride. During refueling, the bed is cooled by passing a coolant through tubes embedded within the bed while during driving, the bed is heated by pumping the radiator fluid through the same set of tubes. The feasibility of using a high-pressure metal hydride storage system for automotive applications is explored. Drive cycle simulations for a fuel cell vehicle are performed and detailed results are presented. A paper discussing this work has been prepared and accepted for publication in the Int. J. Hydrogen Energy (2010).

   The system simulation model for NaAlH\textsubscript{4} is more complicated and employs additional elements. Because of the high enthalpy of hydrogen absorption and desorption, this system requires burning part of the stored hydrogen to heat up the bed for hydrogen desorption. Thus a catalytic heater that burns hydrogen and heats a warming fluid is a necessary part of the NaAlH\textsubscript{4} system. In addition, a buffer volume storing gaseous hydrogen is needed for periods when the bed is unable to meet the fuel cell demand. This occurs when the bed is cold or contains only hex-phase (Na\textsubscript{3}AlH\textsubscript{6}) which has slow hydrogen desorption kinetics. Figure 1 shows a schematic of the sodium alanate-based hydrogen storage system. System simulation results for the US06 drive cycle are shown in Figure 3.

2. System Modeling of Adsorbent System

   A system model for a cryo-adsorber tank employing the activated carbon AX-21 has also been developed. We have selected the lumped parameter model developed earlier at General Motors to develop system simulation models for the processes in the cryo-adsorber tank. A system simulation schematic for the discharge cycle of a cryo-adsorption system is shown in Figure 2. Hydrogen is discharged from the cryo-adsorber 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 either through an electric heater or through a heated sidestream of hydrogen. System simulations for the US06 drive cycle for the case of a constant heat input are shown in Figure 4.

   A preliminary evaluation of the system performance for both sodium alanate and AX-21 systems in relation to the DOE performance targets is shown in Table 1.

3. Storage Media Structuring and Enhancement

   Sodium alanate pellets were prepared using a die and pressures up to 50,000 psi. Use of a binder is not necessary for formation of the alanate pellets. We have studied the hydrogen uptake, thermal conductivity as well as kinetics of sodium alanate pellets of various sizes. Some of the results on hydrogen uptake by the pellets and loose powder are shown in Figures 5. We are also working with AX-21 activated carbon as the adsorbent material for media structuring studies. Results were presented at the 2010 DOE AMR Meeting in Washington, D.C.
Future Directions

- Explore the sensitivity of system performance for the cryo-adsorbent system to various storage pressures.
- Compare the impact of cold-hydrogen and liquid hydrogen refueling on cryo-adsorbent system performance.
- Conduct simulation studies for both the refueling and discharge cycles a new metal hydride system.
- Optimize binders for pelletizing activated carbon and metal hydride materials with respect to engineering properties of interest for hydrogen storage.

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**FIGURE 5.** Hydrogen Uptake by Sodium Alanate Pellets and Loose Powder
| TABLE 1. Preliminary System Performance for the Sodium Alanate and AX-21 Systems in Relation to the DOE Targets |
|---------------------------------------------------------------|---------------|-----------|-----------|---------------|----------------|----------------|---------------|
|                  | NaAlH<sub>4</sub> | Comments | AX-21 | Comments | 2010 | 2015 | Ultimate |
| Gravimetric Density | (Kg H<sub>2</sub>/Kg system) | 0.0105 | composite vessel, aluminum HEX | 0.0308 | Inner and outer vessels aluminum | 0.045 | 0.055 | 0.075 |
| Volumetric Density | (Kg H<sub>2</sub>/liter) | 0.0119 | HEX significant vol and wt fraction | 0.0126 | MLVI between vessels | 0.028 | 0.040 | 0.070 |
| Cost | System Cost ($/KWh net) | 4 | 2 | TBD |
| Fuel Cost | ($/gge) | 133 | 67 | TBD |
| Durability/Operability | Minimum Operating Temperature (°C) | -30 | -30 | -30 | -30 | -40 | -40 |
| | Maximum Operating Temperature (°C) | 50 | 50 | 50 | 60 | 60 | 60 |
| | Min. Delivery Temperature (°C) | -40 | -40 | -40 | -40 | -40 | -40 |
| | Max Delivery Temperature (°C) | 85 | 85 | 85 | 85 | 85 | 85 |
| | Cycle Life (1/4-full) (N) | NA | NA | 1,000 | 1,500 | 1,500 |
| | Cycle Life (90% confidence) (% mean) | NA | NA | 90 | 99 | 99 |
| | Min. Delivery Pressure (PEMFC) (bar) | 4 | 4 | 4 | 3 | 3 |
| | Min. Delivery Pressure (ICE) (bar) | ? | ? | ? | Could be an issue | 35 | 35 | 35 |
| | Max. Delivery Pressure FC/ICE (bar) | 12 | OK | 12 | OK-FC, issue for ICE | 12/100 | 12/100 | 12/100 |
| | On Board Efficiency (%) | 75% | 41 kJ/mole, 90% eff burner, heat media | 95% | 6 kJ/mole + mCp∆T | 90% | 90% | 90% |
| | Well to Power Plant Efficiency (%) | NA | NA | 90% | 90% | 60% |
| Charge/Discharge Rates | Fill Time (5 Kg H<sub>2</sub>) (min.) | 10.5 min | 4.2 min | Cold H<sub>2</sub> | 4.2 | 3.3 | 2.5 |
| | Minimum Full Flow Rate ((g/s)/KW) | 0.02 | H<sub>2</sub>(g) in buffer and void-space | 0.02 | H<sub>2</sub> in gas-phase | 0.02 | 0.02 | 0.02 |
| | Start Time to Full Flow (20°C) (sec,) | 5 | H<sub>2</sub>(g) in buffer and void-space | < 5 | H<sub>2</sub> in gas-phase | 5 | 5 | 5 |
| | Start Time to Full Flow (-20°C) (sec,) | 15 | H<sub>2</sub>(g) in buffer and void-space | < 15 | H<sub>2</sub> in gas-phase | 15 | 15 | 15 |
| | Transient Response (sec,) | 0.75 | H<sub>2</sub>(g) available, mech/elect issue | 0.75 | H<sub>2</sub>(g) available, mech/elect issue | 0.75 | 0.75 | 0.75 |

HEX = heat exchanger; MLVI = multi-layer vacuum insulation; gge = gasoline gallon equivalent; FC = fuel cell; ICE = internal combustion engine; TBD = to be determined; NA = not applicable
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) Create accurate system models that account for realistic interactions between the fuel system and the vehicle powerplant.
- (Task 2) Develop robust cost projections for various hydrogen storage system configurations.
- (Task 3) Assess and optimize the effective engineering properties of framework-based hydrogen storage media (such as metal-organic frameworks).

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) System Costs
- (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. We will address the following technical targets from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L
- Durability (cycle life): 1,000 cycles
- Durability (min. delivery pressure from storage system): 5 bar
- Efficiency (well-to-powerplant): 60%

Accomplishments

Below is a list of accomplishments by-task:

- Task 1. Vehicle Parameter Modeling
  - Determined MATLAB/Simulink as the common platform for building fuel cell and storage system simulation models.
  - Provided key vehicle characteristics parameters to develop the next level of the hydrogen storage simulation model.
  - Initial model and analysis of fuel cell waste heat for initial assessment of target enthalpy.
  - Identified universal modeling framework and interaction assumptions between vehicle, powerplant, and hydrogen storage system models.
  - Evaluated and constructed baseline fuel cell model to support the interaction with the vehicle and hydrogen storage system model.

- Task 2. Manufacturing Cost Modeling
  - Established initial phase of the cost analysis through the pursuit of high level equivalent system studies for the development of a hydrogen storage component cost matrix.
- Supported the manufacturing and cost analysis technology team in the evaluation of the initial cost assessments for the hydrogen storage systems.
- Developed the approach using the cost matrix to decompose the key cost drivers for establishing cost sensitivity and trade-offs.

• Task 3. Assessment of Framework-Based Hydrogen Storage Media
- Completed property screening (e.g., hydrogen capacity, surface area, and pore volume) of five prominent framework powders: MOF-5, MOF-177, IRMOF-8, ZIF-8, HKUST-1.
- Collected and compiled all requisite materials engineering data for Basolite Z-100H, the semi-commercial version of MOF-5 synthesized by BASF. These include: Dubinin-Astakov (D-A) isotherm parameters, thermal properties (e.g., thermal conductivity, heat capacity, etc.), and bulk properties (e.g., bulk density, specific surface area, etc.).
- Designed two preliminary sub-scale hydrogen storage modules to be used for framework material assessment and validation of optimized framework concepts.
- Developed an understanding of, and developed a new measurement protocol which minimizes temperature variation during hydrogen storage experiments at cryogenic temperatures. This allows for more reliable hydrogen capacity measurements and, as a consequence, improved parameterization of adsorption models from experimental data.

Introduction

Widespread adoption of hydrogen as a vehicular fuel depends critically on the development of low-cost, on-board hydrogen storage technologies capable of achieving high energy densities and fast kinetics for hydrogen uptake and release. As present-day technologies -- which rely on physical storage methods such as pressurization or liquefaction -- are unlikely to attain established DOE targets, interest in materials-based approaches for storing hydrogen have garnered increasing attention. To hasten development of these ‘hydride’ materials, the DOE has established three Centers of Excellence for materials-based hydrogen storage research as part of a “Grand Challenge” to the scientific community. While the Centers have made substantial progress in developing new storage materials, significant challenges associated with the engineering of the storage system around a candidate storage material remain largely unresolved.

Approach

As a partner in the Hydrogen Storage Engineering Center of Excellence (HSECoE), Ford is conducting a multi-faceted research project that addresses three of the key engineering challenges associated with the development of materials-based hydrogen storage systems.

First (Task 1), drawing on our extensive expertise in the engineering of fuel cell (FC) and H₂-internal combustion engine (ICE) vehicles, we are evaluating and developing 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 (Task 2), we are leveraging the unique capabilities of the “Ford/MIT 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.

Third (Task 3), we are evaluating and optimizing the “effective engineering properties” of an important class of sorbent materials (metal organic frameworks [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 are being examined (ranging from powders to pelletization to extrusion) in an effort to simultaneously maximize packing density, heat and mass transfer, and hydrogen uptake 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.

Results

Below is a description of our technical results for each task and how these results relate to achieving the DOE targets.

Task 1. Vehicle Parameter Modeling

The Integrated Power Plant/Storage System Modeling Technology Area modeling approach focused on a MATLAB/Simulink platform with a common structure to assist in the exchangeability and interaction
of models within the Center. A modeling interface matrix was further refined and utilized in constructing the top-level HSECoE Simulink model structure (Figure 1).

In support of the HSECoE modeling structure, a fuel cell model was developed to provide the linkage between the vehicle model and hydrogen storage model. The fuel cell model as indicated by the interface matrix for the translation of the vehicle power demand to the hydrogen storage flow requirement. It is also needed to characterize the waste heat available for the hydrogen storage system to avoid the need for external heating devices. The original FC model in the Hydrogen Storage SIMulator (HSSIM) vehicle model was based on a simple polarization curve from Kartha and Grimes in *Fuel Cells: Energy Conversion For The Next Century*, Physics Today (1994). The desire of the team was to refine the FC model to allow for ambient temperature effects and potentially pressure effects. Therefore, a search was conducted to assess available fuel cell models to be utilized in the Simulink framework. The FC performance equations developed by Stefanopoulou (et al. 2004) in *Control-oriented modeling and analysis for automotive fuel cell systems* had the desired thermal term and appeared appropriate for the initial phase of the model.

**Task 2. Manufacturing Cost Modeling**

The hydrogen storage manufacturing cost analysis is included in the Performance Analysis workstream. In particular, the Manufacturing and Cost Analysis Technology Team is being lead by M. Weimar from the Pacific Northwest National Laboratory. A benchmark study was conducted to assess hydrogen storage cost analysis approaches and progress a tool for decomposing the hydrogen storage system into critical elements. The cost modeling effort has evaluated the assumptions of the HSSIM vehicle modeling and approaches to integrate the cost analysis with the performance modeling, which result in consumer preferences based on both performance and cost. The integration assessment allows the HSECoE team to trade-off vehicle architectures (i.e. hybridization levels) and parameters to optimize the hydrogen storage characteristics.

The initial phase of the cost analysis was established through the pursuit of high-level equivalent system studies that support the development of a hydrogen storage component cost matrix. The draft and the approach of the component cost matrix were presented to the HSECoE partners that reinforced the need for the matrix to serve as a foundation for the system architects. The matrix would include the functions to scale the appropriate components. The team developed the cost strategy to provide the matrix of components and then to decompose the key cost drivers to establish cost sensitivity and trade-offs for the system architects.

**Task 3. Assessment of Framework-Based Hydrogen Storage Media**

As a first step we assessed several key properties a series of benchmark framework materials. This was conducted via a brief property screening study, wherein the hydrogen capacity, surface area, and pore volume data for the following powders were measured in our laboratory using a cryogenic Sievert’s apparatus. The compounds studied included: Basolite Z100H (MOF-5), Basolite Z377 (MOF-177), Basolite Z200 (IRMOF-8), Basolite Z1200 (ZIF-8), Basolite C300 (HKUST-1).

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**FIGURE 1.** HSECoE High-Level Universal Simulink Model Structure and Interfaces
The data from these measurements are summarized in Figure 2.

The objective for this phase of our work is to gather existing literature data, and, as appropriate, collect new physical, thermal, and isotherm data to facilitate creation of a materials property “data set.” The contents of the data set are important as they serve as inputs for the HSECoE’s modeling activities. The three primary categories of the data set for an adsorbent material include: Dubinin-Astakov isotherm parameters, thermal properties (e.g., thermal conductivity, heat capacity, etc.), and bulk properties (e.g., bulk density, specific surface area, particle diameter, etc.). Subsequently, MOF-5 was selected by the Center as an initial framework material of interest and thus a complete set of its fundamental and engineering material properties is required. Our experiments were conducted using the semi-commercial form of MOF-5 (Basolite Z100H), synthesized by BASF.

Generation of the Dubinin-Astakov parameters for Basolite Z-100H requires collection of isotherms at several different temperatures (e.g., between -196°C and room temperature). Modification of Ford’s existing sorption instrument (Sievert’s apparatus) to include variable-temperature cryogenic capability was necessary. Upon instrument validation, isotherm data for Basolite Z-100H was collected at five different temperatures, -196°, -190°, -178°, -167°, and -151°C, toward determination of the desired Dubinin-Astakov parameters which fully describe an isotherm and can be used for material modeling. These data are shown in Figure 3 as the filled data points.

A modified version of the Dubinin-Astakov equation (Equation 1) [1], was subsequently used as the model for a non-linear regression analysis on the corrected empirical data.

$$n_{ex} = n_{max} \exp\left[\frac{RT}{\alpha + \beta T}\right] \frac{\rho g}{P} - \rho g V_a$$ \hspace{1cm} (1)

In particular, the empirical data from all five isotherms was simultaneously fit to the above model using five fitted parameters from Equation 1: $n_{max}$ (max. uptake), $\alpha$ (enthalpic factor), $\beta$ (entropic factor), $\rho_g$ (gas phase density), and $V_a$ (adsorbed volume). The values for these parameters, which result in a minimization of the error between model and observed data, are given in Table 1.

Based on these values, the standard error between model and experimental data is 0.46 mol/kg or 0.094 wt%. The residual squared value is 0.998. Using these parameters enables one to determine excess uptake at a variety of temperatures and pressures of interest. Additionally, absolute (or total) uptake and heat...
of adsorption behavior can also be calculated. For example, based on the Basolite Z-100H parameters in Table 1 an absolute uptake of approximately 10 wt% is projected at 70 bar and -196°C. This finalized thermal, bulk property, and Dubinin-Astakov data for powder Basolite Z100H were submitted and distributed to the HSECoE. This established process of compiling and generating all relevant data (i.e. “data set”) for a given framework will be extended to future frameworks of interest as well as extension to compacted/processed forms of a given framework of interest.

Lastly, we have initiated and completed the design work for two preliminary hydrogen storage modules which are necessary for anticipated Phase II framework materials testing. The requirements and specifications for both designs were formulated based on a variety of criteria including von Mises yield stresses at the operating temperatures and pressures, material compatibilities, heat transfer, safety, and data acquisition.

Conclusions and Future Directions

- Task 1. Vehicle Parameter Modeling
  - Complete the integration of the FC stack waste heat model and enhance the FC polarization model at sub-zero temperatures with validation of empirical data.
  - Determine the appropriate integration of static parameters (i.e. cost, weight, volume) within the dynamic performance modeling framework.
  - Support the development of the vehicle and storage system modeling, including the implementation of the waste heat interaction, refinement of the weighting coefficients for the viability index, and confirming the vehicle characteristics parameters for current and projected future levels.

- Task 2. Manufacturing Cost Modeling
  - Support the completion of the hydrogen storage system component cost matrix for the system architects to use as a common reference.
  - Evaluate the key components in order to establish their cost functions in relation to the performance model variables.
  - Decompose the key components into their direct and indirect cost elements for the purpose of assessing cost drivers and opportunities.

- Task 3. Framework-Based Hydrogen Storage Media Properties
  - Continue to monitor and experimentally screen the properties of existing and newly discovered powder framework materials which show promise for hydrogen storage.
  - Pursue detailed densification studies of Basolite Z100H (and other framework materials as appropriate) which includes investigation of the impact of the following processing parameters on the resulting hydrogen storage properties: binder (and/or lubricant), compaction conditions, pellet and particle size, ancillary additives.
  - Continue development of lab-scale testing module including the assembly of the test-bench and data acquisition system.

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References

IV.D.1h SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence

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Start Date:  February 1, 2009
Projected End Date: July 31, 2014

Objectives

SRNL and UQTR will:

- Compile property data for sodium aluminum hydride (NaAlH₄), a metal hydride, and 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 NaAlH₄ and AX-21 based storage systems.
  - Use the models to design optimized storage systems based on NaAlH₄, other metal hydrides, AX-21, and other potential absorbent materials.
- 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 Fuel Cell 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 states 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 the 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

- Metal hydride modeling accomplishments:
  - Developed and validated baseline models for metal hydride storage systems.
  - Incorporated improved models into optimization routines.
  - Identified principal issues for design of metal hydride-based storage systems.
  - Began investigating novel concepts/system designs.
- Adsorbent modeling accomplishments:
  - Developed and validated baseline models.
Developed an adsorbent unit cell model in Comsol® for optimization.
- Began investigating novel concepts/system designs.

• Acceptability envelope accomplishments:
  - Model developed for metal hydrides.

• Material operating requirements: metal hydrides:
  - Selected NaAlH₄ as initial baseline hydride candidate material for transport phenomena and system modeling development,
  - Databases completed for: NaAlH₄ (with and without catalysts), 2:1 LiNH₂:MgH₂, MgH₂ (without catalysts), TiCrMn, Mg₂Ni.

• System architect analyses: metal hydride:
  - Completed system architect analysis of NaAlH₄ vs. DOE 2010 technical hydrogen storage targets.

Introduction

SRNL and UQTR are involved in several critical aspects of the HSECoE. SRNL is focused primarily modeling, validating, and optimizing hydrogen storage designs for metal hydrides, adsorbents, and, to a lesser extent, chemical hydrides, and system architect analyses of metal hydride systems. SRNL is applying 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.

UQTR is developing the governing equations for an adsorbent system that be easily and efficiently implemented by SRNL into a model to accurately predict the adsorption characteristics over a range of temperatures. UQTR is extending its current equations for hydrogen adsorption on activated carbons to any adsorbent used in the storage system design.

Relevance

The ultimate goals of the HSECoE are the design and testing of prototype hydrogen storage vessels, the interpretation of test data, and the implementation for full-scale vessels. Within the HSECoE, the Transport Phenomena Technology area is responsible for the development and application of analyses for storage systems that are necessary to identify and design prototype media and vessel configurations having the best performance relative to the DOE technical targets. Storage vessel models developed by this technology area will be essential to interpret data obtained from prototype testing and to relate it to full-scale systems.

Approach

In Phase I, SRNL and UQTR will:

• Evaluate, interpret, and assimilate data for media and vessel components.
• Develop and apply an “Acceptability Envelope” based on DOE targets.
• Develop, validate and test general models for scoping and detailed evaluation of storage system designs.
• Obtain material operating requirements for metal hydride and AX-21 materials.
• Perform system architect analysis on candidate metal hydride systems for Phase I Go/No-Go decision.

Results

SRNL and UQTR to date have met and or exceeded their Phase I objectives for all of their major technical areas for the HSECoE. These major technical areas include: transport phenomena, material operating requirements and system architecture. Transport phenomena results are shown below and are divided into metal hydride and adsorbent modeling as well as acceptability envelope development and applications. Results for activities under material operating requirements and system architecture are shown for metal hydrides systems.

Transport Phenomena

Metal Hydride modeling accomplishments:

• Developed and validated baseline models for metal hydride storage systems
  - 0-dimensional kinetics models in MathCad® (Figure 1)
  - 1-, 2-, and 3-dimensional models in Comsol®
    - Consolidated all models into Comsol®
• Incorporated improved models into optimization routines
  - Used Nelder-Mead (Downhill Simplex) optimization scheme
    - With given constraints, optimal designs require very small spacing of heat transfer surfaces
Methods can be easily extended to new metal hydride systems
- New hydrides, such as 2:1 and 1:1 LiNH$_2$-MgH$_2$
- New catalysts for existing hydrides
- New tank designs
- Adsorbent systems

- Identified principal issues for design of metal hydride-based storage systems
  - Variations in powder composition and catalyst materials
  - Large impact on the charging and discharging kinetics
  - Large impact on capacity
  - Substantial increase (x50) in NaAlH$_4$ kinetics required to meet 2010 DOE targets for refueling time
    - Heat removal becomes an issue for $\Delta H$ associated with most metal hydrides
  - Short refueling times (e.g., 4.2 min vs. 15 min) for the current NaAlH$_4$ kinetics impact
    - System gravimetric capacities
    - System volumetric capacities

- Began investigating novel concepts/system designs (Figure 2)

Adorsbent modeling accomplishments:
- Model development and validation
  - Numerical models within Comsol®
  - Model validation against experimental data for MaxSorb® (Figure 3)
- Developed baseline scoping models for an adsorbent unit cell in Comsol®

**FIGURE 1.** Fill times calculated from the 0-dimensional Mathcad Kinetics Model for NaAlH$_4$ based on the UTRC Prototype 2 Kinetics.

**FIGURE 2.** Novel concepts for tank designs, such as (a) longitudinal fins or (b) a metallic honeycomb structure.
Began investigating novel concepts/system designs

Acceptability envelope accomplishments (Figure 4):
- Model developed for metal hydrides
  - Based on energy balance
  - Constraints are from DOE technical targets

Model should be used in conjunction with media kinetics
- Can be used to identify range of media and component parameters required to meet operational targets

Application
- Has been applied to NaAlH$_4$ and other metal hydrides

Material Operating Requirements: Metal Hydrides
- Selected NaAlH$_4$ material as initial baseline hydride candidate material for transport phenomena and system modeling development
- Databases completed for:
  - NaAlH$_4$ (with and without catalysts)
  - 2:1 LiNH$_2$:MgH$_2$
  - MgH$_2$ (without catalysts)
  - TiCrMn
  - Mg$_2$Ni

System Architect Analyses: Metal Hydride
- Completed system architect analysis of NaAlH$_4$ vs. DOE 2010 technical hydrogen storage targets
- Completed preliminary analysis on other potential metal hydride candidates (Mg, Mg$_2$Ni, 2:1 LiNH$_2$:MgH$_2$, and 1:1 LiNH$_2$:MgH$_2$)

Explanation of terms:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>Distance between heat transfer surfaces</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Temperature range for acceptable chemical kinetics (to give charge/discharge rate of DmH$_2$/Dt)</td>
</tr>
<tr>
<td>$M_{\text{Hd, eff}}$</td>
<td>Mass of hydride (in reference form) required to load target amount of hydrogen in specified time (relates to kinetics)</td>
</tr>
<tr>
<td>$\Delta H_{\text{overall}}$</td>
<td>Overall heat of reaction</td>
</tr>
<tr>
<td>$\rho_{\text{hydride}}$</td>
<td>Hydride density (in reference form)</td>
</tr>
<tr>
<td>$k$</td>
<td>Bed thermal conductivity</td>
</tr>
<tr>
<td>$\Delta m_{\text{Hd}}/\Delta t$</td>
<td>Required rate of charging/discharging from DOE Technical Targets</td>
</tr>
</tbody>
</table>

FIGURE 3. Adsorbent model validation showing the total hydrogen concentration (mol/m$^3$) during loading for a MaxSorb® bed.

FIGURE 4. Basic Equation and Concept for the Acceptability Envelope
Conclusions and Future Directions

Proposed future work for metal hydrides:

- All future work will be dependent upon the results from the acceptability envelope
- More detailed models, as needed
  - Consider mass transfer limitations
  - Include hydrogen stored in gas phase
  - Include cooling at tank wall/surface
  - Identify minimum coolant tube thickness
    - Dependent on operating pressure and tube internal diameter
  - Use convection heat transfer coefficient in coolant tubes dependent on internal diameter and coolant flow rate
  - Include pressure vessel mass
    - Important for hydride (high pressure) storage
  - Incorporate limits based on manufacturability constraints
- Model additional metal hydrides suggested by System Architect and Acceptability Envelope calculations
- Evaluate novel concepts and other unique configurations
  - Longitudinal fins
  - Metal honeycomb structures (UQTR)
    - Cell size
    - Addition of cooling channels
  - Hybrid systems – Combination of high pressure tanks and metal hydrides
- For likely viable systems, convert models to form suitable for Simulink system models

Proposed future work for adsorbents:

- Conduct validation experiments that reduce parasitic heat transfer
  - Use N₂ at temperatures closer to ambient
- Compare performance of MOF-5® and MaxSorb®
- Use baseline models in two and three dimensions for design and sensitivity studies
  - Vessel design
  - Structured media
  - Novel concepts

Proposed future work for the acceptability envelope:

- Include balance of plant contributions
  - Mass and volume of storage vessels, fins, tubes, and other structures and fittings
- Complete the application to metal hydrides
  - Include coupled parameter ranges
  - Evaluate candidate metal hydrides (2:1 and 1:1 LiNH₂-MgH₂)
- Develop and apply model for adsorbents

Proposed future work material operating requirements:

- Complete databases for 1:1 LiNH₂-MgH₂ material with and without catalysts
- Determine needed engineering properties for all up selected materials

Proposed future work metal hydride system architect analysis:

- Extend system architect analysis from sodium alanate to other metal hydride systems
- Complete system architect analysis on metal hydride candidate systems for Phase I Go/No-Go Decision

FY 2010 Publications/Presentations

IV.D.1i Key Technologies, Thermal Management, and Prototype Testing for Advanced Solid-State Hydrogen Storage Systems

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 Hydrogen Storage section of the Fuel Cell 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 g H$_2$/kg$_{sys}$, 40 g H$_2$/L$_{sys}$

(C) Efficiency: 90% on-board/60% off-board

(D) Durability/Operability: <1% degradation @ 1,500 cycles, etc.

(G) Materials of Construction

(H) Balance-of-Plant 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

The efforts at JPL during the previous year have centered on a technology development role in the Enabling Technologies area of the Center, specifically the identification, analysis, and characterization of thermal insulating materials for hydrogen storage systems. This effort will extend into Fiscal Year (FY) 2011, featuring the testing of thermal materials in order to inform the modeling/validation effort ongoing within the Center.

JPL has also taken on the role of System Architect for Adsorbent System technology development. In this role, JPL provides oversight and coordination of the various technology areas within the Center that have responsibility for developing credible paths toward satisfying the DOE hydrogen storage targets (2010/2015/ultimate). JPL will also have direct responsibility for a notional “system engineering” role, providing guidance and oversight for conceptual system design.

Specific Accomplishments:

- Initial “insulative materials” database has been developed and deployed within the Center; database contains thermal performance parameters, mass, volume, and cost where possible. Candidate materials continue to be added as they are identified, or as potential vendors/technologies are found.
- Preliminary plans for a low-k material thermal characterization facility are complete; this facility will be used to fully characterize candidate insulative materials across a large temperature range; the potential also exists for this facility to be...
used to analyze the thermal characteristics of bulk hydrogen storage materials, especially cryosorbents. The facility will be hosted in JPL’s Hydrogen Storage Engineering Laboratory.

- **JPL hosted the Center’s Face-to-Face Meeting 4 in Pasadena, CA (March, 2010).** This meeting solidified the System Architect roles and reviewed the first calendar year of Center activity (start date February, 2009). Crucial teaming activities were accomplished between JPL and other Center partners; first high-level system designs shown and preliminary performance numbers reviewed.

Introduction

Activities at 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 Center; the present effort at JPL is divided into several tasks:

- **Advanced Technology Development.** JPL has a lead role in the Center as a technology area lead 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 Center’s duration, and involves collaborations with a majority of the Center’s partners and a responsibility at the center coordinating council level.

- **System Architect/System Engineer.** JPL provides technical guidance and engineering oversight to the Adsorbent System design team in its Center role as System Architect/System Engineer. Additionally, and in coordination with the Center’s conceptual design effort, JPL will provide assistance with overall system design, component selection, and design review for the adsorbent system, especially as it applies to cryogenic system design and operation.

- **Material/Media Evaluation.** JPL is contributing to the evaluation of the engineering properties of candidate hydrogen storage materials. A subcontract with Caltech allows assistance with evaluation of hydrogen sorption materials (cryosorbents).

- **Thermal Modeling & Validation.** JPL will provide modeling support to the Center via parametric and other types of analysis for hydrogen storage systems. This effort includes thermal/thermodynamic/performance modeling of cryogenic storage vessels and associated hardware, both specific to and independent of storage material type. This task is integrated into the overall Center modeling effort. JPL will collaborate with partners Savannah River National Laboratory (SRNL) and United Technologies Research Center (UTRC). This task may involve validation of model results via bench-top testing of novel designs and configurations.

- **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 Center 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 Center, and will be led by LANL.

Via the task breakdown summarized here, JPL will mix management and direct engineering in a three-phase project of roughly 1.5 years per phase. Much of this effort is being accomplished in an “emergent” manner, allowing for changes to scope, approach, and technology basis. The Center’s technology area lead structure is designed to account for this type of operation.

Approach

Within the HSECoE, JPL’s participation covers a wide variety of tasks and activities, spanning technology management and active research and development. In the latter case, JPL relies on in-house expertise in the areas of thermal engineering, cryogenic system design, systems engineering, and hydrogen storage system testing and evaluation. The overall approach involves well-organized and managed communication pathways and closed loops among the other Center partners collaborating with JPL as well as with the Center lead at SRNL. This management approach is built around the technology area concept, wherein key Center partners
IV.D Hydrogen Storage / Hydrogen Storage Engineering CoE

Reiter – Jet Propulsion Laboratory

including JPL – are responsible for sub-management and direction of agile technical teams, each charged with a particular task in the engineering scope. Within this structure, JPL 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.

The Center has also developed the System Architect model for managing the development and configuration of individual storage system designs; as such, there are three Center partners responsible for the guidance and oversight of the design teams assigned to the metal hydride design, the cryo-adsorbent design, and the chemical hydride design, respectively. JPL is the Center partner responsible for the adsorbent system overall design and architecture. The System Architect relationship to the Center is as a matrix organization, utilizing the analytical products of the technology areas in order to reach a system design that credibly satisfies the appropriate DOE Hydrogen Storage targets. This relationship is illustrated schematically in Figure 1.

HSECoE is a widespread effort technically, geographically, and with regard to expertise. JPL maintains a central cognizance within the Center by virtue of its status as an System Architect and technology area lead, working closely with Center partners SRNL, LANL, Pacific Northwest National Laboratory, and UTRC, as well as with Oregon State University, General Motors, Ford, and, via subcontract, Caltech.

Results

Key results of the work during the reporting period are summarized as follows:

- Insulative materials literature/vendor search has resulted in the categorization of potential materials by temperature range (elevated, ambient, and cryogenic) and material type (rigid, blanket, loose-fill). Such materials are considered “physical” or “bulk” insulation, typified by low thermal conductivity and (occasionally) low density. Considering as an example a design for storing a cryogenic (77 K) material, performance of these insulators would be compared to the “standard” approach of using multi-layer vacuum insulation, with regard to cost, mass, and volume. A first-step algorithm for measuring performance in this way has been developed.
  - Key material parameters for solid-aerogel insulation has been obtained internally from JPL where this material is manufactured. These parameters have been included in initial scoping models of tank/storage vessel thermal performance, but data are required for radiative transmissivity and temperature-dependent thermal conductivity data. The means to acquire this information for aerogel and other insulative materials is being developed at JPL in the form of a novel test facility.

Conclusions and Future Directions

The overall HSECoE effort will be continuing through early 2014. At the time of this writing, Center efforts are focused on the near-term goal of demonstrating the performance of several conceptual systems against the 2010 DOE Storage targets; a Center-wide milestone for this achievement is set for the end of the second quarter of FY 2011. With this in mind, there are several broad areas in which JPL plans specific accomplishments:

- Additional physical/bulk insulative materials will be added into the Insulative Materials Database, which continues to be available internally to the Center. It is planned that the database, along with analytical tools, results, and general metrics, will be made publicly available at some point in the future.

- The low-k material thermal characterization facility will be brought on-line and used to validate literature values for several candidate materials in the database. In addition, the facility will allow JPL to acquire temperature-dependent data for these materials, which in many cases is not otherwise available elsewhere. The facility will also be used to directly validate the thermal material properties of storage materials; superactivated carbon and certain candidate metal-organic frameworks are good examples of such materials. Figure 2 shows the current status of the hardware being assembled for this effort.

- Initial scoping models for determining thermal performance of the storage vessel will be integrated into the Center model framework. The models will address issues for cryogenic vessels such as low-temperature dormancy, parasitic heat loads, and passive thermal design approaches. These models will initially be designed for the cryo-adsorbent

[Figure 1: Graphic representation of the System Architect concept, showing the flow-down and cross-reporting paths as well as hierarchical responsibilities within the Center. This concept maintains the goal of aligning notional system design concepts with the overall storage targets as set by DOE.]
system, but will be extensible for the metal hydride and chemical hydride systems as well. Parametric data from the insulative materials search/analysis will feed directly into this effort.

FIGURE 2. In-process photo of the hardware being assembled for the low-k material thermal characterization facility being developed for testing/validation of both insulative materials and low-temperature storage materials. The facility will be a JPL/Center asset capable, for example, of obtaining temperature-dependent data from low-conductivity materials.

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Contract Number: DE-FC36-08GO19005
Project Start Date: February 1, 2009
Project End Date: January 31, 2014

Objectives

Use microchannel techniques 1) to demonstrate reduction in storage system size and weight, 2) for improvement of charge and discharge rates, and 3) to reduce size and weight and increase performance of thermal balance of plant components.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(E) Charging/Discharging Rates
(H) Balance of Plant (BOP) Components

Technical Targets

This project focuses on optimization of the performance characteristics and reduction in the size, weight, and cost of metal hydride and adsorption hydrogen storage systems. We will achieve these goals through careful design of thermal integration to efficiently harness “waste heat”, and by applying microscale techniques to enhance heat and mass transfer. More efficient heat transfer through microscale combustors, heat exchangers and recuperators allows for substantial reductions in the size and weight of balance-of-plant components. Microchannel-based hydrogen storage systems offer enhanced heat and mass transfer, possibly allowing more rapid charging and startup, quick response to changing driving conditions. In addition, the excellent heat transfer control achievable with microscale components allows for efficient removal of thermal energy generated during charging. These experimental and simulation studies are expected to guide the design of high-efficiency metal hydride and adsorption-based hydrogen storage systems toward meeting the following DOE 2010/2015 targets:

- System gravimetric capacity: 1.5/1.8 kWh/kg
- System volumetric capacity: 0.9/1.3 kWh/L
- Charging/discharging rates: 1.2/1.5 kg/min, 5–15 sec start time to full flow

Accomplishments

- Completed preliminary design of ~1 mm-thick microchannel-based tank insert plate for liquid-cooling and hydrogen distribution. A unit cell in the model in-tank system consists of two of these liquid-cooled distribution plates, separated by adsorbent or metal hydride. (Barriers A and E)
- Completed design and fabrication of a test apparatus that will be used to test the tank insert unit cell. (Barriers A and E)
- Completed simulation tool and a preliminary design of a microchannel combustor/heat exchanger to heat oil used to discharge hydrogen from storage. High-efficiency (>90%) microscale device integrates a flame-proof combustor, oil heat exchanger and thermal recuperator. (Barrier H)
- Completed simulation tools to support the experimental investigations of the tank insert and microchannel combustor/heat exchanger. (Barriers A, E and H)

Introduction

Hydrogen storage involves coupled heat and mass transfer processes that significantly impact the size,
weight, cost, and performance of system components. Micro-technology devices that contain channels of 10 to 500 microns characteristic length offer substantial heat and mass transfer enhancements, by greatly increasing the surface to volume ratio, and reducing the distance that heat or molecules must traverse. These enhancements often result in a reduction in the size of energy and chemical systems by a factor of 5 to 10 over the conventional designs, while attaining substantially higher heat and mass transfer efficiency. In cooperation with the OSU Microproducts Breakthrough Institute and groups at Pacific Northwest National Laboratory, Savannah River National Laboratory (SRNL) and Los Alamos National Laboratory, we are developing: 1) advanced tank inserts for enhanced and mass transfer during charge and discharge of metal hydride and adsorbent hydrogen storage systems; and 2) microchannel-based thermal balance of plant components such as combustors, heat exchangers and chemical reactors.

Approach

Our technical approach to meet the Phase I goals involves: 1) OSU will focus on simulation and experimental investigations to identify and prioritize opportunities for applying microscale heat and mass transfer enhancement techniques; 2) Working with other team members, OSU will identify the highest value applications and conduct experimental investigations and modeling to collect data necessary to support the Go/No-Go decision to proceed to Phase 2.

For each high priority component we plan to use microchannel technology to reduce the relevant barriers to heat and mass transfer. Our approach involves: 1) the optimization of the performance of a single unit cell (i.e. an individual microchannel) and then “number up” using appropriate simulation tools and which are validated by experimental investigations; and 2) developing microlamination methods as a path to “numbering up” by low-cost high-volume manufacturing.

Results

Relative to our Phase 1 technical targets, we identified two high value applications of microchannel technology. The first application is the development of a microchannel tank insert for cooling during charging, heating during discharging and hydrogen distribution. The tank insert can be used with either metal hydride or adsorbing material. The second application is the development of a microchannel combustor/heat exchanger that can be used for on-board oil heating during discharge of a metal hydride hydrogen storage system. Results relative to these two applications are summarized below.

Microchannel-Based Tank Insert - A tank insert that integrates storage media, microchannel heat exchangers and microchannel hydrogen distribution plates may provide improved charging of the storage system, rapid startup, and quicker response to changing driving conditions. Progress to date on the development of the microchannel-based tank insert includes:

- A test apparatus for a tank insert unit cell that includes the storage media, microchannel cooling and microchannel hydrogen distribution has been designed, and is being assembled. This system, expected to be operational in August 2010, will support experiments to determine the kinetics of adsorption and desorption of hydrogen on metal hydrides and carbon-based adsorbents, and also serve as a testbed for developing an optimized hydrogen storage unit cell.
- A microchannel unit cell for metal hydride and adsorbing materials has been designed and the integrated microchannel cooling and hydrogen distribution plates have been fabricated (Figure 1).
- Computational simulation of the unit cell is being performed in parallel with the physical experiments. A multi-phase flow simulation in FLUENT, incorporating full Navier-Stokes equations and sodium alanate reaction kinetics (provided by

![FIGURE 1. Schematic design of ~1 mm-thick high-efficiency microchannel-based storage tank insert, with integrated liquid-cooled heat exchanger (left), and H₂ distribution (right) systems.](image-url)
SRNL), was used to model hydrogen flow in the porous storage medium. The simulation was validated by comparison with published data [1]. The results indicate that particle size is a major factor, and that multi-phase flow components must be included in simulations dealing with small (<2 μm) particles. This and related computational models are also being used to simulate adsorption/desorption processes on single-particle and whole-bed scales, and further validation and optimization studies for the test bed integrated microscale unit cell are currently under way.

**Integrated Microscale Combustor/Heat Exchanger (μCHX)** - The microscale combustor/heat exchanger (μCHX, Figure 2) will be used to safely and efficiently produce heated oil, which is used to discharge hydrogen from the storage bed. Combining the combustion and heat exchanger systems, and the use of microchannels for enhanced heat and mass transfer can drastically reduce the size and weight required for this function, while simultaneously increasing efficiency. A substantial safety benefit of a microscale combustor is that flames cannot be sustained in the sub-millimeter microchannels. Progress to date on the development of the μCHX includes:

- A simulation of the μCHX has been completed, including a detailed model of the kinetics of the combustion reactions. The code has been used to predict the performance of the device and current results suggest the μCHX will be significantly smaller, lighter and more efficient than current compact combustion systems.
- A design of the test apparatus and a μCHX unit cell test article has been completed. Currently, we are assembling the test apparatus and having the μCHX unit cell test article fabricated.

**Conclusions and Future Directions**

- A FLUENT-based two-dimensional computational simulation of hydrogen desorption rates has been completed and used to model the desorption process. A 1 m long, 15 cm radius tank containing 75 kg of sodium alanate bed was modeled, using literature data and accounting for thermal effects on physical properties. The results suggest that two sources of thermal energy one located at each end of the tank, produces acceptable desorption (Figure 3).
- Complete the assembly of the tank insert unit cell test apparatus, assembly of unit cell test articles for metal hydride and adsorbing materials, and validate simulation models and unit cell performance.
- Develop a conceptual design and identify high volume, low cost fabrication approaches for the tank inset.
- Complete the assembly of the μCHX test apparatus and μCHX unit cell test article, and validate simulation model and unit cell performance.
- Provide support for other center partners on applications where microchannel technology can provide significant improvement over existing technology.

**References**

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 adsorbants.
- To evaluate design, materials, or manufacturing process improvements necessary for containing metal hydrides, chemical hydrides, or adsorbants.
- 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:

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric capacity</td>
<td>&gt;4.5%</td>
<td>&gt;6%</td>
</tr>
<tr>
<td>Volumetric capacity</td>
<td>&gt;0.045 kg H₂/L</td>
<td>&gt;0.081 kg H₂/L</td>
</tr>
<tr>
<td>Storage system cost</td>
<td>To be determined</td>
<td>To be determined</td>
</tr>
</tbody>
</table>

Introduction

Lincoln Composites is conducting research to meet DOE 2010 and 2015 Hydrogen Storage Goals for a storage system by identifying appropriate materials and design approaches for the composite container. At the same time, continue to maintain durability, operability and safety characteristics that already meet DOE guidelines for 2010 and 2015. There is a continuation of work with Hydrogen Storage Engineering Center of Excellence partners to identify pressure vessel characteristics and opportunities for performance improvement. Lincoln Composites is working to develop high-pressure vessels as are required to enable hybrid tank approaches to meet weight and volume goals and to allow metal hydrides with slow charging kinetics to meet charging goals.

Approach

Lincoln Composites is establishing and documenting a baseline design as a means to compare and 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 which will then be evaluated to meet Go/No-Go requirements for moving forward.

The following areas will be researched and documented:

- Evaluation of alternate fiber reinforcement
- Evaluation of boss materials and designs
- Evaluation of resin toughening agents
- Evaluation of alternate liner materials
- Evaluation of damage vs. impact
- Evaluation of stress rupture characteristics
- Evaluation of in situ non-destructive examination (NDE) methods to detect damage
Results

Lincoln Composites has completed the documentation of a baseline design as a means to compare and evaluate potential improvements in design, materials and process to achieve cylinder performance improvements for weight, volume and cost. Baseline characteristics are shown in Table 1.

Lincoln Composites is in the process of conducting testing on alternate fibers relative to fiber strength and impact tolerance. Baseline fiber was selected as Toray T700. Five alternative fibers were selected as part of the study. Vessels were constructed with each of the five fibers using the same parameters on each: mandrel, wind patterns, tooling and processing. Tow count was adjusted, per fiber, to maintain consistent band cross-sectional area. One vessel constructed of each fiber was hydrostatically burst. Stress in the fiber at failure is calculated based on fiber certifications and normalized to Toray T700. Further testing of alternative fibers is being completed. Vessels, that were manufactured along with the burst vessels, are in the process of being impacted (drop testing), cycled and then burst tested. This testing is in process and following the completion of this testing, strength versus cost will be evaluated.

Lincoln Composites is looking into alternative boss materials as part of this project. Specifically, investigation methods are underway to create bosses constructed with Aluminum 7075-T73. Properties, of which, are difficult to acquire through entire thickness. High strength would allow reduction in boss size and allow aluminum use at high temperatures. To date, near net shaped bosses have been machined from 7075-T6 aluminum with the following surface finishes: smooth machining, rough machining, sand blasted and chemical etching. These bosses were then heat treated to a T73 condition. Bosses have been sectioned for review and locations mapped for hardness testing. Results of hardness testing have been received and are in the process of being evaluated. Results to date indicate that heat treating will be sufficient if the parts are rough machined first. Plans are being made for testing of the boss material with respect to stress corrosion cracking.

Investigations into alternate resin compilation are underway to determine effects on the toughening properties of a full-scale vessel. First phase was to research and perform testing on alternate hardeners that could be used with our current baseline resin. Several experiments were run with alternate hardeners with an end result that our current hardener performs best. Next step is to use this hardener to begin looking at different resin formulations. First step is to down-select based on screening of viscosity and $T_g$ results. Further testing is planned to determine mechanical and environmental/chemical properties. Upon completion, a down-select activity will determine what resin formulations will be used to produce coupons for further testing. The last activity will then be to build full-scale vessels with the alternate resin formulations and to perform further testing such as impact.

Studies are ongoing with respect to alternate materials to minimize the permeability of gas through the high density polyethylene (HDPE) liners that Lincoln Composites currently uses. Evaluation of coatings and surface treatments has shown blistering following a hydrogen soak and blow down. Treatments have not been shown to be effective. The first investigation into Nanoclay gave unsuccessful results. The molecular properties of HDPE did not promote dispersion. However, new material found from an alternate vendor has shown some improvements. HDPE with titanium dioxide has resulted in a 25% reduction in permeation. Lincoln Composites has also worked with the addition of ethylene vinyl alcohol (EVOH). We encountered problems with layered materials including the ability to weld. We looked at adding an outside

<table>
<thead>
<tr>
<th>TABLE 1. Service Conditions and Nominal Cylinder Properties</th>
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<tbody>
<tr>
<td><strong>Service Pressure</strong></td>
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<tr>
<td><strong>Gas Setting Temperature</strong></td>
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<tr>
<td><strong>Maximum Fill Pressure</strong></td>
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<td><strong>Service Life</strong></td>
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<td><strong>Gas Fill Temperature Limits</strong></td>
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<td><strong>Operating Temperature Limits</strong></td>
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<td><strong>Proof Test Pressure</strong></td>
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<td><strong>Minimum Rupture Pressure</strong></td>
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<td><strong>Cylinder Diameter</strong></td>
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<td><strong>Cylinder Length (unpressurized)</strong></td>
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<td><strong>Cylinder Length at Maximum Fill Pressure</strong></td>
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<td><strong>Cylinder Empty Weight (excluding hardware)</strong></td>
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<td><strong>Cylinder Volume at Service Pressure</strong></td>
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<td><strong>Cylinder interior diameter</strong></td>
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layer to keep the material away from the weld joint, however, issues with adhesion of the EVOH to the HDPE were experienced. Lincoln Composites is in the process of looking at EVOH that has been modified to increase ductility. The evaluation of nylon as a filler has also been targeted. The cost of nylon, when compared with HDPE, would generate a large cost increase. Liners have been built with the following conditions: HDPE (baseline), HDPE/standard nanoclay, HDPE/development nanoclay, and HDPE/titanium dioxide. These will be wound into full vessels and testing will then move forward on full-scale models. A permeation rate versus cost relative to HDPE is shown in Figure 1. HDPE is the baseline at 1.1. HDPE fillers show 40% reduction with limited cost increase. Alternate materials show promise of significant permeation reduction while others are prohibitively expensive.

Lincoln Composites is looking into an improved database for stress rupture of carbon fiber that may allow for reduced safety factors. This will in turn maintain projected reliability and reduce cost, weight and increase volumetric efficiency with thinner walls. A stress rupture project presented at an industry workshop to gain feedback and support was conducted. This project is currently being refined with some collaborators and funding identified. Additional collaboration and funding is being sought. Stress rupture, fatigue and damage tolerance are all being considered in the study. The evaluation of damage vs. impact is being considered to characterize safety and ability to remain in service after damage. NDE as a means of monitoring the structural integrity is being considered which will allow for thinner laminates and removal from service before rupture.

**Conclusions and Future Directions**

Future work for this project will be to continue progress on evaluating potential improvements. This is work that is being completed in Phase 1 of the project. After completion of Phase 1, Lincoln Composites will down-select most promising engineering concepts and evaluate against DOE 2010 and 2015 Hydrogen Storage Go/No-Go criteria. Phase 2 is continuation of container development in support of system requirements and finally, Phase 3 will be the fabrication of subscale vessels to support assembly of prototype systems for evaluation.

**FY 2010 Publications/Presentations**

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 (FY) 2010 included:

- Model various developmental hydrogen storage systems.
- Provide results to Centers of Excellence 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 Storage section of the Fuel Cell 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 gravimetric and volumetric capacities of Type-3 (metal liner) and Type-4 (high density polyethylene [HDPE] liner), 350- and 700-bar compressed hydrogen (cH₂) physical storage systems.
- Updated the analysis of storage capacity and system performance of the cryo-compressed hydrogen (CcH₂) storage systems to include liner fatigue considerations.
- Analyzing the storage capacity of liquid hydrogen storage systems (LH₂) with advanced vapor shields to extend dormancy.
- Revised the on-board and off-board analyses of the metal-organic framework (MOF-177) system with adiabatic LH₂ refueling and cryogenic liner fatigue considerations.
- Initiated system analysis of on-board hydrogen storage systems that use ammonia borane (AB) in ionic liquids (ILs) as the hydrogen storage medium.
- Conducting off-board analysis of AB regeneration using hydrazine.

Introduction

Several different approaches are being pursued to develop on-board hydrogen storage systems with the goal of meeting the 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 the various 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 analysis projects 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.

**Results**

Figure 1 summarizes the storage capacities and well-to-engine efficiencies of some storage options that have been analyzed. The results in Figure 1 are only for reference and should not be compared directly since the systems are at different stages of development and have been analyzed to different levels of sophistication. The specific results given here are subject to revision as the models continue to be refined and additional data become available to help validate them.

**Physical Storage**

We modified our physical storage model to include the effects of autofrettage on the fatigue life of metal liners in Type-3 pressure vessels and on the load distribution between the liner and the carbon fiber (CF). We modeled the autofrettage process applied to composite tanks for service at ambient and cryogenic temperatures [1]. For service at ambient temperatures, we determined the induced residual compressive stresses in the metal liner and tensile stresses in the CF. We also modeled the post-autofrettage thermal stresses, the reversal of the residual stresses, and the resulting liner yield at lower loads even though the liner yield and tensile strength are higher at cryogenic temperatures. We used the model to determine the liner and CF thicknesses to meet the target life of 5,500 pressure cycles at 25% over the normal working pressure (SAE J2579). In addition, based on recent data and feedback from tank developers, we reduced the CF strength in our analysis by 10% to account for the variability in CF quality at high-volume manufacturing, and significantly increased the CF translation efficiency from 63% to 82% for 700-bar storage.

The fraction of the tensile load borne by the CF in Type-3 tanks affects the weight and cost of the tank. It is desirable to shift as much of the load to the CF as possible within the constraint of the autofrettage proof pressure. Figure 2 shows the calculated gravimetric and volumetric capacities for the Type-3 and Type-4, ch₂, single-tank systems. We calculate that the CF in a 350-bar, 5.6-kg usable H₂, Type-3 tank system can carry 90% of the total load, the Al liner thickness is 7.4 mm, and the usable storage capacities are 4.2 wt% and 17.4 g/L. The corresponding capacities for the Type-4 tank system (5-mm HDPE liner) are higher, 5.5 wt% and 17.6 g/L. At 700-bar storage pressure, the liner thickness for the Type-3 tank increases to 12.1 mm, the gravimetric capacity decreases to 5.6 wt%, and the volumetric capacity increases to 25 g/L. The storage capacities for the 700 bar, Type-4 tank system are higher.
5.2 wt% and 26.3 g/L. Because the HDPE liner carries negligible load, the liner thickness is unchanged between 350-bar and 700-bar pressures. We conclude that among the various cH2 tank systems analyzed, only the 350-bar, Type-4 system can potentially meet the 2015 gravimetric target of 5.5 wt% for 5.6 kg of recoverable hydrogen. None of the analyzed systems was found capable of meeting the 2015 volumetric target of 40 g/L.

We used the autofrettage model to revise the projected capacities of the Gen-3 CcH2 system with an in-tank heat exchanger and a 276-bar pressure vessel rating [2,3]. We determined that the unloading of the residual stresses during post-autofrettage cooling to cryogenic temperatures limits the maximum CF load share to 85%. The maximum load share is constrained by the proof pressure, which in turn depends on the safety factor (2.25) and the assumed approach to the burst pressure (80%). We estimate that a 9.3-mm liner is needed to withstand 5,500 pressure cycles. The liner thickness would increase if the analysis had considered deep temperature cycling due to refueling with compressed and liquid hydrogen (dual-mode storage). As shown in Figure 2, we project that a 5.6-kg recoverable CcH2 system can achieve capacities of 5.5 wt% and 41.1 g/L, meeting the DOE 2015 targets. Furthermore, with an aluminum outer shell instead of the steel shell, the gravimetric capacity of the 5.6-kg CcH2 system can exceed 9 wt% (but at a higher cost).

### Sorption Storage

We updated and expanded our analysis of on-board hydrogen storage in MOF-177. We investigated the adiabatic refueling option in which the MOF tank is evaporatively cooled by refueling it with LH2. We considered that hydrogen is recirculated through a small ex-tank heat exchanger during discharge to provide the heat of desorption and the temperature swing in the sorbent bed. We conducted fatigue analyses to estimate the required liner and CF thicknesses to meet the target life of 5,500 pressure cycles. We performed life cycle analyses to determine the well-to-tank energy efficiency, greenhouse gas emissions and fuel and ownership costs.

Figure 3 shows the calculated system gravimetric and volumetric capacities and the optimum storage temperature and temperature swing as functions of storage pressure. The optimum storage temperature and temperature swing depend on the storage pressure. The maximum gravimetric capacity of ~5.2 wt% is achieved at 150 atm and 80 K. The maximum volumetric capacity
increases with increasing pressure, reaching \( \sim 35 \text{g-H}_2/\text{L} \) at 350 atm and 100 K.

We estimated that 29% of the weight of the MOF-177 system (250-bar storage pressure, 80-K storage temperature) is in the storage medium, 25% in the liner, 11% in the CF composite, 11% in the aluminum shell, 1% in the multi-layer vacuum superinsulation, and 23% in other miscellaneous components. The corresponding volume distribution is 68% for MOF-177 bed, 6% for the liner, 5% for CF, 3% for the shell, 11% for the multi-layer vacuum superinsulation, and 7% for other miscellaneous components.

Analysis of the refueling dynamics showed that the total cooling load is 7.1 MJ (maximum, from completely empty to completely full). Of this, 62% is to remove the heat of hydrogen adsorption on MOF-177 and 38% is for sensible cooling of the thermal mass and the pressure-volume work of compressing the hydrogen in the tank. During discharge, a constant heat input rate of 1.9 kW is needed to provide \( \text{H}_2 \) continuously at 1.6 g/s full flow rate for an 80-kW fuel cell system. The peak heat input rate increases to 6.3 kW if the heat is supplied only as the tank pressure tends to fall below 4 atm. The system dormancy is a function of the amount of \( \text{H}_2 \) stored in the tank and the tank pressure and temperature at the start of the dormancy period. The minimum dormancy is 16 W-days, or ~3 days with a 5-W heat in-leakage rate.

The effects of varying different parameters on the system gravimetric and volumetric capacities were assessed. The parameter values (base case value in boldface) in the sensitivity study were 100, 250 and 300 atm storage pressure; 3, 4 and 8 atm minimum discharge pressure; and 0.4, 0.6 and 0.8 MOF packing fraction. In addition, the effects of a hypothetical increase in the absolute adsorption capacity by 0%, 20%, and 50% were evaluated. The resultant gravimetric capacities ranged from 4.6 to 5.75 wt% and the volumetric capacities ranged from 24 to 43 g/L. The sensitivity analyses showed that the adsorption capacity was the most significant parameter for the gravimetric capacity, whereas the storage pressure and the adsorption capacity were the two most significant parameters for volumetric capacity. Over the range of parameter values studied, the gravimetric capacity was the least affected by the minimum \( \text{H}_2 \) delivery pressure and the storage pressure, while the volumetric capacity was the least sensitive to the minimum \( \text{H}_2 \) delivery pressure and the MOF packing fraction.

The MOF-177 system, as analyzed, can meet the 2010 storage targets, but a 50% increase in sorption capacity is needed to meet the 2015 targets. With hydrogen obtained by steam-methane reforming and electricity drawn from the Energy Information Agency-projected U.S. grid mix for 2015, our analysis showed that the well-to-tank efficiency is about 41%, which falls well short of the DOE target of 60%. The total greenhouse gas emissions were estimated to be 19.7 kg CO\(_2\) equivalent/kg-H\(_2\), or \( \sim 0.51 \text{kg CO}_2/\text{mile} \) (63-gasoline gallon equivalent fuel economy) which is slightly less than the emissions for a conventional gasoline internal combustion engine vehicle (\( \sim 0.35 \text{kg CO}_2/\text{mile} \) for 50 mpg fuel economy). The ownership cost was $0.15/mile, which is 50% higher than that for conventional gasoline vehicles ($0.10/mile, 30 mpg and $3/gallon gasoline untaxed).

### Chemical Storage

We performed a preliminary on-board analysis for hydrogen storage in a 50:50 liquid mixture by weight of AB and an IL, bmimCl (1-butyl-3-methylimidazolium chloride, C\(_8\)H\(_{15}\)ClN\(_2\)). This AB solution is a stirrable, viscous liquid at room temperature, with a freezing point below \(-10^\circ\text{C}\). However, the solution foams once \( \text{H}_2 \) is released from the AB in the exothermic process; the foam begins to convert to a white solid after releasing 1 \( \text{H}_2 \) equivalent, with the entire mixture becoming solid after releasing 2 \( \text{H}_2 \) equivalents [4]. We fitted the dehydrogenation kinetics data [4] to the Arram-Erofeyev kinetics model with \( n=1.5 \) for the first \( \text{H}_2 \) equivalent released (Step 1) and \( n=2.5 \) for the next 1.55 \( \text{H}_2 \) equivalents released (Step 2). In our model, 100% AB conversion implies the release of 2.35 \( \text{H}_2 \) equivalents from AB. The kinetics model fits the measured data well for temperatures of 75°C, 85°C, 95°C, 105°C, and 110°C. The model could then be used to estimate hydrogen release at higher temperatures. The modeled kinetics showed that a temperature higher than 150°C is needed to release 2 equivalents of \( \text{H}_2 \) in 30 s (average release rate of 67 mEq/s) with a liquid-hourly space velocity (LHSV) of 120 h\(^{-1}\); for comparison, the highest measured release rate is 6 mEq/s at 110°C.

Assuming that an alternate IL (or mixture of ILs) is found such that the solution does not foam or solidify, we developed a conceptual on-board dehydrogenation reactor model using the kinetic data for the AB-bmimCl mixture. The main challenge is to control the peak temperature in this exothermic process, as too high a temperature may lead to undesirable side reactions, as well as issues of solvent stability and AB conversion (complete AB conversion would impede regenerability). The adiabatic temperature rise is in excess of 500°C, which, with an inlet temperature of 150°C, would lead to peak temperatures of 650°C or higher. The reactor temperatures can be controlled by using a heat transfer coolant, product recycle, or a combination of the two, as shown in the system schematic diagram in Figure 4. The reactor model was set up to yield 1.6 g/s of \( \text{H}_2 \) at 100% conversion using ethylene glycol as the coolant with a 10°C temperature rise through the reactor. To limit the maximum temperature to 200°C, the recycle ratio needs to be between 0.90 and 0.95 for an inlet temperature of 150°C and an LHSV of 150 h\(^{-1}\). The
IV.E Hydrogen Storage / Storage Testing, Safety and Analysis

Our analysis of CH₂ storage in Type-3 tanks indicates that the maximum load share in carbon fiber is limited to 90% because of the liner fatigue life requirement and the constraint on proof pressure. We project a gravimetric capacity of 4.2 wt% at 350 bar, decreasing to 3.6 wt% at 700 bar for 5.6 kg recoverable hydrogen. The corresponding volumetric capacity is 17.4 g/L at 350 bar, increasing to 25 g/L at 700 bar. With Type-4 tanks, the gravimetric capacity improves to 5.5 wt% at 350 bar and 5.2 wt% at 700 bar; the volumetric capacity is marginally higher at 350 bar and improves to 26.3 g/L at 700 bar.

- Our analysis of CcH₂ storage in Type-3 tanks indicates that the maximum load share in carbon fiber is limited to 85% because of the unloading of residual stresses at cryogenic conditions. We project a gravimetric capacity of 5.5 wt% and a volumetric capacity of 41.8 g/L for 5.6 kg recoverable hydrogen. The gravimetric capacity can be significantly higher if the steel outer shell is replaced with an aluminum shell.

- We project that an on-board MOF-177 system with adiabatic LH₂ refueling and 5.6 kg recoverable H₂ can achieve 4.8 wt% gravimetric capacity and 34.6 g/L volumetric capacity at 250 bar. The loss-free time and hydrogen loss rate are functions of the amount of hydrogen stored and the pressure and temperature at the start of the dormancy event.

- In FY 2011, we will continue our system analysis of hydrogen storage in liquid ammonia boranes. We will investigate reactor startup, buffer hydrogen storage, fuel stability, and supplemental heat rejection.

- In FY 2011, we will complete our analysis of the single-pot scheme developed by CHCoE for regenerating AB with hydrazine. We will determine the process efficiencies, well-to-tank efficiency and greenhouse gas emissions.

- Also in FY 2011, we will further extend our systems analysis work on physical, sorbent and metal-hydride storage methods.

Conclusions and Future Directions

- Our analysis of CH₂ storage in Type-3 tanks indicates that the maximum load share in carbon fiber is limited to 90% because of the liner fatigue life requirement and the constraint on proof pressure. We project a gravimetric capacity of 4.2 wt% at 350 bar, decreasing to 3.6 wt% at 700 bar for 5.6 kg recoverable hydrogen. The corresponding volumetric capacity is 17.4 g/L at 350 bar, increasing to 25 g/L at 700 bar. With Type-4 tanks, the gravimetric capacity improves to 5.5 wt% at 350 bar and 5.2 wt% at 700 bar; the volumetric capacity is marginally higher at 350 bar and improves to 26.3 g/L at 700 bar.
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- Also in FY 2011, we will further extend our systems analysis work on physical, sorbent and metal-hydride storage methods.

FY 2010 Publications/Presentations


References


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 Fuel Cell 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 preliminary, high-volume (500,000 units/yr) on-board system factory cost assessments of metal organic framework (MOF) 177 and liquid hydrogen tank systems. The MOF-177 system is projected to cost $16/kWh for a 5.6 kg hydrogen tank and $12/kWh for a 10.4 kg hydrogen tank. The liquid hydrogen system is projected to cost $8/kWh for a 5.6 kg tank and $5.4/kWh for a 10.4 kg tank.
- Revised high-volume on-board system factory cost assessments of cryo-compressed and 350 bar and 700 bar compressed tank systems. For the compressed systems, the analysis was extended to include Type 3 and Type 4 tanks, and single and dual tank systems.
- Supported the Storage Systems Analysis Working Group (SSAWG) evaluation of the well-to-tank energy use and greenhouse gas (GHG) emissions for MOF-177 tanks, cryo-compressed tanks, 350 and 700 bar tanks, and cold gas tanks.
- Completed review of Dow Chemical’s Ammonia Borate 1st fill cost projections.
**Introduction**

DOE is funding the development of a number of hydrogen storage technologies as part of its “Grand Challenge.” 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); and 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 Argonne National Laboratory (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 SSAWG 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**

TIAX developed preliminary cost estimates for a MOF-177 storage system and a liquid hydrogen storage system, and updated previous cost estimates for compressed and cryo-compressed storage systems. Each of the storage system cost projections are estimated based on on-board system designs developed by ANL [1].

The high volume (~500,000 units per year) cost of the MOF-177 system was estimated to be $16/kWh for a 5.6 kg useable hydrogen tank and $12/kWh for a 10.4 kg useable hydrogen tank (Figure 1). The modeled MOF-177 tank consists of a Type 3 carbon fiber pressure vessel surrounded by multi-layer vacuum insulation and an aluminum outer shell. The pressure vessel is filled with a metal organic framework storage media (Figure 2), which stores hydrogen at 250 bar and 100 K. The single biggest contributors to the system cost are the carbon fiber (19%), the aluminum tank liner (14%), and the storage media (14%). It should be noted that the MOF storage media is not yet available at high commercial volumes. As such, our preliminary estimate of the storage media is based on the high volume cost of activated carbon (AX-21); subsequent revisions will revisit this assumption.

The liquid hydrogen storage system was estimated to cost $8/kWh for a 5.6 kg tank and $5.4/kWh for a 10.4 kg tank (Figure 1). The liquid hydrogen tank consists of an aluminum inner shell and steel outer shell.

![FIGURE 1. Preliminary On-board Storage System Cost Comparison Results](image-url)

1 Costs were estimated for both a 5.6 kg useable hydrogen tank and a 10.4 kg useable hydrogen tank for the cryogenic systems. Due to space constraints, only the results for the 5.6 kg tanks are shown. The two different tank sizes reflect two different bases for comparison that were suggested by various stakeholders: the 5.6 kg tank is consistent with other cost analyses performed as part of this project, and reflects the amount of hydrogen needed for a passenger vehicle to achieve 350 mile range. The larger tank is more consistent with the specifications of cryogenic tanks that have been tested to date, which tend to be larger to help mitigate the effects of boil-off.
with multi layer vacuum insulation sandwiched between. The tank is sized to include 7.5% ullage and assumes 40% boil off of hydrogen. The major costs are relatively evenly distributed between the tank (46%, primarily the liner and vacuum insulation), and the balance of plant (54%).

In addition to the new cost analyses described above, TIAX updated previous cost assessments of compressed and cryo-compressed storage systems. The revised cryo-compressed storage system is based on Lawrence Livermore National Laboratory’s Gen 3 tank design [1]. Key changes between the current design and the Gen 2 design used for TIAX’s prior assessment include changes in the liner and vacuum insulation thickness, and a reduction to the system’s nominal pressure (to 272 Bar). The updated estimates for the cryo-compressed system project a system cost of $12/kWh for a 5.6 kg tank and $8.4/kWh for a 10.4 kg tank (Figure 1). The tank, primarily due to the cost of carbon fiber and the aluminum liner, accounts for 55% of the total cost, while the balance of plant accounts for an additional 34% of the total.

The revised compressed hydrogen system cost estimates project that a 350 bar Type 4 tank will cost $15/kWh and a 700 bar Type 4 tank will cost $19/kWh (Figure 1). Both tanks were sized to store 5.6 kg of useable hydrogen. These calculations include a number of revised assumptions compared to TIAX’s prior analysis, the net effect of which was a 10% decrease in the cost of the 350 bar system and a 30% decrease in the cost of the 700 bar system. The revised calculations continue to show that the cost of carbon fiber is the dominant cost component for both the 350 and 700 bar systems, accounting for 75 to 80% of the system cost; the balance of plant accounts for an additional 18%.

In addition to the Type 4, single tank compressed hydrogen storage system, TIAX estimated the system costs for Type 3 tanks and for multi-tank systems. In total, eight different compressed hydrogen tanks were evaluated (i.e., each combination of 350 and 700 bar, Type 3 and Type 4, and single and multi-tank systems). The cost results of this analysis are shown in Figure 3. As shown, the multi-tank systems lead to a minor cost increase in system costs (approximately $0.5/kWh). Although the two tank system has additional surface area compared to a single tank, the carbon fiber thickness may be decreased due to the smaller dimensions. As such, the single and dual tank systems use a very similar quantity of carbon fiber. Moreover, it was assumed that the two tank system uses the same balance of plant as the one tank system. The Type 3 tanks are projected to lead to a modest cost increase compared to the Type 4 baseline: for the 350 bar tank, the system cost increases by $1.3/kWh, while the 700 bar tank cost increases by $2.2/kWh compared to a Type 4 tank. This difference reflects a large increase in the cost of the aluminum Type 3 liner compared to the HDPE Type 4 liner, coupled with a minor decrease in the carbon fiber required.

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. While this project focuses on the onboard hydrogen storage system cost, the results of TIAX’s onboard cost assessments were used as inputs to well-to-wheel lifecycle analysis of system performance cost conducted by the SSAWG (Table 1).

\[\text{i.e., none of the balance of plant components are duplicated.}\]

\[\text{The aluminum liner is able to support a portion of the carbon fiber’s pressure load.}\]
TABLE 1. Hydrogen Storage System Performance and Cost Metrics for 5.6 kg Tanks

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</tr>
<tr>
<td>2010 Targets</td>
<td>4.5 28 4 2 to 3 60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2015 Targets</td>
<td>5.5 40 2 2 to 3 60</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ultimate Targets</td>
<td>7.5 70 TBD 2 to 3 60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

WTT = well-to-tank; TBD = to be determined

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.

- None of the systems assessed meet the Department of Energy’s 2010 cost target of $4/Wh. The cost of the 5.6 kg 350 bar, 700 bar, cryo-compressed, liquid, and MOF-177 storage systems range from 2 to 5 times the cost of the DOE target. Key factors influencing system costs are the carbon fiber material cost, the cost of aluminum, and in the case of the MOF system, the storage media.
- The MOF-177 system cost is 3 and 4 times the 2010 DOE target of $4/kWh for the 10.4 and 5.6 kg systems, respectively. Achieving the DOE cost targets will require large reductions in the cost of the storage media and the tank materials (aluminum and carbon fiber).
- The onboard liquid hydrogen system cost is 1.3 and 2 times the 2010 DOE target for the 10.4 and 5.6 kg systems, respectively. While the liquid system has amongst the lowest onboard storage system cost, it has low volumetric efficiency, well-to-tank efficiency, and high fuel costs. These shortcomings are a function of fuel boil-off and the high energy requirement associated with liquefaction.
- The cryo-compressed system is 2 and 3 times the 2010 DOE target for the 10.4 and 5.6 kg systems, but meets the 2010 volumetric and gravimetric targets. The base case 350 bar and 700 bar systems are 4 and 5 times higher than the 2010 DOE targets for the 350 bar Type 4 and 700 bar Type 4 systems, respectively, and both systems fall short of the 2010 volumetric capacity targets. Additional analysis of 350 and 700 bar dual tank systems showed minor cost increases of less than 5%; 350 and 700 bar Type 3 systems showed moderate cost increases on the order of 10%. The major cost driver for the compressed system is carbon fiber, while the cryo-compressed system cost is driven by carbon fiber, aluminum liner, and balance of plant component costs.

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 and finalize our analysis of storage technology options. Specifically, we plan to:

- Incorporate feedback and finalize on-board cost assessments and reports (with ANL) for MOF177 and liquefied hydrogen options. In parallel, we will update previously completed final reports for 350 bar, 700 bar and cryo-compressed systems.
- Complete updated assessments and final reports (with ANL) for previously evaluated technologies, including liquid hydrogen carrier and Gen 4 cryo-compressed systems.
- Complete new assessments and final reports (with ANL) for activated carbon systems.
- Complete off-board cost review for ammonia borane and other technologies as requested by DOE and integrate with overall performance and on-board cost results.
- Continue to work with DOE, SSAWG, Centers of Excellence, other analysis projects, developers, Tech Teams and other stakeholders (as necessary) to revise and improve system models.

FY 2010 Publications/Presentations


References

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, 2010

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 Fuel Cell 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 (U.N.) hazard analysis tests completed for all promised hydrides except alane.
- Modeling has been used to determine a critical radius for pelletization of 2LiBH₄-MgH₂.
- Calorimetric characterization of NH₃BH₃ is completed and the accompanying modeling work is nearly completed.
- A modified burn rate test has been developed and verified using less than one-half the material required for the standard U.N. burn rate test.
- The U.N. self-heating test has been modified to a cylindrical geometry to more thoroughly support the modeling effort.
- Environmental exposure risk mitigation strategy invention disclosure filed.
- Four mitigation strategies have been evaluated preliminarily and several have been promising enough to be evaluated under cyclic sorption conditions.
- Initial thermal and chemical kinetic model completed having predictive capabilities for environmental exposure and reactivity scenarios.

Introduction

This report gives a summary of standardized U.N. 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 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 U.N. 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$_3$BH$_3$, Mg(NH$_2$+LiH, AlH$_3$, and 2LiBH$_4$+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**

**U.N. Tests**

The standard materials testing procedures employed are based on existing U.N. 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. The U.N. tests were modified to include visual recording of the testing event, and the addition of thermocouples in those experiments where this was possible. Table 1 shows the U.N. test results for ammonia borane, alane, lithium borohydride-magnesium hydride (2:1 ratio), and the lithium hydride and magnesium hydride (8:3 ratio) hydrogen storage systems. The 8LiH·3MgH$_2$ system is the only material that failed the pyrophoricity test. All materials, with the exception of ammonia borane, showed reactivity towards water.

**Risk Mitigation**

Four risk mitigation strategies have been identify to mitigate the risks associates with air and water reactivity in this type of materials. Currently, invention disclosures

<table>
<thead>
<tr>
<th>Material / UN Test</th>
<th>Pyrophoricity</th>
<th>Self-Heat</th>
<th>Burn Rate</th>
<th>Water Drop</th>
<th>Surface Contact</th>
<th>Water Immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$BH$_3$ SRNL</td>
<td>No ignition event.</td>
<td>Self-heated -300°C within 10 min, 5 min at T$_{max}$ = 150°C</td>
<td>Flame propagated in 6 sec with burn rate of 33 mm/sec</td>
<td>No reactivity detected</td>
<td>No ignition event recorded. Gas evolved for about 5 min</td>
<td>No reactivity detected</td>
</tr>
<tr>
<td>AIH$_3$ SRNL (chemically synthesized)</td>
<td>No ignition event.</td>
<td>Not Tested</td>
<td>Flame Propagates at 250 mm/sec</td>
<td>Material ignited</td>
<td>Material sparked upon contact with wet surface.</td>
<td>Material sparked upon contact with wet surface.</td>
</tr>
<tr>
<td>2LiBH$_4$·MgH$_2$ SRNL</td>
<td>No ignition event. Hygroscopic material absorbed H$_2$O from air.</td>
<td>Self-heated -300°C within 5 min at T$_{max}$ = 150°C is approached.</td>
<td>Flame propagated in 5 sec with burn rate of 52 mm/sec.</td>
<td>2 drops required for near-instant ignition.</td>
<td>Material ignited</td>
<td>No ignition event recorded. Gas evolved for about 5 min</td>
</tr>
<tr>
<td>8LiH·3Mg(NH$_2$)$_2$ AIST</td>
<td>Ignition event recorded in room temp experiment</td>
<td>Not Tested</td>
<td>Flame Propagates at 463 mm/sec</td>
<td>Material ignited</td>
<td>Material ignited</td>
<td>No Ignition detected.</td>
</tr>
<tr>
<td>NaAlH$_4$ (UTRC)</td>
<td>No ignition event</td>
<td>Not Tested</td>
<td>Flame propagated with burn rate of 51 mm/sec.</td>
<td>Material ignited</td>
<td>Not Tested</td>
<td>Not Tested</td>
</tr>
</tbody>
</table>

* Reported values from the Japanese National Institute of Advanced Industrial Science and Technology (JNAIST) (Kuriyama).
are being prepared addressing the use of these strategies for these purposes. The $\text{8LiH} \cdot 3\text{Mg(NH}_2\text{)}_2$ system, supplied by JNAIST was used for testing these strategies. Experiments performed at JNAIST and SRNL show that the systems exhibits high reactivity to both air and water. Figure 1 shows the water drop test for this system as well as a modified sample utilizing one of the strategies pursued. As it can be observed, the original sample ignites upon in contact with the first drop of water. In contrast, the modified sample shows significant charring but did not undergo an ignition event even after being in contact with five drops of water.

**Calorimeter Experiments**

Alane calorimetric measurements (refer to Figure 2) were conducted under dry air as well as 30% relative humidity and 40°C. While the dry air environmental displayed a typical exothermic behavior, the presence of 30% water vapor caused a distinct behavior change in the alane. An exothermic peak is initially observed upon exposure humid air attributed the interaction of moisture with the material. Subsequently, a competing effect is then observed between the dehydrogenation of alane (endothermic peaks) and the oxidation of aluminum metal (exothermic peak). In situ X-ray diffraction studies are underway to further understand changes in crystal structure upon exposure to humid air condition.

**Numerical Simulations**

The numerical simulation examined an environmental exposure of storage material, where the hydride has been released from its containment vessel and is falling through the ambient air. The governing equations solved for each analysis include mass, momentum, and energy balances, plus additional kinetics equations based on isothermal calorimetry data at 70°C for porous $2\text{LiBH}_4\cdot\text{MgH}_2$ exposed to water. FLUENT, a general purpose computational fluid dynamics package, was used to solve the equations using the finite volume approximation method [2]. Further details of the mathematical model are available in the publications list below.

Two sets of initial conditions were used to evaluate the different release scenarios. For the first set of scenarios, the hydride is initialized with ambient air filling the porous media. This assumes the hydride has been out of the container for a short amount of time prior to a reaction occurring, which allows all of the hydrogen gas within the hydride to dissipate (replaced by ambient air) prior to the reaction. Typical results from these simulations are shown in Figure 3 and summarized in Table 2. The smallest diameter hydride spheres (0.05 inch and 0.25 inch radius models) never reach the lower flammability limit (LFL = 0.04) for hydrogen concentration, which means no ignition event occurs. For the larger spheres (0.50 inch and higher radius models), the LFL and/or the auto-ignition temperature (500°C or 571°C depending on the $\text{H}_2$ concentration)
of hydrogen is reached and an ignition event occurs. Figure 3 highlights the species concentrations before and after the hydrogen ignition event occurs for the 0.50 inch hydride sphere model. The $H_2$ concentration (26.6% mole fraction, $m_f$) is well above the LFL prior to the ignition event and then drops off rapidly after the event (~1.5% $m_f$). Note that as the $H_2$ and $O_2$ burn away, water vapor ($H_2O$) increases in their place. Similar results are seen for the larger spheres (1 inch and greater models), but are not shown for brevity.

For the second set of scenarios, the hydride is initialized with hydrogen gas filling the porous media. These scenarios assume that the reaction occurs immediately after the hydride is released from its container, which means the porous space within the hydride is still full of 100% hydrogen gas at the start of the numerical simulation. However, due to the high dissipation rate of $H_2$ into the ambient, most or all of the hydrogen has been expelled from the hydride prior to the start of the chemical reaction (mass/heat generation) within the simulation. Thus, the hydrogen-initialized hydride models have similar results to the air-initialized hydride models and are not shown for brevity. As is shown from the preceding results, small amounts of hydride have a lower chance of ignition compared to the larger amounts of hydride.
Conclusions and Future Directions

Conclusions

• Calorimetric measurements for alane show a competing effect between the dehydrogenation of alane and the oxidation of aluminum.
• NH₃BH₃ poses significantly less risk of ignition than the other materials tested for environmental exposure.
• Four risk mitigation strategies have been identified. Preliminary results on the 8LiH 3Mg(NH₂)₂ showed significantly reduced reactivity upon exposure to water.
• The mathematical modeling is an effective method of determining heat and hydrogen concentrations developed during simulated accident scenarios.

Future Directions

• Conclude standardized testing of AlH₃ as decided in consultation with the centers of excellence.
• Continue the thermodynamic and kinetic testing with AlH₃ and 8LiH 3Mg(NH₂)₂ to feed information into the numerical simulations.
• Continue modeling effort to include actual chemical kinetics to render predictive capabilities
• Evaluate proposed mitigation strategies utilizing calorimetry and modified U.N. tests.

Special Recognitions, Awards/Patents Issued

This project has been recognized by the International Partnership for the Hydrogen Economy. Partners in the project include 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.

This project has been recognized by the International Energy Agency-Hydrogen Implementation Agreement with award of the Annual Project Prize for 2010 for “Fundamental research characterized by technical excellence and harmony in international cooperation that contributes to the understanding and advancement of basic and applied hydrogen science.”

FY 2010 Presentations/Publications

Presentations


Publications


Endnotes

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-FG36-07GO1 7032
Subcontractor: Kidde-Fenwal, Combustion Research Center,
Holliston, MA

Project Start Date: June 1, 2007
Project End Date: May 31, 2011

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), liquid reactivity and other specialized testing.
- 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

- Qualitative risk analysis (QLRA): identified potential safety-significant failure modes that challenge the integrity of the storage vessel in an on-board reversible system.
- Quantitative risk analysis (QRA):
  - Used the fault tree methodology to perform system-level failure analysis of a baseline design of an on-board reversible storage system.
  - Defined a probabilistic importance measure to estimate contributions of system components to the total failure probability of the on-board system.
  - Developed and quantified a fault tree model to assess the consequences of accidental air intrusion into a hydride-based storage vessel.
  - Developed and applied a stochastic approach using interactive simulation in conjunction with Monte Carlo sampling to manage uncertain inputs in quantitative risk analysis.
  - Defined a probabilistic risk reduction importance measure to quantify the magnitude of safety improvement that can be achieved by reducing the probability of occurrence of undesired events and failure of components credited in the risk model.
- Risk mitigation: experimentally evaluated hydride powder compaction as a potential risk mitigation method.
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 codes and standards. 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 (QLRA and QRA).
- Materials reactivity testing.
- Chemical reaction kinetics testing and modeling.
- Risk mitigation.
- Limited scope prototype testing.

Figure 1 outlines the risk analysis framework of this project.

Results

1. QLRA

Identified safety-significant failure modes associated with the on-board reversible storage vessel (Figure 2). These failure modes include catastrophic vessel rupture due to a vehicular collision and vessel burst due to an external fire in conjunction with failure to vent the vessel. Other failure modes include accidental intrusion of air or water into the storage vessel and the potential for stored hydrogen diffusion/permeation through the vessel walls.

2. QRA

2.1 Developed a system-level fault tree (FT) model for a baseline design of an on-board vehicle reversible hydrogen storage system (Figures 3 and 4). The hydride storage vessels and associated pressure relief devices are among the key components credited in

![Fault Tree / Event Tree Linking]

![Hydride Powder Compaction]

**FIGURE 1. Risk Analysis Framework**
Safety-Significant Failure Modes that Challenge Vessel Integrity of On-Board Reversible Storage Systems

1. Catastrophic Failure of the Hydride Storage Vessel
   1.1 Vessel Rupture Caused by Vehicular Collision
   1.2 Vessel Burst Due to External Fire & TPRD Fails to Vent

2. Hydrogen Permeation or Leakage Leading to Early/late Ignition and/or Explosion
   2.1 Pipe Break
   2.2 TPRD Spurious Venting
   2.3 Loose Joints / Fittings
   2.4 Hydrogen Permeation

3. Fluid Intrusion into Storage Vessel Leading to Chemical Reaction with Hydride Material
   3.1 Water Intrusion into Storage Vessel Leading to Chemical Reaction with Hydride Material
   3.2 Air Intrusion into Storage Vessel Leading to Chemical Reaction with Hydride Material

FIGURE 2. Safety-Significant Failure Modes of On-Board Reversible Storage Vessels

FIGURE 3. Baseline Design of an On-Board Reversible Hydrogen Storage System
2.2 Developed a fault tree model which quantifies the consequences of accidental air intrusion into a hydride storage vessel. In this model, air leakage into the vessel was the initiating event and vessel burst was conditional on failure of the safety relief device to open and vent the vessel.

3. Risk Mitigation – Experimental Studies

3.1 A series of scoping tests were conducted to evaluate the hydride material reactivity under selected environmental conditions that could be encountered during a vehicular accident. Catalyzed sodium alanate (NaAlH$_4$+4mole% TiCl$_3$) was used in these experiments.

3.1.1 In immersion tests, loose powder as well as powder compacts (wafers) were immersed in different liquids at room temperature. The liquids selected were water, windshield washing fluid, engine coolant (antifreeze), engine oil and NaCl solution (brine), respectively. These tests were repeated using powder compacts.

3.1.2. In the droplet tests, water, windshield washing fluid, engine coolant (antifreeze), engine oil and brine, respectively, were dropped on loose powder and powder compacts (wafers).

Test results demonstrated that powder compaction has the potential to reduce risk by suppressing material reactivity (in the liquids tested) and preventing consequential ignition of the evolved reaction gases. Additional validation tests are in progress.

3.2 The scope of our risk mitigation scoping tests was extended to include the following high-temperature tests:

3.2.1 Sodium alanate wafers (1-gram each) were immersed in 50-ml hot water at 80°C and in 50-ml thermo-oil at 100°C, respectively. In both cases, only a benign reaction at the wafer’s surface was observed and the evolved reaction gases did not ignite.

3.2.2 The consequences of contacting powder compacts with hot surfaces in the presence of air were investigated; a condition that could be encountered during postulated accident scenarios. In this test, the hydride wafer was placed on an electrically-heated surface. Thermocouples were used to measure the wafer’s temperature. When the temperature of the wafer reached ≈85°C, it ignited and the evolved gases burned but the wafer did not disintegrate. The insights gained from this test will drive the development of additional risk mitigation to prevent the observed hydride fires.

3.3 Experimentally investigated the impact of extended immersion time of catalyzed sodium alanate wafers in different liquids. In these tests, hydride wafers (1-gram each) were immersed for 8 hours (soaking time) in water and in windshield washing fluid, respectively. The experimental observations showed very mild hydride/liquid reactions and the emitted reaction gases did not ignite.

3.4 Performed fast blowdown tests using our project’s specially designed and fabricated test rig that mimics hydride storage vessel rupture. The pressure profile during each blowdown test was recorded and the results showed that depressurization from 100 bars to 20 bars was completed in ≈40 msec. Results of tests with NaAlH$_4$ powder showed that ≈16% of the initial powder mass (30 grams) was entrained to the collection vessel of the rig as a result of the blowdown. Future tests will be conducted using powder compacts instead of the loose powder which was used for establishing a baseline for comparison purposes.
Conclusions and Future Directions

The work conducted in this year included QLRA, QRA and risk mitigation tests. The QLRA identified key safety significant failure modes of the hydride storage vessel (which represents a single point failure in the on-board system). The QRA covered: a) fault tree modeling and quantification of consequences of accidental air intrusion into the storage vessel, b) system-level failure analysis of a baseline design of a hydrogen storage system and c) developing a stochastic approach for managing uncertainties in risk quantification. The experimental work focused on risk mitigation tests to evaluate the hydride material reactivity (both loose powder and powder compacts) under wide ranges of environmental conditions and postulated accident scenarios.

Future work will focus on:

- **Risk Analysis**
  - Continue accident sequences development and quantification for the remaining risk-dominant initiating events.
  - Complete risk analysis framework (both QLRA and QRA) incorporating results from dust cloud tests, experimental and modeling activities at SNL and SRNL.
  - Evaluate candidate risk mitigation methods (material reactivity based and system-based).

- **Economic Consequence Analysis**
  - Perform economic consequence analysis for the identified most probable and worst-case scenarios and assign monetary safety benefits of selected risk mitigation methods.

- **Experimental Studies (including those planned and coordinated with SNL material reactivity project)**
  - Complete dust explosion tests for at least one mitigated material structure.
  - Complete X-ray diffraction characterization test for at least one mitigated material structure.
  - Perform material reactivity tests for selected mitigated and unmitigated material structures. Conduct fast depressurization tests on selected unmitigated and mitigated material structures.

**FY 2010 Publications/Presentations**


**References**

IV.E.5 The Reactivity Properties of Hydrogen Storage Materials in the Context of Systems

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Project Start Date: July 5, 2007
Project End Date: September 30, 2010

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

Objectives

- Develop generalized methods and procedures required to quantify the effects of hydrogen storage material contamination in a 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 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(D) Durability/Operability
(F) Codes and Standards
(Q) Reproducibility of Standards
(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 codes and standards efforts, thus enabling the design, handling and operation of effective hydrogen storage systems.

Environmental Health and Safety

<table>
<thead>
<tr>
<th>Toxicity</th>
<th>Meets or exceeds applicable standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safety</td>
<td>Meets or exceeds applicable standards</td>
</tr>
</tbody>
</table>

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

- We have found that the hazard presented by the breach-in-tank scenario is significantly minimized when loss of hydrogen was considered.
- We have determined that over-pressures and over-temperatures are probable during a pool fire scenario involving an un-mitigated metal hydride bed.
- We have polymerized both catalyzed and uncatalyzed complex metal hydrides, sodium alanates with vinyl monomers at 10 and 20 wt% (mitigated samples produced).
- We have demonstrated that mitigated samples show a nearly a 70% reduction in energy released during oxidation.
• We have successfully hydrogen cycled polymerized and mitigated samples nearly 160 times.
• We have quantified the impact of cross-linking density on the structural properties of mitigated materials.
• We have scaled up synthesis of mitigated materials to 10 g to enable larger scale testing and analysis.

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 solid-state 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 of the identification of hazard mitigation strategies, and eventually development of appropriate codes and standards. 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.

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 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

Prediction of processes during accident scenarios and the development of mitigation technologies for solid state hydrogen storage systems were the focus of efforts in Fiscal Year (FY) 2010.

Efforts to predict processes during accident scenarios investigated the impact of hydrogen evolution on the breach-in-tank contamination scenario, and the fire impingement scenario. In brief, we have determined that the evolution of hydrogen from the bed reduces the extent of the oxidation reaction during a breach-in-tank scenario. We have also determined that a pool fire scenario can lead to a system over-temperature and over-pressure event within a short time of exposure. As a result of this analysis we have identified to mitigation strategies for further development (1) additives that limit the extent and rate of oxidation and, (2) thermal shielding design to limit the reduce the rate of temperature rise within the system during a fire.

Breach-In-Tank Scenario Modeling – We have considered the case in which an accident results in air exposure of alane contained within a tank. We have built our models using desorption kinetics of alane combined with our model parameters developed for permeability and oxidation kinetics. We considered the realistic case for the alane bed breach-in-tank where heat losses to the environment at 5 W/m²-K cool the bed after the initiating event. Considering a one inch diameter, one foot long cylinder (characteristic geometry utilized in the simulations) filled with alane at 0.33 g/cc, calculations indicate that the oxidation reaction is significantly inhibited by the evolution of hydrogen. The loss of hydrogen from the system initially cools the bed to ~85°C prior to any inclusion of air into the bed (Figure 1). These results indicate that an alane breach-in-tank event may present a minimal hazard during an accident. Of course, this analysis is specific to this formulation of alane and the characteristic tank geometry.

Other materials may be much more reactive compared to the alane system. Catalyzed sodium alanates, for example, are materials that represent a prototypical alkali-metal containing complex metal hydride. Our experimental measurements utilizing our contamination flow-through reactor show that catalyzed sodium alanates and their decomposition products are significantly more reactive. Exotherms in excess of 100°C are sustained for nearly 250 s upon exposing a 300 mg sample of hydrogen-depleted material to dry air. Analysis of the products indicates the formation of sodium hydroxide (NaOH) at these temperatures. Mitigation technologies to reduce the extent and rate of reaction during the breach-in-tank scenario are considered below.

Fire Impingement Scenario Modeling - Exposure to a pool fire is one of the potential scenarios associated with solid-state hydride storage systems that might result from a vehicle accident.

The sodium alanate containing system provides an opportunity to observe the processes of a complex hydride during exposure to a pool or impinging fire. For
this system, it is assumed that the formation of sodium metal due to overheating is the outcome requiring management. Using measured heat transfer, mass transfer, and chemical kinetics, an axisymmetric model was assembled for analysis (Figure 2). The results show that a thin desorption front develops in the sodium alanate starting at the outer tube wall, which is heated directly by the fire, and then propagates radially inward. The calculations account for the rapid desorption of the sodium alanate resulting from the fire. Assuming that sodium metal would begin to form at near 350°C, the unshielded case achieves this temperature very quickly, after 180 s. A small amount of shielding (a thin air gap formed by a metal plate) extends this over-temperature event to 300 s – providing good management of the over-temperature hazard. Similar analysis can be performed for a variety to materials, such as alane or interstitial hydrides, to manage the resulting over-temperature or over-pressure hazard. The pool fire scenario may be one of the more important safety design considerations for metal hydride containing systems. This effort scopes details such as pressure relief device and insulation design characteristics required to allow for an adequate delay in loss-of-containment during an accident scenario.

**Mitigation Technology Development** – Towards the goal of mitigating and managing the hazards presented by solid state storage systems, we have demonstrated the ability to polymerize vinyl monomers in the presence of complex metal hydrides, sodium alanates and produce composite materials.

Composite materials were made with 10–20 wt% polymer. Characterization of the composite polymer/metal hydride material was done by scanning electron microscopy and thermal methods. Figure 1 and the accompanying energy dispersive spectrum (EDS) analyses show that the polymer is intimately mixed with the metal hydride particle. The inorganic portion was identified by the strong Na, Al and O signals in the accompanying EDS. The polymer surrounding the inorganic material was identified by the absence of Na and Al signals and the shoulder at low energy for carbon, C. Thermal analysis of composite materials compared to free sodium alanate suggests slower kinetics for mass-transport properties of the melted metal hydride above 150°C.

To test the mitigating properties of the polymer supported material, 360 mg of the polymerized material were analyzed using flow-through calorimetry. The
exotherm resulting from dry gas exposure at 200°C and 0.1 SLPM air was compared to the un-mitigated “neat” material results (Figure 3). It was observed that the energy release was reduced by nearly 70%, indicating that a significant portion of the sample was excluded from oxidation. This was confirmed by product analysis indicating very little formation of NaOH in the mitigated sample compared to the un-mitigated sample. In parallel, catalyzed and supported samples of sodium alanate were hydrogen cycled. Initial results indicate that hydrogen uptake/release is not significantly hindered and even at high cycles (in excess of 30 hydrogen sorption cycles executed). The cycled material was then analyzed by thermal gravimetric analysis (TGA). Results show that the cycled material has an 11% weight loss upon heating, similar to the uncycled material. Our conclusion from this study is that the polymer matrix withstands at least 30 cycles of charging with no indication in loss of polymer matrix.

To optimize the structural properties of the material, the cross-linking density of the added polymer has been varied to determine the effect on mechanical properties. Monomer/cross-linker ratios of 10:1 to 1:1 have been explored. Our results show that with higher cross-linker ratios, the composite materials are more brittle and are easily crushed into a powder. In contrast, the composite materials with a lower cross-linker ratio (10:1 monomer/cross-linker) give very hard solids that are not easily crushed into powders. Little change in decomposition behavior is observed despite large structural properties changes. TGA of the composite materials in argon shows polymer decomposition occurring above 220°C with approximately 11–12 wt% loss (Figure 4). This mass loss is expected since significant char formation occurs in cross-linked polymer networks upon thermal decomposition.

Conclusions and Future Directions

- This project has developed the tools and understanding for eventual codes and standards development and market penetration of metal hydride systems.
- Over-temperature and over-pressure events caused by exposure to air or fire are hazards that need to be managed to enable the widespread utilization of advance hydrogen storage materials.
- Mitigation technologies are being developed that are able to:
  - Contribute a small weight penalty
  - Withstand hydrogen cycling
  - Mitigate unfavorable reactions
  - Structurally support fine reactive solids
- Future work will focus on:
  - Optimization of composite materials
  - Validation at full-scale
  - Enabling design-for-safety of advanced storage systems

Special Recognitions & Awards/Patents Issued


FY 2010 Publications/Presentations


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

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/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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(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).

Accomplishments

• Established new collaborations with: Université Paris-Sud, Texas A&M University, Los Alamos National Laboratory, VU University Amsterdam/Delft University of Technology and University of Nevada, Reno.
• Compiled example measurements from the literature, to illustrate key issues associated with the four tasks outlined above.
• Performed example measurements to illustrate key issues associated 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.
• Final Capacity section 100% complete.
• Draft Thermodynamic section in progress 85% complete.
IV.E Hydrogen Storage / Storage Testing, Safety and Analysis

- Draft Cycle-Life Properties section in progress 50% complete.

Introduction

The Hydrogen Storage sub-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 Hydrogen Storage sub-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 measurement, incorporating examples from the literature, performing experimental measurements to demonstrate important issues, and finally, condensing key information into a concise reference guide. Each section covers such topics as the overall purpose of the measurements, some basic theory, experimental consideration, methods of measurement, and many details on both material properties and experimental factors that may strongly influence the final results and conclusions. Participation from other experts in the field is being sought out for input, relevant examples, and critical review at all levels.

In Fiscal Year (FY) 2010 sections of the document were reviewed by many experts from around the world. We greatly appreciate the collaborative efforts of all of the reviewers: Dr. Thomas Gennett of the National Renewable Energy Laboratory, Dr. Gary Sandrock and Dr. George Thomas, consultants to the U.S. Department of Energy, Dr. Michael Miller of Southwest Research Institute®, Dr. Anne Dailly and Dr. Frederick Pinkerton of General Motors R&D Center, Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller, Norway, Dr. Eric Poirier of NRC Canadian Neutron Beam Centre Chalk River Laboratories, Professor Channing Ahn of the California Institute of Technology, Dr. Kevin Ott, Dr. Anthony Burrell, and Dr. Troy Semelsberger of Los Alamos National Laboratory, Professor Richard Chahine, Université du Québec à Trois-Rivières, Professor Klaus Yvon, University of Geneva, Professor Sam Mao of the University of California, Berkeley, 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.

Results

The second task in this project focused on creating a best practices document for capacity measurements. This has been completed reviewed and public commentary has be received and addressed. The final version including a preface, introduction, kinetics and capacity measurement sections is now posted on the DOE Web site.

In addition, this year’s work covered the Thermodynamics and Cycle-Life measurements sections of the “Best Practices” document. For this work collaborations were established with the following contributing authors: Pierre Dantzer, Université Paris-Sud, Shengqian Ma and Hong-Cai Zhou, Texas A&M University, Kevin Ott, Tony Burrell and Troy Semesbgerger, Los Alamos National Laboratory, Yevheniy Pivak and Bernard Dam, VU University Amsterdam and Delft University of Technology and Dahnesh Chandra of the University of Nevada, Reno. Through these collaborations the document has added perspectives of critical measurement issues from the three main materials research areas: on-board rechargeable hydrides, off-board regenerable hydrides, and hydrogen physisorption storage materials.

Examples are included below of important considerations when making thermodynamic measurements. Figures 1 shows the classic conversion of pressure-concentration-temperature (PCT) isotherms of a reversible hydride to a van’t Hoff plot for the determination of the enthalpy and entropy of hydride formation.

This simplified example does not take into consideration, irreversibilities that lead to hysteresis between absorption and desorption measurements. It also depicts the thermodynamic behavior a highly ordered crystalline material as opposed to real materials which range from some structural defects, may also include multiple partial substitutions, to fully amorphous materials. As an example of this, Figure 2 shows...
The heat of reaction in storing hydrogen in a hydride consists of the heats of hydrogen solution as well as hydride formation. In this respect the total heat produced (as measured by calorimetry) will not necessarily be the same as the enthalpy of hydride formation (as measured by the van’t Hoff method). Figure 3 depicts the complete hydrogen absorption of a material where hydrogen is absorbed first in solution, then forms a hydride and finally further dissolution of hydrogen into the hydride. In this sense, the Van’t Hoff measurements based on plateau pressures only are useful in comparing the stability differences between hydrogenated compounds, however they may not fully represent the heat produced (or required) in real hydrogen storage applications.

With physisorption storage materials, the determination of isosteric heat of adsorption for hydrogen is an important aspect of characterizing the potential of porous materials for on-board hydrogen storage applications. By drawing the In pressure vs. 1/temperature plot of H₂ at various hydrogen concentrations, the isosteric heat of adsorption can be determined (Figure 4).

Conclusions and Future Directions

In FY 2010 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 Capacity section in a timely manner. We are currently working on the Thermodynamic and Cycle-Life measurement sections. We expect to complete the draft version these sections in this fiscal year.

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FIGURE 4. (a) Excess adsorption isotherm data of H₂ in the MOF-5 metal-organic framework storage material, used in the heat of adsorption calculation. Dotted lines indicate pressure-temperature data at fixed hydrogen concentrations. (b) The ln pressure vs. 1/temperature plot of H₂ in MOF-5 at various wt%. According to the Clausius-Claperyon equation, the isosteric heat of adsorption \( Q_{st} = -\text{slope} \times R \). (c) \( Q_{st} \) plot for H₂ adsorption in MOF-5, as derived from (b) [3].


References

Objectives

- Synergistic work between Yaghi (UCLA) and Goddard (California Institute of Technology [Caltech]).
- Build high-throughput preparation setups for covalent-organic framework (COF) synthesis (high temperature and pressure).
- Develop chemistry to realize stable frameworks.
- Introduce potential metal binding sites through the COF synthesis.
- Determine atomistic connectivity of COFs using an ab initio charge-flipping method using powder X-ray diffraction (PXRD) data.
- Predict adsorption enthalpy of H₂ on various metal sites.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(E) Charging/Discharging Rates

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project consists of conducting fundamental studies of COFs. 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 targets:

- Volumetric density: 40 g L⁻¹
- Gravimetric density: 5.5 wt%

Accomplishments

- Build high-throughput preparation setups.
- Develop structural determination technique using ab initio charge-flipping method.
- Synthesis of new COFs through hydrazone condensation.
- Began modeling study for optimal binding energy.

Introduction

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. We are therefore undertaking efforts to discover highly porous materials with strong affinity for hydrogen.

Approach

To meet the DOE 2010 targets by physisorption, adsorbents must have high surface area (>3,500 m² g⁻¹) and relatively high density (>0.75 g cm⁻³). We have already demonstrated how to design high surface area MOFs and COFs; however, in many cases, these materials do not show steep H₂ uptake in the low pressure region indicative of the weak interaction with
Hydrogen Storage / New Materials-Independent Projects

Yaghi – University of California, Los Angeles

It is predicted that the impregnation of COFs with metals should enhance the adsorption enthalpy; therefore, we explore methods for the preparation of metalated COFs using high-throughput techniques. In this fiscal year, we developed a new class of COFs for metal impregnation and applied an ab initio charge-flipping method for structural analysis.

Results

Metal impregnation is one of the most promising strategies to improve the adsorption enthalpy of COFs. However, before the metal impregnation experiments, it is necessary to prepare stable COFs, and it is preferable to introduce metal binding sites in the framework through the condensation reaction. To this end, we designed and prepared new COFs having hydrazone and imine moieties. In addition, we applied a new technique to the structural analysis of COFs, which can be useful in determining the structure from low-resolution PXRD data. With regard to the simulation calculations, we demonstrated a method based on accurate quantum mechanics that allows us to screen different metal complexes to determine the enthalpy of adsorption at 298 K and 1 atm. We proposed a way to tune the $H_{ads}$ based on the degree of metalation of our linkers.

1. Synthesis of Crystalline Hydrazone COF (UCLA)

We have developed the synthesis of new COFs constructed from the dehydration of aromatic carbohydrazides and aldehydes to form carbohydrazones (Figure 1A). This functional group shows interesting features such as the presence of both of amides and imines, resulting in materials with high thermal and chemical stability as well as dynamic reversibility forming libraries of polymers that exchange monomers in solution; moreover, hydrazones possess both carbonyls and nitrogen atoms that can be available for metal coordination/impregnation. An additional advantage for the synthesis of hydrazide-based materials is the easy synthesis of the hydrazide building blocks, which are prepared from the condensation of hydrazine and a carboxylic acid ester in refluxing alcohols with high yields.

A new COF, termed COF-41 was crystallized by reacting terephthalohydrazide with 1,3,5-tris(4-formyl-phenyl)-benzene through solvothermal conditions in mesitylene/dioxane/acetic acid/water mixtures (Figure 1A). The formation of the hydrazone linkages was determined by solid state Fourier transform infrared (FTIR) and $^{13}$C nuclear magnetic resonance (NMR) of synthesized COF-41, starting materials, and model compound $N'$-benzylidene-benzohydrazide. The FTIR spectrum of COF-41 shows the characteristic C=N vibrational modes at 1,558 and 1,273 cm$^{-1}$ (1,550 and 1,288 cm$^{-1}$ in model compound). The solid-state $^{13}$C NMR spectrum shows a chemical shift for the C=N of 149.2 ppm, compared to shifts of 150.2 ppm for the model compound and 192.5 ppm for the aldehyde in the starting material. The crystallinity of COF-41 was confirmed by PXRD from which the diffraction peaks were indexed into a primitive hexagonal unit cell ($a = 43.52$ Å, $c = 3.62$ Å) and compared to simulated patterns from crystal models of hexagonal layers packing in bnn (eclipsed) and gra (staggered) topologies.

In order to ascertain the correct structure, we performed porosity studies in which information such as surface area and pore size distribution will confirm one structural model or another. Preliminary porosity measurements on COF-41 (Figure 1B) give the Brunauer-Emmett-Teller (BET) surface area of 110 m$^2$ g$^{-1}$ with a Type IV isotherm, characteristic of a mesoporous material. It seems that the obtained surface area was smaller than that of ideal value; therefore, we plan to optimize the synthetic and sample activation conditions.

2. Synthesis of Porphyrin Containing COF (UCLA)

In the pursuit for the preparation of a material in which different metals can be inserted, we are exploring the synthesis of COFs containing porphyrin rings. Porphyrin is a well-defined molecule and much effort has been devoted to study nature of metal substituted porphyrins. Therefore, we implemented the imine condensation of tetra(4-aminophenyl)porphyrin with terephthaldehyde to obtain a new...
porphyrin COF (termed COF-366, Figure 2A) whose condensation manor is the same as COF-300 [1]. COF-366 was prepared by the following procedure: tetra(4-aminophenyl) porphyrin and terephthalaldehyde in a solvent mixture of ethanol/mesitylene/acetic acid were placed in a pyrex tube. The tube was sealed at 77 K and under vacuum, and heated at 120°C for three days. The obtained purple powder was washed with absolute ethanol and immersed in anhydrous tetrahydrofuran for 24 h. The solvent was removed under vacuum at room temperature, yielding a porous material (yield: 79% based on the porphyrin).

A PXRD pattern of COF-366 showed an intense peak at 3.5° matching the unit cell of the simulated crystal, indicating that the distance between neighboring porphyrin rings is roughly 25.6 Å. It is likely that the connectivity of obtained COF has a sql topology (i.e. 4,4-grid type layered material). However, it is not clear if the layers are piled by an eclipsed fashion based on the PXRD data. We will discuss this point later in conjunction with gas adsorption measurements.

This solvent exchanged sample was activated on a supercritical CO2 dryer to obtain porous crystalline solids. The Langmuir and BET surface areas of COF-366 were estimated based on the N2 isotherm measured at 77 K (1,270 and 990 m2 g⁻¹, respectively). It should be noted that the profile of the isotherm is classified into Type I. If the sample has a one-dimensional channel, the isotherm should show a significant step around \( P/P_0 = 0.1 \) to 0.2, because the distance between neighboring porphyrins (\( >20 \) Å) will be large enough to cause micropore filling of \( \text{N}_2 \). The lack of step in isotherms implies that the porphyrin layers are staggered, leading to the micropore. We also tested low-pressure \( \text{H}_2 \) uptake capacity for COF-366 (Figure 2B). The \( \text{H}_2 \) uptake at 1 bar and 77 K is 1.0 wt%. Based on the 77 and 87 K isotherms, the \( Q_{st} \) was estimated. Calculated \( Q_{st} \) at the zero coverage (6.6 kJ mol⁻¹) is better than other COFs (COF-1, 5, 10, 102, 103) except COF-6 (7.0 kJ mol⁻¹). To improve the number, we plan to perform a metalation reaction.

3. Pore Structure from Low-Resolution PXRD Data (UCLA)

One of the difficulties in the COF projects is precise structure determination. Since COFs are synthesized by a condensation reaction of organic materials, it is possible to predict the connectivity of these building units. However unlike MOFs, COFs are comprised of light elements; therefore, obtained PXRD patterns may not provide enough diffraction lines and resolutions to resolve the structure. Indeed, we have encountered the problem when we prepared COF-300 [1]. Recently, ab initio charge-flipping method was developed [2,3]. In this method, unit cell parameters are required (i.e. hkl indices with intensity); while no information related to the connectivity and space group is necessary. Since it can be possible to determine the atomistic connectivity based on the PXRD data, we applied this technique to solve the COF structure.

Originally, we tried to solve the structure of as-synthesized COF-300, because the degree of interpenetration is not clear. However, due to the disordered solvent molecules, we could not obtain meaningful result. Therefore, we used activated COF-300. Figure 3 demonstrates the PXRD pattern of COF-300. We refined the pattern with 2-Å resolution. Using obtained hkl information (including intensity of each diffraction), electron density map was generated on Superflip [3]. Figure 3 (left) demonstrates the electron density map for COF-300 along the c-axis. As we expected, square channel was observed, and the dimension of the pore is almost identical to the space filling model of COF-300.

For the structure determination, reasonable resolution (preferably shorter than bond distance) and intense diffraction lines (at least 10 lines, although it depends the space group) are required. So far, we could not solve COF-366 structure due to the insufficient X-ray diffraction pattern. However, we believe that
pore structure should be revealed when a better PXRD pattern is obtained.

4. Interaction Energies for Imine COFs (Caltech)

We performed ab initio quantum mechanics to investigate the interaction of the H₂ molecules with different building blocks for potential COFs. We decided to use density functional theory (DFT) at M06 level which has been shown to predict accurately interaction energies for non-covalent interactions [4,5] including that of H₂. We used the algorithm as implemented in Jaguar 7.0 [6] using the LACVP basis set.

We chose the structures shown in Figure 4, because we found similar building blocks in the literature that have been synthesized and are reported in the Cambridge structural database [7]. We chose the metals in the light on the easiness of synthesis and handling; such as, Cu, Pt, Cu, and Zn. We also propose to use some other lighter early transition metals like Cr, Mn, Fe, Co, and Ni that given the lighter mass character can help us in gravimetric units. The reasoning behind selection of such targets is that we want the metal site to interact as direct as possible with H₂ molecules, so we chose metal that can form square planar or tetrahedral geometries.

Using our DFT-MO6 method we calculated the adsorption enthalpy ($H_{ads}$) at 298 K and 1 atm (Figure 4, right). From these calculations, the best performers are Cu, Pt, Co, and Zn (i.e., Models P, N, G, A, and J, respectively). The $H_{ads}$ of these complexes are greater than 15 kJ/mol, but these values are still below threshold interaction energy for an optimal H₂ adsorption.

It is worth noting that the degree of metalation is directly related to the value of $H_{ads}$. This can be seen when we compare similar models such as: B vs. F, C vs. G. This is more obvious when comparing D vs. E and L vs. P, where the $H_{ads}$ increased by roughly 5 and 10 kJ/mol, respectively. Considering that the similar trend (addition of more metals to the complex improves the $H_{ads}$) is presented in other systems, it can be said that the H₂ near the metal complexes is stabilized by metals. This behavior can be potentially used to tune the $H_{ads}$ and obtain a desirable system with the adequate degree of soft chemisorption. We can keep increasing our $H_{ads}$ in systems such as models I to P.

Conclusions and Future Directions

This year we experimentally demonstrated how to connect di-, tri-, and tetra-topic building units through condensation reactions (i.e. hydrazone, imine, and boronate COFs). Since the atomistic connectivity and pore structure can be predicted based on the reticular concept, we plan to find candidates for metalation reactions of COFs through modeling studies. In addition, we will predict the binding energy between H₂ and metal unit.

- Material design assisted by the reticular synthesis.
- Theoretical prediction of the binding energy between H₂ and metalated COFs.
- Employ metals to create strong binding sites.
- Supercritical CO₂ drying to optimize the porosity.

Special Recognitions & Awards/Patents Issued

1. The 2010 Centenary Prize from the Royal Society of Chemistry.
2. The 2009 Izatt-Christensen Award.
3. Three of world’s leading chemistry scholars in UCLA.

FY 2010 Publications/Presentations

FIGURE 4. Model structures used for $H_{\text{ads}}$ calculation. The red line indicates the 15 kJ/mol threshold.

References

IV.F.2 New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

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 H\(_2\)/kg system
  - System Volumetric Capacity: 0.9 kWh/L = 0.028 kg H\(_2\)/L system

Accomplishments
- Synthesized a new MOF that exhibits an 11 kJ/mol heat of adsorption for hydrogen. As a comparison, note that unfunctionalized MOFs and carbon-based sorbents typically have hydrogen heats of adsorption around 4-5 kJ/mol. Modeling from several groups indicates that heats of 15-20 kJ/mol will be required to meet DOE hydrogen storage targets.
- Synthesized a variety of new POFs, some with surface areas over 1,500 m\(^2\)/g. These materials have functional groups that can be tailored to increase the hydrogen heat of adsorption. One material synthesized has a hydrogen heat of adsorption of 8 kJ/mol before functionalization.
- Used molecular modeling to rule out catenation as a viable strategy for achieving room temperature hydrogen storage targets in unfunctionalized MOFs.
- Developed a model for MOFs containing alkoxide groups. Identified alkaline earth alkoxides as promising synthetic targets.
- Computationally constructed and subsequently experimentally synthesized a MOF material showing: a) record-high gravimetric uptake of H\(_2\) under cryogenic (77 K) conditions (99.5 mg excess H\(_2\) per g of MOF; 164 mg total H\(_2\) per g of MOF at 70 bar) and b) record-high Brunauer-Emmett-Teller surface area (6,500 m\(^2\)/g [modeled]; 6,200 m\(^2\)/g [measured]).
- Showed that a recently published claim of 6 wt% uptake of H\(_2\) by a comparatively low-area POF material is in error.

Introduction

One option for storing hydrogen on vehicles is to use tanks filled with porous materials that act as
“sponges” to take up large quantities of hydrogen without the need for extremely high pressures. The materials must meet many requirements to make this possible. This project is developing two related classes of porous materials to meet these requirements. All materials are synthesized from molecular constituents in a building-block approach. This allows us to create a wide variety of materials in a tailorabilf fashion. The materials have extremely high surface areas, to provide many locations for hydrogen to adsorb. In addition, they are designed to contain cations that create large electric fields to bind hydrogen strongly but not too strongly.

Approach

The approach in this project is to introduce cations into MOFs and POFs to increase the hydrogen heats of adsorption, which will, in turn, increase the amount of hydrogen that can be stored near room temperature. Many MOFs have enough surface area to meet the DOE hydrogen storage targets if the entire surface were covered with a monolayer of hydrogen. However, at room temperature, the energetic interactions between hydrogen and the surfaces are too weak to bind hydrogen. Thus, we are focused on increasing these energetic interactions. A variety of synthetic chemistries are being explored to increase the chances of success. In addition, molecular modeling is used to help explain experimental observations and provide guidance to the synthetic efforts.

Results

We designed and synthesized the first two examples of unique zwitterionic MOF materials (2H-BTBA and 2Br-BTBA). These materials are permanently microporous and feature fixed cationic sites on vertical struts and fixed anionic sites on horizontal struts. Together the struts (and associated metal nodes) define cavities having sizable electric fields. We reasoned that these cavities might stabilize polarizable molecules (dihydrogen has a small, but finite, polarizability), resulting in enhanced heats of adsorption. As shown in Figure 1, the limiting (low pressure) isosteric heat of adsorption is 11 kJ/mol for H₂ uptake by 2H-BTBA. To our knowledge, this is the first time the zwitterionic concept has been proposed or explored for enhancing framework/gas interactions.

Figure 2 shows the behavior of a new ultra-higharea MOF that was computationally characterized prior to experimental synthesis. Importantly, the computational studies promised record-high uptake of hydrogen by the new material (at 77 K). Using a supercritical activation methodology pioneered at Northwestern we were able to access essentially all of the MOF interior, i.e. little, if any, framework collapse or blockage occurred. The activated MOF exhibited, as predicted, exceptionally high hydrogen uptake. Ultimately, to reach desired ambient-temperature hydrogen storage goals, it will be important to combine the findings here with the advances we are making in the area of improvement of heats of adsorption.

We have synthesized an important new variant of a well-known single-channel MOF. The variant features substituent alcohols that are amenable to conversion to metal alkoxides. We anticipate that this new MOF will enable us to test our computational predictions regarding enhanced interactions between H₂ and MOF components.
We have developed two new families of microporous POFs. The first family of POFs (imine-linked) were synthesized via Schiff base condensation between 1,3,5-triformylbenzene and several readily available diamine monomers. Our facile, one-pot approach results in quantitative yields (~90%) of POFs with the flexibility to incorporate several functional groups in their pores for tuning the interaction of their surface with different guest molecules.

We initially prepared POFs using *para* diaminobenzene and *meta* diaminobenzene. Because the specific surface area of the POF prepared using *meta* diaminobenzene (POF-2) was higher than the POF prepared using *para* diaminobenzene (POF-1), we focused on *meta* diamines as the amine building blocks most likely to give rise to materials with high surface areas. We also optimized the reaction conditions to maximize surface area and micropore volume. A surface area of 1,063 m² g⁻¹ (POF-2) was initially obtained by combining monomers at the beginning of the reaction. Notably, slowly adding amine monomer to a solution of aldehyde monomer significantly increased this surface area by ~50%, to 1,521 m² g⁻¹ (POF-3), which is the highest specific surface area obtained among our synthesized POFs. POF-3 was found to possess H₂ adsorption capacity of 1.5 wt%, at 1 bar and 77 K and a good isosteric heat of H₂ adsorption of 8.2 kJ mol⁻¹ at low coverage (Figure 3a). In addition, the H₂ adsorption measurement performed for this POF, at high pressures and 77 K, shows an increase in H₂ uptake with the increase in pressure giving maximum H₂ uptake of 4.3 wt% at 70 bar (Figure 3b). Pore size distribution analysis for POF-3, performed using non-local density functional theory, confirms a primary pore width of 6 Å. Interestingly, even though the synthesized POFs are amorphous, their pore size distributions are not wide.

The second POF family is based on reaction between phloroglucinol and aldehydes. This is a straightforward reaction that produces highly cross-linked polymers. The polymerization took place under solvothermal conditions using dioxane as solvent at 220°C producing solid materials in high yield (~90%). These synthesized POFs contain large numbers of hydroxyl groups which are available for functionalization. All these POFs are microporous materials, and they exhibit specific surface areas from 600 to 900 m² g⁻¹ and a main pore width of 6 Å. Scanning electron microscope images of POF-4 show spherical particles with smooth surfaces in the range of 1–3 μm. Phloroglucinol POF samples were tested for H₂ adsorption at 77 and 87 K up to atmospheric pressure (Figure 4a). POF-4 shows H₂ uptake of 1.25 wt%; POF-5 and POF-6 show uptake of 1 wt%. Heat of H₂ adsorption is estimated to ~8.3 kJmol⁻¹ at low coverage for all samples (Figure 4b).

A rather astonishing experimental and computational report of very substantially enhanced uptake of H₂ by a permanently microporous, organic framework material appeared earlier this year in the literature (*Angew. Chem., Int. Ed.* 2010, 49, 3330-3333). The report was remarkable on three counts. First, doping with a very small amount of lithium led to a quadrupling of hydrogen uptake. Secondly, the material features only a modest internal surface area – raising the question of how the material could imbibe such large amounts of H₂. Thirdly, we had previously examined a related material (unpublished) but not encountered the spectacular enhancements reported in the new article. While we have previously described large lithium-based enhancement effects upon sorption of hydrogen by three MOF materials, the mechanism invoked to account for the MOF results is inapplicable to the new POF material. Follow-up work in our labs has now clearly established that the stunning new results described in
Using classical grand canonical Monte Carlo (GCMC) simulations, hydrogen storage and delivery in eight representative MOFs was investigated. The simulations demonstrate that the optimal isosteric heat of adsorption (Qst) for maximum hydrogen delivery using MOFs is approximately 20 kJ/mol. We considered the delivered hydrogen as the amount adsorbed at 120 bar minus the amount adsorbed at 1.5 bar. The results also suggest that increasing Qst for MOFs with large surface areas is required to attain current hydrogen storage targets in terms of deliverable capacity. Using the same model, hydrogen adsorption isotherms in 20 MOFs were obtained from GCMC simulations and used to develop quantitative correlations to quickly estimate the H₂ uptake of MOFs at 120 bar from the free volume of the adsorbent. These correlations were subsequently validated with a diverse set of 22 MOFs that were not used in developing the correlations.

We also used classical GCMC simulations to assess whether catenation is a viable strategy for meeting DOE hydrogen storage targets. We simulated hydrogen uptake in a series of catenated MOFs along with their non-catenated counterparts. The MOFs were chosen to cover a wide range of pore sizes and free volumes. The results indicate that catenation does increase the heats of adsorption, as expected. However, the effect is not enough, at room temperature, to compensate the loss of free volume that also arises from catenation. These results indicate that catenation is not a viable strategy for meeting room temperature hydrogen storage targets in unfunctionalized MOFs. Strong binding sites that increase the heats of adsorption will be required. These calculations support the main premise of this project.

Finally, we have developed a model for simulating hydrogen uptake in MOFs containing alkoxide groups. MP2 calculations with a large basis set (6-311+G**) were performed for a hydrogen molecule in 200 different geometries near the alkoxide group, and these energies were fit with a combined Morse + Coulomb + Lennard-Jones potential. Models were developed for a range of metal alkoxides, including Na, Li, Mg, and some transition metals. GCMC simulations have been performed using these models to predict the hydrogen adsorption isotherms. In addition, the Second-order Møller-Plesset perturbation theory calculations provide useful details of the orbitals involved in the hydrogen-metal interactions. There has been much attention in the literature on Li-functionalized MOFs, but our calculations indicate that Mg provides a larger enhancement in hydrogen uptake. Based on these calculations, synthetic efforts in the group are now focused on Mg alkoxides in addition to Li.

**Conclusions and Future Directions**

**Conclusions**

- Multiple strategies have now been demonstrated in our labs for introducing sites into MOFs that increase hydrogen heats of adsorption, including framework reduction, alkoxide formation, and zwitterionic cavities. These provide a powerful platform for tailoring MOFs to increase the heats of adsorption toward meeting DOE hydrogen storage targets.
- One MOF synthesized in our labs exhibits an 11 kJ/mol heat of adsorption for hydrogen.
- A variety of new POFs, some with surface areas over 1,500 m²/g, have been synthesized in this project. These materials have functional groups that can be tailored to increase the hydrogen heat of adsorption. One material synthesized has a hydrogen heat of...
adsorption of 8.3 kJ/mol at low coverage before functionalization.
- We showed that a remarkable new claim in the literature of 6 wt% uptake of hydrogen by a comparatively low-area POF material is, in fact, in error.
- Catenation is not a viable strategy for achieving room temperature hydrogen storage targets in unfunctionalized MOFs.
- A new MOF displaying record-high internal surface area and record-high (cryogenic) uptake of H₂ (total H₂ of 14.4 wt%) has been synthesized.
- Modeling indicates that alkaline earth cations may be more promising than alkalis for increasing hydrogen heats of adsorption in alkoxide-containing MOFs.

Future Directions
- Synthesis of Mg and other alkaline earth alkoxide MOFs.
- Characterization of a new “framework reducible” MOF designed to localize added dications (i.e. alkaline earth and transition-metal species) on the reduced strut, rather than at comparatively inaccessible metal-carboxylate node sites.
- Functionalization of POFs, especially with alkaline and alkaline earth alkoxides.
- Initiation of POF synthesis using “click” chemistry.
- Combination of strategies for introducing cations into MOFs and POFs and strategies for producing MOFs and POFs with very large surface areas.
- Modeling of additional metal-substituted MOFs.
- Modeling of POFs.

Special Recognitions & Awards/Patents Issued
1. Profile of Randy Snurr and his group’s work on hydrogen storage in the May/June 2010 issue of The Pennsylvania Gazette, the alumni magazine of the University of Pennsylvania.
2. Joseph Hupp, Distinguished Alumni Lectureship, Department of Chemistry, Michigan State University, April, 2010.

FY 2010 Publications/Presentations
6. Multiple Presentations at universities and conferences
IV.F.3 Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

Objectives

- Synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H₂ storage at 300 K to 400 K and moderate pressures.
- Adapted volumetric measurements to enable rapid screening tests (RSTs) at high-pressure, towards Go/No-Go decision point. Validate RSTs against published activated carbon and spillover materials at P<80 bar and 298 K.
- Use RST to down-select MMOFs and determine effect of structure and surface chemistry.
- Explore methods for pressure-induced hydrogen/gas trapping.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (bar)</th>
<th>wt% of Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMOF-8</td>
<td>20,70, &amp; 100</td>
<td>0.09,0.37,0.52</td>
</tr>
<tr>
<td>+5% Pt/AC</td>
<td>20,80, &amp; 100</td>
<td>0.38,1.4,1.80</td>
</tr>
<tr>
<td>+Bridge</td>
<td>20,70, &amp; 100</td>
<td>0.74,2.68,3.94</td>
</tr>
<tr>
<td>+IRMOF-8*</td>
<td>80</td>
<td>1.5</td>
</tr>
<tr>
<td>+IRMOF-8</td>
<td>75-85</td>
<td>0.306 ± 0.026</td>
</tr>
<tr>
<td>+IRMOF-8*</td>
<td>75</td>
<td>0.78</td>
</tr>
<tr>
<td>+Zn(NDC)(TED)</td>
<td>82</td>
<td>1.12</td>
</tr>
<tr>
<td>+Zn,(bpdcl),(bpy)</td>
<td>20</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.63</td>
</tr>
<tr>
<td>+Ni(HCOO)₆[Ni-FA]</td>
<td>20</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.93</td>
</tr>
<tr>
<td>CuBTC (HKUST-1)</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>+5% Pt/AC</td>
<td>20</td>
<td>0.165</td>
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<tr>
<td>+5% Pt/AC</td>
<td>20, 80</td>
<td>0.61, 1.32</td>
</tr>
<tr>
<td>+MMOF=0*</td>
<td>80</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*Meets or Exceeds Benchmark for PtC/IRMOF8 in Ref. 1.
†Reproducibility Measurements, four measurements
‡Increased mixing intensity relative to b

Accomplishments

- A total number of eight MMOFs synthesized, with variations in surface chemistry and porosity.
- RST was developed and validated against published data for GX-21 activated carbon. Propagation of error and reproducibility measurements insured precision of method and demonstrated effect of preparation conditions when mixing with standard catalyst.
- IRMOF-8 with Pt/C confirms literature data; multiple tests indicate reproducibility of volumetric RST method and track how subtle variations in synthesis leading to increased/decreased uptake.
- PtC/CuBTC and PtC/IRMOF8 showed importance of preparation conditions: pretreatment, handling, mixing, and gas exposure are key parameters to ensure reproducibility.
- Oxygenated ligand exceeds uptake of IRMOF-8 benchmark with rapid initial uptake.
- On-going development of models to understand P-switching behavior and validate experiment with theory.
Introduction

The term hydrogen spillover has been used to describe a synergistic effect between high-surface area adsorbents and associated catalysts. The associated catalyst may act to dissociate molecular H\textsubscript{2} 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 to a much higher uptake than expected for the metal catalyst alone. To date, hydrogen storage reports for spillover systems suggest moderate temperature adsorption (i.e. 300 K) can be achieved, with uptake approaching DOE goals at 298 K and 100 bar. The highest uptake reported for spillover materials has utilized MMOFs as the receptor for spilled over hydrogen: bridged (‘br’) PtC/IRMOF8 achieved 4 wt% excess adsorption at 100 bar and 298 K [1]. Independent groups have demonstrated up to 4.2 wt% at 6.9 MPa after extended equilibration for brPtC/IRMOF8 [2]. As the process is highly dependent upon synthesis, measurement, and catalytic particle size, [3,4] the process remains poorly understood. It is anticipated that optimization of the MMOF structure, surface chemistry, and porosity will further increase uptake via spillover. Meeting DOE hydrogen storage targets at moderate temperature will have significant engineering advantages for mobile applications, as temperature of operation has implications for system weight.

Approach

The project relates to materials development and optimization of surface chemistry, crystal and pore structure, catalyst, and system parameters for the hydrogen spillover phenomenon. In this stage of the project, we are screening materials against benchmark spillover data for brPtC/IRMOF8 mentioned above. Our current gravimetric goals are relative to this benchmark in the literature, with the assumption that bridging will further improve excess adsorption to bring total uptake to DOE goals. Prior to bridging, the PtC/IRMOF8 material had 1.4 wt% and 1.8 wt% of hydrogen uptake at 298 K and 80 and 100 bar, respectively [1]. Other relevant literature data listed in Table 1 include variation of MMOF structures in Ref 5. The project is currently exploring materials without bridging, as bridging has unknown effects on the surface chemistry and structural parameters we hope to optimize. The project is currently using secondary spillover studies such that the catalyst, or H species ‘supply’, remains constant in order to independently determine the effect of MMOF structure. A later phase will explore direct incorporation of catalytic sites into the MMOF structure for further optimization of the hydrogen spillover process. As spillover equilibration times may be significant, a RST (i.e., one-point isotherm at 80 bar) has been developed and validated against published data [6] for GX-31 superactivated carbon. Materials that exceed benchmark uptake, or are deemed interesting from a mechanistic standpoint, are moved from the volumetric RST to a gravimetric unit equipped with mass spectrometry for more detailed mechanistic and temperature studies. The latter, along with rate determinations, are relevant to the temperature-switching for decoupled adsorption-desorption optimization, outlined above.

Our approach for optimization of system parameters for spillover considers decoupling of adsorption and desorption, such that optimization of temperature and pressure for each may be considered separately. Towards this end, we are exploring MMOF structural changes that are pressure-induced in order to incorporate this phenomenon into hydrogen trapping, via both physisorption and hydrogen spillover. We are validating theoretical models with extensive adsorption isotherms for a MMOF with demonstrated pressure-induced structural changes (Zn\textsubscript{2}(bpdc)\textsubscript{2}(bpee)), and exploring the effect of adsorption time, adsorbate, pressure, and temperature. Once validated, it is anticipated the theoretical model will be able to predict the feasibility of using various MMOFs for hydrogen trapping at pressures and temperatures of interest.

Results

A total of eight MMOFs were synthesized in 2009-10 (Figure 1), with variations in ligands and secondary building units (i.e. corners) leading to expected differences in structure, surface area, pore dimension, and surface chemistry. RST adsorption results (Figure 2) show no real trend with surface area or pore dimension, contradicting previous claims, [5] and suggesting coverage from spillover is not related to surface area in a simple fashion. Two PtC/MMOFs had uptake exceeding that of literature benchmarks (IRMOF8 and MMOF=O, Figures 1-2 a-b). The latter significantly exceeded benchmark data, with 2.4% at 80 bar and 298 K, suggesting that surface chemistry will play a predominant role in surface coverage via spillover. These findings (correlation with surface chemistry not area) are consistent with a chemical kinetic consideration of spillover, in which the relative rates of adsorption, desorption, and surface diffusion must be considered [7].

Previous published spillover data has suffered from reproducibility issues. Recent data for brPtC/IRMOF8 varies from 1.5-4.0 wt% at 298 K and 100 bar; [4] with little concrete explanation provided to explain the discrepancy. Therefore, PtC/IRMOF8 was chosen to
study the effect of various synthesis and measurement parameters on instrument precision and material reproducibility. The accuracy of the RST measurement is calculated at ±0.026 mmol (±0.05 wt% for 100 mg sample) via propagation of error when a He blank measurement is done to determine the differential pressure due to volume differences. Validation of the equipment with GX31 shows agreement within 20% relative to published data [6] at 80 bar, a difference which can be attributed (in part) to slight variations in pretreatment and sample. When equipment, sample, and pretreatment are the same, the RST reproduces a multiple point isotherm within 8% at 80 bar. For PtC/IRMOF8, multiple experimental RST replicates with identical procedural and temporal conditions show a standard deviation of less than 10% (i.e. 0.31 ± 0.03 wt%, Table 1), even with a 10 bar variation in the equilibrium adsorption pressure (i.e. 75-85 bar). With this level of precision in uptake, we were able to confirm that increased mixing intensity leads to increased uptake via spillover for PtC/IRMOF8: from 0.31 wt% to 0.78 wt%. The increase cannot be directly attributed to differences in catalyst size, as the catalyst source is identical in the secondary spillover studies, unlike previous reports [4,8]. Despite the increased uptake, no significant changes in MMOF structure were detected by power X-ray diffraction, suggesting

FIGURE 1. Structures of MMOFs synthesized and tested in 2009-10: (a) MMOF=O; (b) Zn\textsubscript{10}(NDC)\textsubscript{10} or IRMOF-8; (c) Zn(NDC)(TED)\textsubscript{5.5}; (d) Cu\textsubscript{2}(BTC)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3} or Cu-BTC; (e) Ni(NCOO)\textsubscript{5} or Ni-FA; (f) Zn(BDC-OH)(TED)\textsubscript{5.5}; (g) Zn\textsubscript{3}(BPDC)\textsubscript{3}(BPY).

FIGURE 2. Rate data for one-step adsorption isotherm, i.e. 'rapid-screening test'. Data is labeled as in Figure 1.
mixing intensity may affect particle size and/or interface. Currently, additional mixing parameters are being tested with alternate characterization of the physical properties after mixing. Sample handling for PtC/CuBTC is also shown to drastically affect overall uptake and material integrity. When mixed in an inert environment, PtC/CuBTC has 0.61 wt% at 20 bar, exceeding published reports by a factor of three. The uptake due to spillover at low-pressure is found to be pronounced using gravimetric methods (Figure 3).

In an attempt to develop a means for hydrogen trapping and to facilitate decoupled optimization of adsorption vs. desorption, work to validate and understand pressure-induced MMOF structural changes is ongoing. Although adsorption-induced gate opening (GO) in MMOFs is well documented, it is poorly understood. Experimental data collected for Zn₄(bpdc)₂(bppe) suggest the process is highly sensitive to adsorbate, time, temperature, and pressure. The process behaves consistently, but in a unique and often unpredictable way. Parallel theoretical studies are seeking to understand experimental data and validate models, and further, to use the concepts towards predictive understanding of the phenomenon. Current studies have used well-defined and analogous systems to demonstrate that GO is favored when the relative gas-solid interaction energy exceeds the energetic cost of structural rearrangement. Parametric studies with mean-field theory are also on-going. We anticipate the modeling will provide a means to expedite experimental studies such that the behavior of a MMOF can be correlated to its adsorption potential. Such modeling is intended to provide a road map to utilize this process for hydrogen trapping.

Conclusions

Hydrogen spillover continues to show promise for considerable excess adsorption at moderate temperatures and pressures (i.e. 300 K, 100 bar). On-going studies aim to provide a mechanistic understanding of the spillover process. Current data suggest that surface chemistry, rather than surface area or structure, is the controlling factor in maximizing surface coverage via spillover. Further tests are on-going to validate this finding and increase mechanistic understanding. First, however, tests with PtC/IRMOF suggest laboratory environment and mixing conditions—rather than (or in addition to) catalyst particle size—may lead to significant differences in uptake via catalytic spillover and the effect is now being studied in a systematic way. Similarly, uptake for PtC/CuBTC is increased 3-fold (at 20 bar; 298 K) relative to published literature data when mixed in an inert environment. With the validated RST, introduction of a carbonyl group to the ligand led to 2.4 wt% (80 bar, 298 K), and significantly exceeded

![Figure 3](image-url)

**FIGURE 3.** (i) Hydrogen uptake for (a) Cu-BTC, and (b) Cu-BTC+PtAC, mixed 9:1 in an inert atmosphere, with adsorption temperature as noted. (ii) X-ray diffraction of (a) and (b) shows crystalline structure, whereas (c) mixing in atmosphere destroys crystallinity; (d) crystal structure in sample 'b' is retained after H₂ measurement shown in (i). Mixing in inert environment contributes to the three-fold increase in H₂ uptake for 'b' relative to published literature, shown as dotted lines in (i) at 20 bar and 298 K for (e) Cu-BTC, and (f) PtC+Cu-BTC. (iii) Adsorption isotherms for (a) at 77 K.
benchmark data (1.4 wt%, 80 bar, 298 K), prior to bridging. We anticipate uptake can be further increased with additional modifications of structure, bridging, and careful consideration of synthesis conditions. Methods to incorporate pressure-induced hydrogen trapping into the materials is on-going, and will provide a further means to increase pressure savings for the storage system relative to system targets.

**Future Directions**

- Finalize systematic studies of mixing environment on uptake.
- Detailed study of ligands with modified surface chemistry.
- Introduce pore modification in synthesis of like compounds.
- With validated measurements and optimized mixing conditions, develop correlations between porosity, surface area, and surface chemistry of PtC/MMOFs with overall H₂ uptake, kinetics, and hysteric adsorption-desorption.
- Write and submit papers on: (1) methods validation and reproducibility with a focus on PtC/IRMOF8 and brPtC/IRMOF8; (2) sample preparation on PtC/CuBTC; and (3) variation of MOF structure/chemistry with secondary spillover studies.
- Validate theoretical imbibition study with experiment; evaluate pressure-trapping of MOF structures at ambient conditions; assess opening via spilled over H.
- Evaluate potential for temperature trapping with PtC/MMOFs that exceed benchmarks using combined multiple temperature adsorption isotherms and temperature-programmed desorption studies.
- Develop MOF containing built-in catalytic functionality using metalloligands.
- Independent measurement of Tsao et al. sample.

**2010 Publications/Presentations**

5. A. Lueking, Invited Department Seminar at Chemical Engineering Penn State University, February 11, 2010.

**References**

Objectives

To develop storage materials that enable high H₂ loading under more economical temperature and pressure ranges; that have more controllable uptake/release dynamics; and that have moderate losses over a charge/discharge cycle. By using electric field enhanced adsorption, we expect to:

- Enhance adsorption binding energy (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 hydrogen charge/discharge dynamics using field strength as a control variable in addition to thermal and/or pressure modulation.

Technical Barriers

Several technical barriers from the Storage section (part 3.3) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan are addressed by this project:

(C) Efficiency
(E) Charging/Discharging Rates
(J) Thermal Management
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The project centers on the fundamentals of hydrogen adsorption in porous adsorbents under the influence of externally applied electric fields. Electric-field enhancement of binding (capacitive storage) can integrate well with electric drive systems and the insights gained from these studies will be applied toward the design and synthesis of storage materials more likely meet DOE hydrogen storage targets. Outcomes of this work are expected to include:

- New insights into H₂ 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 using field strength as a control variable in addition to thermal and/or pressure modulation.

Accomplishments

- Continued of ab initio computations exploring effects of external field on electron density in organic constituents typical of metal organic frameworks. Modeling results are being used to guide chemical synthesis effort (e.g. organic linker selection).
- Refined capacitor test-cell design for use in measuring sorption under an applied electric field. Fabricated custom sorption rig – measurements underway.
- Substrate synthesis efforts now include more polarizable organic linkers. Focus remains on metal organic framework and related substrates.
- Modified dielectric properties of substrates and characterized using electrochemical impedance spectroscopy. Static dielectric constant, loss tangent, and leakage current are being measured and used to estimate time constants and losses over a charge-discharge cycle.
- Conducted experiments where dielectric breakdown was intentionally induced across the capacitor in the presence of hydrogen (addresses an important safety issue).
- Designed a neutron diffraction cell for use with static electric fields. Cell will ultimately provide insight into specific binding site locations.
Introduction

Capacitive storage involves establishing an electric field across a porous dielectric material designed to adsorb hydrogen. The field acts on localized regions of high polarizability to enhance binding within the cavities of the porous network through induction and dispersion forces (we hope by 10-15 kJ/mol). The enhanced binding energy, induced by the substrate’s response to the field, should allow storage goals to be met at more practical combinations of temperature and pressure. Upon discharge of the “capacitor” the electric field is removed, and in turn, the induced electrostatic moment stabilizing hydrogen dissipates. Thus a portion of the thermodynamic driving force for binding can in principle be switched on and off at will. Furthermore, some of the energy required to bind and release hydrogen is reversibly introduced into the system in the form of an electric field. Losses are expected to include dielectric losses and any leakage current through the capacitor during storage. As the field is removed, desorption will be promoted and cooling the substrate is expected. The decrease in temperature provides a larger driving force for heat diffusion into the substrate. Thus, improvements in the release dynamics and improved control over the release are anticipated. 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 more practically accessible temperatures and pressures. For example, operating over the range –40 to 60°C should become less onerous. Charging and discharging, system cycling, and transient system response can now involve field modulation in addition to thermal and/or pressure swings and heat exchange within the adsorbent bed. The other outstanding challenges detailed in the On-Board Hydrogen Storage System Technical Targets, such as delivery pressure, charging/discharging kinetics, and system fill time may also benefit directly.

Approach

It is well-known that manipulation of temperature and pressure provides benefits in gas storage, however, it appears that combinations of these two intensive variables alone will not likely yield the desired end result, namely, high hydrogen 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 should enhance the hydrogen binding energy. This may involve a combination of enhanced binding energies, creation of new binding sites and/or formation of hydrogen clusters (as is reported in both clathrate-hydrate cages [1] and metal organic frameworks [2]). The key challenge is to determine how best to create localized polarizability within porous adsorbents. Electrostatic stabilizing forces can be locally enhanced by judiciously increasing the polarization of the host substrate at specific sites, or within sub-structures (cavities) favorable to molecular clustering. The metal organic frameworks (MOFs) are serving as the starting point for developing the new dielectric materials [3]. 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 (of specific interest to us is the local polarizability). Thus in addition to being high surface area structures (>3,000 m²/g), MOFs can be chemically tailored by modifying the organic linkers between metal centers. This can potentially be done through introduction of more polarizable atoms and functional groups, tuning the band gap, and/or varying core metal electronic properties. Related materials such as the zeolitic imidazolate frameworks are also being examined. Other potential 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 [4]. Our approach to developing these materials (structured dielectrics) combines both computational guidance and experimental probes/testing.

Results

Our recent computational modeling has focused on simple models for the structural motifs featured in the Cu-1,3,5-benzenetricarboxylate (BTC) MOFs and the effect on an applied electric on their interaction with hydrogen. For this purpose, we chose the copper acetate structure since it shares several structural similarities with Cu-BTC while consisting of discrete molecular units in the solid state. For example, the pinwheel coordination geometry is present about the copper center. Figure 1(a) shows a candidate binding geometry for the hydrogen molecule at the copper site. Quantum chemical calculations have been performed on this model in vacuum and with an applied electric field. In Figure 1(b), the calculated electrostatic potential has been projected onto the calculated total electron density for the molecule. It can be clearly seen that applied electric field induces a dipole in the molecule, and the calculated binding energy is enhanced by around 5 kJ/mol for an applied field of 20 MV/cm. The computations suggest that in order to effect the desired change at more modest field strengths, higher polarizability and/or low band gap ligands (linkers) are needed (Figure 2). Thus, new
ligands are being incorporated into MOFs with the aim of altering framework polarizability (e.g. replacing the 1,3,5-benzenetribenzoate [BTB] links in MOF-177 with more polarizable ring motifs or phosphazene derivatives). Known MOFs were also synthesized for baseline testing. A custom gas adsorption rig was also commissioned. Experiments are now underway using this rig and the matching capacitor assembly (Figure 3). We will also explore the role played by the electrostatic moment in the gas by comparing field-induced adsorption of hydrogen and carbon dioxide, which have very different electrostatic moments than hydrogen (e.g. relative quadrupole moments: CO$_2$ 4.3 esu; H$_2$ 0.662 esu [5]). We expect to have a robust quantitative assessment of the electric field enhancement on hydrogen adsorption in selected MOFs next year. Electrochemical impedance spectroscopy is being used to determine dielectric properties and estimate losses. Losses specific to electric field swing adsorption include the dielectric losses upon a charge-discharge cycle, which involves a time-varying (periodic) electric field. A simple (idealized) way to envision these is energy dissipation as a result of dipole rotation generating friction in the time-varying field. Dielectric losses over a charge-discharge cycle for a uniform dielectric in a periodic field can be estimated from classical
electrostatics \[6\] as: dielectric loss = \(\varepsilon'' E^2 \omega / 8\pi\)
where \(\varepsilon''\) is the imaginary part of the complex dielectric constant, \(E\) the electric field strength (e.g. MV/m), and \(\omega\) is the frequency of the periodic electric field. Calculations suggest that dielectric losses should be small (<1 watt/liter of dielectric) in the hydrogen storage systems, due primarily to the low frequency variation in the electric field over a charge-discharge cycle. Estimates of the leakage current have been made using electrochemical impedance spectroscopy and results fit to the Randles "equivalent circuit" model for a real capacitor. Initial estimates of leakage in MOFs placed in our current test rig were too high, but by increasing dielectric constants (via molecular design) and altering the electrode area to electrode gap ratio in the capacitor, it appears be possible to maintain charge for days. The ability to favorably modify the dielectric properties of MOFs were demonstrated (Figure 4). A capacitor cell for use in neutron diffraction experiment was also built. It will ultimately allow us to monitor hydrogen adsorption at specific sites. Hydrogen bonding sites will be refined from the neutron diffraction data and used to improve the next iteration in materials design/synthesis.

Conclusions and Future Directions

- Capacitive storage appears to offer a practical means of enhancing hydrogen storage. 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).
- The energy used to establish the field can largely be recovered upon discharge (the dielectric losses, and leakage currents are within acceptable limits).

Work in progress:
- Conducting quantitative demonstration of enhanced hydrogen loading.
Further assessments of H₂/substrate compatibility under dielectric breakdown.

Design/synthesis of high polarizability porous adsorbent frameworks.

Results will ultimately position us for design and testing of an integrated storage system.

Special Recognitions & Awards/Patents Issued


FY 2010 Publications/Presentations


References


IV.G.1 Extended Dormancy, Vacuum Stability, and Para-Ortho Hydrogen Conversion in Cryogenic Pressure Vessels

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Start Date:  October 1, 2004
Projected End Date:  September 30, 2013

Objectives

- Test thermal endurance and heat transfer rate.
- Test composite vessel outgassing and vacuum stability.
- Test para-ortho conversion at cryogenic temperatures and full scale (10 kg H₂).

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(D) Durability/Operability
(H) Balance of Plant (BOP) Components
(O) Hydrogen Boil-Off

Accomplishments

- Held 10.2 kg liquefied hydrogen (LH₂) in a 95% full vessel for eight days with no evaporative losses or hydrogen extraction.
- Demonstrated that para to ortho hydrogen conversion stabilized vessel temperature for about one week.
- Demonstrated capacity to maintain 75% of the liquid hydrogen stored in vessel after one-month parking.
- Directly measured para-ortho hydrogen conversion with rotational Raman spectroscopy.
- Developed and tested a kinetic model for para-ortho hydrogen conversion.
- Conducted vacuum stability tests and chemically analyzed composite outgassing.

Introduction

Cryogenic pressure vessels have potential for enabling practical vehicle 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. Low sensitivity to heat transfer enables 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. Further increases in thermal endurance may result from endothermic para-ortho conversion during long parking periods.

TABLE 1. Progress toward Meeting DOE On-Board Hydrogen Storage Technical Targets

<table>
<thead>
<tr>
<th>Lawrence Livermore Cryogenic Pressure Vessels</th>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010 Target</th>
<th>2015 Target</th>
<th>2007, Gen-2</th>
<th>2009, Gen-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>kWh/kg</td>
<td>1.5</td>
<td>1.8</td>
<td>1.8</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>Energy Density</td>
<td>kWh/L</td>
<td>0.9</td>
<td>1.3</td>
<td>1.04</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>Storage System Cost</td>
<td>$/kWh</td>
<td>4</td>
<td>2</td>
<td>9</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

§From Argonne and TIAX [1,2,3]
Approach

In previous years we dedicated our effort to demonstrating cryogenic pressure vessel weight and volume performance by building a prototype that met the DOE 2015 targets. This year we directed our attention to other critical issues: evaporative losses and long-term vacuum stability. The key experiment consisted on parking a vehicle with a nearly full (95%) cryogenic pressure vessel for a month to determine (1) heat transfer rate; (2) vacuum stability; and (3) para-ortho conversion. The results indicate that high performance thermal insulation, heat absorption due to para-ortho conversion, and favorable thermodynamics enabled completion of the 30-day experiment while retaining 75% of the initial hydrogen.

Results

Hydrogen has two phases of nuclear spin orientation: para-H₂ and ortho-H₂. Para-H₂ is the low energy form stable at liquid hydrogen temperature (20 K). As the hydrogen heats up from 20 K equilibrium shifts toward ortho-H₂, reaching normal composition (25% para and 75% ortho) at room temperature [4]. Liquid hydrogen (typically delivered as para-H₂ for stability) will therefore convert to ortho-H₂ as it warms up, absorbing considerable thermal energy (700 kJ/kg – comparable to vaporization) in the process. Para-ortho H₂ conversion has therefore much potential for augmenting thermal endurance.

While it may be possible to detect and quantify para-ortho H₂ conversion from calorimetry alone, LLNL has directly measured para-ortho population ratios using rotational Raman spectroscopy. In this approach, a hydrogen sample is collected inside a Raman cell (a small pressure vessel with windows at each end). A frequency-doubled Nd-YAG laser enters through a window in the Raman cell and the light is analyzed after interacting with the hydrogen (Figure 1). Most of the light leaving the Raman cell has the same frequency as the laser. This is filtered out leaving only light of different frequencies (inelastic scattering). A very small portion of the incident laser light scatters off the hydrogen molecules. An even smaller portion of the scattered photons give up some of their energy to the molecules. Thus they scatter with slightly less energy and are therefore shifted to slightly longer wavelengths. This is the Raman effect. The amount of this Raman scattered light is directly proportional to the number of molecules in each rotation energy state. Each energy state yields a slightly different Raman wavelength. Thus we are able to make a direct measurement of the relative populations of para (even quantum number rotational energy states) and the ortho (odd quantum number energy states) molecules.

The para-ortho conversion experiment was conducted onboard LLNL’s hydrogen-fueled Prius. The vessel was filled to 95% capacity (10.2 kg) with LH₂ and parked outside, exposed to the daily sun, to capture worst-case conditions. The vessel warmed due to ~4.5 Watts of environmental heat transfer, until reaching maximum working pressure of 5,000 psi after 8.25 days of parking (Figure 2). At this point, we released 1.2 kg H₂. This both reduced the pressure to 3,000 psi and cooled the remaining 9 kg of H₂ from ~70 K to ~60 K.

Para-ortho conversion occurred during the second pressurization cycle (days 12-24) as indicated from rotational Raman spectroscopy measurements (blue line in Figure 2). During this time, endothermic para-ortho conversion absorbs most of the environmental heat transfer, leading to a considerable reduction (from ~4.5 Watts to ~1 Watt) in apparent heat transfer into the vessel. Apparent heat transfer is calculated from the pressurization rate assuming no para-ortho conversion. Calculating the total internal energy absorbed (blue area in Figure 2) and dividing it by the baseline heat transfer rate (4.5 W), we were able to determine that para-ortho conversion increased vessel dormancy by ~1 week.

After day 24, para-ortho H₂ conversion was nearly complete as the composition approached equilibrium (Figure 3), and apparent heat transfer returned to the baseline level (4.5 W). After a few more H₂ extractions,
In addition to conducting the first (to the authors’ knowledge) full-scale para-ortho hydrogen conversion experiments, we also developed and tested a para-ortho conversion model. This model is derived from ortho-para conversion experiments in a small vessel (2 cm³) [4] and solves a set of differential equations that determine para-ortho composition as a function of density, temperature, and initial composition. After appropriate tuning, the model performed well for the full-scale vessel (Figure 3) accurately predicting para-ortho composition during the experiment. Further experiments are planned to validate the model under varying densities, with the final goal of determining how to best design cryogenic pressure vessels that take advantage of para-ortho conversion for considerable increases in thermal endurance.

In addition to the para-ortho experimental and modeling activities, we also completed outgassing experiments from fiber-wound pressure vessels. In these experiments, we tested the outgassing behavior of composite pressure vessels by storing them inside a steel vacuum chamber at specified temperatures (20, 60 and 80°C). We tested 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 results can be summarized as follows:

1. Temperature is the most important factor in determining outgassing.
2. Vacuum quality remains high if the vessel remains cold (below 250 K).
3. Pressure cycling plays a relatively minor role in outgassing.
4. Vacuum curing did little to reduce outgassing and it is most likely not worth the effort. UV coating considerably increased outgassing and is therefore not recommended for cryogenic pressure vessels.
5. Chemical composition reveals a series of ~10 hydrocarbons that are produced in all experiments. The main species produced are n-heptanone, acetic acid butyl ester, and acetone – all oxygenated hydrocarbons most likely derived from the epoxy used in the tank.

Detailed composition and outgassing amounts are now being used for selecting appropriate getters that may preserve vacuum during long periods of operation.

**Conclusions and Future Directions**

- Demonstrated 1-month cryogenic vessel dormancy while extracting only 2.5 kg H₂.
Para-ortho conversion proved synergistic with cryogenic pressure vessel operation, extending vessel dormancy by approximately 1 week by absorbing heat during endothermic conversion. Developed and tested a kinetic conversion model of para-ortho conversion. Completed outgassing experiments that characterized the effect of temperature, surface treatment, and pressure cycles. Outgassing composition was also determined and is being used to find appropriate getters for long-term vacuum stability.

References


FY 2010 Publications/Presentations


2. High Density Hydrogen Storage in Cryogenic Capable Pressure vessels, Salvador Aceves, Invited presentation, Purdue Hydrogen Symposium, Purdue University, Indiana, April 2009.


IV.G.2 Lifecycle Verification of Polymeric Storage Liners

Objectives

Perform durability qualification measurements on specimens of Type IV storage tank liners (polymers) at the nominal working pressure using thermal cycling commensurate with the design lifetime, followed by permeation measurements to determine if the steady-state leakage rate in the tank could potentially exceed the specification for hydrogen fuel cell passenger vehicles.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Storage section (3.2.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(D) Durability/Operability

Technical Targets

This project 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 (FY) 2010: 90/90; FY 2015: 99/90
- Environmental Health and Safety:
  - Permeation and leakage: meet or exceeds applicable standards.
  - Loss of usable H₂ (g/h/kg H₂ stored): FY 2010: 0.1; FY 2015: 0.05.

Accomplishments

- Completed 3,000 temperature cycles on a specimen of Lincoln Composites Type IV tank liner (high-density polyethylene, HDPE) and performed periodic permeation measurements on liner specimen to assess temperature-cycling induced changes in permeation coefficients.
- Verified that permeability coefficients have changed only slightly through 3,000 temperature cycles.
- Observed small systematic changes in activation energy $E_a$ and constant $P_0$ in the liner during temperature cycling.
- Designed and assembled improved temperature-cycling apparatus. First temperature cycling results with new apparatus expected in 4th quarter of FY 2010.

Introduction

Modern high-pressure hydrogen storage tanks use a polymeric liner as a permeation barrier to hydrogen, typically 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 internally heated high-pressure permeation test vessel (IHPV). The IHPV was previously used in the Hydrogen Delivery sub-program to measure real-time hydrogen permeation in low-carbon steels and polymer materials at constant temperatures. Materials properties 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. In the previous project year we modified the IHPV to enable rapid temperature cycling in polymer specimens.

We are using the relevant portion of the test protocol specified in SAE J2579 to guide our performance of durability test cycling measurements of high-pressure polymeric tank liners [2]. 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 -30 to 85°C at hydrogen pressurizations of 43 MPa (6,250 psia) and then 86 MPa (12,500 psia). Testing at 43 and 86 MPa, with cycling between -30 and 85°C, requires an automated temperature control strategy. To replicate the rapid temperature rise in the tank liner during fill cycles (approximately 100°C rise in 3 minutes) we decoupled the cooling and heating control systems in the IHPV. A low-temperature chiller with low-temperature refrigerant circulating to and from a sealed reservoir cools the IHPV’s exterior containment vessel to approximately -40°C. A resistive heater situated in the permeation cell is used to ramp the specimen temperature from -30°C to 85°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. A complete heating and cooling cycle requires 33.3 minutes (see temperature cycle profile in Figure 1), and approximately 127 days are required to perform 5,500 temperature cycles.

The verification measurements occur at regular intervals during the 5,500 temperature cycles. The hydrogen flux is to be measured at three temperatures (-30, 25 and 85°C) at each interval, if practicable. The first measurements occur after the completion of 250, 500, 750, 1,000, 1,250 and 1500 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

Permeation measurements on the specimen of Lincoln Composites Type IV tank liner (HDPE) indicate that permeability coefficients $P$ are relatively unchanged through 3,000 temperature cycles (see Figure 2). Small systematic changes in activation energy $E_A$ and constant $P_0$ in Arrhenius relationship $P = P_0 \exp(-E_A/kT)$ as a function of the number of temperature cycles were observed, which could indicate microstructural changes are occurring in the polymer during temperature cycling (see Figures 3 and 4). Assembled and tested an improved temperature-cycling apparatus that will enable us to complete cycling measurements faster. First results temperature cycling results using new apparatus expected in 4th quarter of FY 2010.

Conclusions and Future Directions

Through 3,000 temperature cycles we have observed no statistically significant departures from the Arrhenius relationship between permeation coefficient and temperature that would indicate the occurrence of microcracking or changes in glass transition temperature in the Lincoln Composites HDPE liner specimen.

FY 2010

- Complete initial lifecycle verification measurements and report durability assessments of Lincoln Composites specimen through 5,500 cycles.
Begin temperature cycling of Lincoln Composites specimen at 860 bar (12,500 psia).

Begin temperature cycling of Quantum Technologies specimen at 430 bar (6,250 psia).

Complete all lifecycle verification measurements and report assessments for Lincoln Composites and Quantum Technologies.

Complete temperature cycle testing of an alternative liner material (PA-6, PA-11, PPS) and compare to HDPE liner materials.

Measure hydrogen solubility in tank liner materials.

**FY 2010 Publications/Presentations**


**References**

**IV.G.3 High Strength Carbon Fibers**

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Project Start Date: November 2006
Project End Date: Project continuation and direction determined annually by DOE

**Objectives**

- Reduce the manufacturing cost of high-strength carbon fibers by using melt-spun polycrylonitrile (PAN) precursor technology which has the potential to reduce the production cost by >30%.
- Develop advanced conversion techniques that will significantly reduce the production cost of high-strength carbon fibers suitable for use in compressed hydrogen storage vessels by an additional 20%.

**Technical Barriers**

High-strength carbon fibers account for approximately 65% of the cost of the high-pressure storage tanks. This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **System Weight and Volume**
- **System Cost**
- **Durability/Operatability**
- **Materials of Construction**

**Introduction**

The exceptional strength-to-weight ratio of carbon fiber composite tanks makes them prime candidates for use with materials-based, cryogenic, or high-pressure gas for both vehicular and stationary storage applications. Cost is the primary issue with composite tank technology. A critical challenge lies in the cost of the fiber and the manufacture of composite tanks. Current projections of the manufactured cost per unit for high production volumes are about a factor of nine above storage system targets, and it is estimated that about 40-70% of the unit cost is due to the base cost of the carbon fiber (approximately 40% of the fiber cost is
due to the precursor and the remainder due to thermal processing). Costs for compressed gas storage systems stored at 350 and 700 bar (5,000 and 10,000 psi) can be reduced by lowering the cost of carbon fiber through materials and process improvements and moving to higher volume manufacturing processes through advanced manufacturing research and development (R&D). R&D is needed as composite storage technology is most likely to be employed in the near term for transportation applications and will be needed for most materials-based approaches for hydrogen storage.

Currently, composite tanks require high-strength fiber made from carbon-fiber grade polyacrylonitrile precursor. Manufacturing R&D is needed to develop lower cost, high quality polyacrylonitrile or alternate precursors and reduced energy or faster carbonization process for carbon fiber, such as microwave or plasma processing. In addition to improved carbonization processes, other steps in the process, such as oxidation and graphitization need to be improved. Developing and implementing advanced fiber processing methods has the potential to reduce cost by 50% as well as provide the technology basis to expand U. S. competitiveness in high-strength fiber manufacturing [1].

Most carbon fiber in use today is based on the technology developed over many years for production of aerospace grade materials where performance requirements clearly justifies higher costs than for other structural materials. The major contributors to the cost of high strength fiber are: 1) presently, all high-strength carbon fibers are manufactured from relatively costly PAN precursor which is wet spun into fiber in an expensive process; 2) precursor fiber is converted into carbon fiber in bundles, or “tows”, which are optimized for performance versus cost; 3) carbon fiber is typically processed at line speeds optimized for “conservative” production of aerospace properties; 4) conventional fiber production utilizes large, massive furnaces in which most energy is lost to the environment; and 5) rigorous qualification, certification, inspection, and documentation requirements can contribute very significantly to the cost of aerospace grade fibers. This project addresses all of these factors, the most critical of which is the raw material and processing costs involved with precursor production.

This project will leverage previous and ongoing work of the FreedomCAR’s program to develop a low-cost, high-strength carbon fiber. At this time, the cost and property targets needed for compressed hydrogen storage are not well understood. Analysis is underway at DOE to determine appropriate targets. Until targets are definitively established, this project will seek to develop carbon fibers with properties equivalent to Toray’s T700/24k fiber (24k tow, 700 ksi ultimate tensile strength, 33 Msi tensile modulus), and reduce production costs by at least 25%.

Approach

This project is structured into tasks focused on precursor development, conversion process improvements, process integration, and business analysis. Development and demonstration of melt-spinnable PAN is the project’s primary precursor option. This requires concurrent activities in both development of melt-stable PAN copolymer and blends as well as the processes necessary to successfully spin the formulations into filamentary tows. Backup options include textile PAN, polyolefins, and incorporation of nanomaterials. Demonstrating and down-selecting a precursor capable of meeting performance targets utilizing conventional conversion processing defines the pathway for the balance of project activities. In conversion, critical processability parameters include: (i) highly controlled stretching, especially during pre-treatment and stabilization; (ii) residence time in various conversion modules; (iii) optimal graphitization for maximum strength; (iv) uniform treatment of fibers throughout the tow; and (v) characterization of filaments at various stages of conversion operation. Related ORNL work in advanced processing technologies address these issues, with a focus on increasing line speed in a reduced footprint, with reduced energy consumption. Means to adapt these emerging processes will be developed and evaluated for applicability to meeting requirements of this program area. As these technological advances are demonstrated independently, work will also be initiated to make all the modules work together as a robust system focusing on the implementation of an optimized system design and operating procedures to satisfy technical targets at minimum cost. As the system integration is completed, the energy efficiency and overall economics of the complete system will be evaluated and forecast for production scale up.

Results

As described in the approach, our initial focus is on developing and demonstrating melt-spinnable PAN, the necessary processes to spin these material into fibers, and projecting converted carbon fiber properties adequate for down-selecting this or other candidate precursor materials for system integration and technology demonstration. Accordingly, ORNL and its project partners at Virginia Tech have devoted most project resources to this effort as described below.

Alternative Precursor Synthesis

Earlier research has shown that partially sulfonated PAN copolymers (PAN-AMPS) affords highly miscible blends with poly(ethylene glycol) (PEG) due to an apparent intermolecular interaction between the sulfonated groups and PEG. This enables effective depression of the Tg of the blends. In addition to this
The characterization results of the grafted copolymers are summarized in Table 1. From the gel permeation chromatography (GPC) and 1H-nuclear magnetic resonance (NMR) results, it has been confirmed that copolymers with sufficiently high molecular weight and target compositions were synthesized. Our differential scanning calorimetry (DSC) results also indicates that copolymerization of the macromonomers with AN can lead to effective Tg depression. Molecular weight characterization of the graft copolymer is in progress.

The next step is to control the molecular weight which is critical for melt processing. Both initiator concentration and the use of chain transfer agents such as dodecyl mercaptan will be employed.

**Fiber Spinning**

A key accomplishment was successful generation of a four-filament mini-tow with AN/VA copolymer. The scanning electron microscope (SEM) micrographs from this work showed that the fibers have void size similar to that of as-spun fibers produced by BASF as reported in their patent. At the conclusion of this period we are working to generate a 10-filament mini-tow using a new 10-hole spinneret to meet the new milestone. The new spinneret works but more work needs to be done to get filaments with the desired size. We also tried using PAN/methyl acrylate (MA) copolymers in fiber spinning and succeeded in generating some fibers from polymers containing 95% AN. To investigate the stability of hydrated PAN/VA melt, the time dependence of melt pressure was measured during the fiber spinning. The result showed that, under the spinning condition (195°C), the hydrated P(AN/VA) melt was stable as long as the residence time was less than 30 minutes (a time that is long enough for melt spinning). In addition, the DSC thermogram of PAN/VA fibers was measured and compared with that of pristine copolymer. The two thermograms observed are quite similar, indicating that no serious degradation took place during the fiber spinning process.

**TABLE 1. Preliminary Characterization of PAN-PEGMEMA and PAN-HEMA-g-PCL Copolymers**

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mn of macromonomer (g/mol)</th>
<th>IV (dL/g)</th>
<th>Weight fraction of PEG/PCL (%)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Target From 1H-NMR</td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>-</td>
<td>2.38</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>PAN-PEGMEMA(5)</td>
<td>475</td>
<td>1.89</td>
<td>5.0</td>
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<td>PAN-PEGMEMA(10)</td>
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<td>10.0</td>
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<tr>
<td>PAN-HEMA-g-PCL(5)</td>
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<td>TBD</td>
</tr>
</tbody>
</table>

TBD – to be determined
SEM Micrograph of As-Spun PAN/VA Fibers

SEM analysis was carried out to study the morphology of melt-spun PAN/VA fibers, including single filament and four-filament fibers produced in the last quarter. The as-spun fibers are substantially void free when examined in cross section at 2,000X or lower magnification (see Figures 1a and 2a). Any voids which are observed in the as-spun fibers when a cross section is examined are generally \( \leq 0.2 \) micron (see Figures 1b and 2b). Note that this size of voids is at the same level as that observed in the as-spun acrylic fibers produced by BASF (see U.S. Patent 5,168,004). That is, we were able to use just water to produce precursor fibers with the same void size as that generated by using water and acetonitrile.

Spinning of PAN/VA 10-Filament Mini Tow

In order to meet the milestone on spinning of the 10-filament mini-tow, we designed and fabricated a new spinneret with 10 holes (0.01” in diameter). We have made trial spinning runs with the new spinneret several times. Some 10-filament mini-tows were generated successfully with PAN/VA mixed with 17 wt% water. However, we still could not produce a 10-filament tow with fibers of diameter \( \leq 50 \) microns continuously. Some filaments broke easily as we tried to increase the take-up speed and the draw ratios. We are working to find the solution and generate a 10-filament tow with filaments of desired size and properties. The appropriate conditions seem to be a function of the melt temperature and the subsequent drawing and cooling conditions.

Spinning of PAN/MA Copolymer Fibers

We also tried to spin PAN/MA fibers with three copolymer samples (see Table 2) made available to us. Fiber spinning was carried out by using the same conditions as were used for generating PAN/VA copolymer fibers. It turned out that neither sample #1 nor #2 worked. The molecular weight (and viscosity)
of sample #2 is so high that we could not even extrude the melt out of the capillary. In contrast, the spinning of sample #3 went quite well. Some fibers were generated successfully. Because the PAN/MA sample has higher AN content and is more stable in comparison with the PAN/VA samples, using new PAN/MA samples could improve the properties of PAN fibers as carbon fiber precursors.

Stability of Hydrated P(AN/VA) Melt

The viscosity of the polymer melt is sensitive to the polymer structure. Under constant extrusion temperature and speed, the shear viscosity of the polymer is proportional to the pressure drop over the die hole (capillary) and approximately proportional to the melt pressure in the barrel. For this reason, if molten polymer undergoes structural change or becomes unstable, the viscosity of the melt may change and so would the melt pressure. So time dependence of melt pressure could provide information about melt stability or degradation of polymer melt.

Figure 3 presents the time dependence of the hydrated AN/VA copolymer melt pressure during the fiber spinning at an extrusion temperature of 195°C. The extrusion (plunger) speed is 0.06 cm/min. Note that t=0 was set as 6 minutes after the sample was inserted into heated barrel of an Instron Rheometer. It shows that, when t is less than 30 minutes, the melt pressure was approximately constant, suggesting that the melt was stable during this period of time. In contrast, when t is greater than 30 minutes, the melt pressure went up quickly, indicating that the polymer might undergo structural change and become unstable. As 30 minutes should be long enough for melt spinning, it can be concluded that the P(AN/VA) – water system is suitable for application in the melt-spinning process.

DSC Analysis of Melt-Spun AN/VA Copolymer Fibers

The DSC analysis was carried out for both AN/VA copolymer (pristine powder) and melt-spun AN/VA fibers (as-spun fibers with t < 30 min). Both samples were dried in a vacuum oven at 80°C for 20 hours before testing to remove any residual water/moisture in the polymer or fibers. A heating rate of 20°C/min was used in the analysis. The result is shown in Figure 4. It is apparent that the thermograms for the two samples are quite similar, especially in the temperature range less than 280°C. At temperatures higher than 280°C there is a large exotherm produced by the cyclization reaction of adjacent nitrile groups. Both samples exhibited the same glass transition temperature (102–103°C) and the exothermic reaction (cyclization reaction) which starts at

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Provider</th>
<th>Composition (mol/mol)</th>
<th>IV (dL/g)</th>
<th>Spinnability with hydrated melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aldrich Co.</td>
<td>AN/MA=96/4</td>
<td>90.7/9.3</td>
<td>5.41  Unable to draw fibers</td>
</tr>
<tr>
<td>2</td>
<td>Exlan Co.</td>
<td>AN/MA=95/5</td>
<td>92.7/7.3</td>
<td>4.09  Unable to extrude</td>
</tr>
<tr>
<td>3</td>
<td>ORNL 6/22/10</td>
<td>AN/MA=95/5</td>
<td>95.0/5.0</td>
<td>1.13  OK</td>
</tr>
</tbody>
</table>

Table 2. Spinnability of Hydrated Melt of PAN/MA Copolymers
about 280°C. However, the positions (temperatures) of the exothermic peaks are different. For the fiber sample, the peak temperature is 324°C, which is some 14°C lower than that of the pristine polymer sample. It suggests that the cyclization reaction of fiber is faster than that of pristine polymer. From this result and the fact that the fiber sample has much higher molecular orientation than the pristine sample, it is possible that the orientation of polyacrylonitrile molecules may accelerate the cyclization reaction of adjacent nitrile groups.

Based on the above thermal analysis and melt pressure data, we believe that the melt-spun fiber generated with the continuous technology (t <30 minutes) would have a chemical structure similar to or very close to that of the pristine polymer samples.

Conclusions and Future Directions

Significant accomplishments were achieved in precursor development during the past year in successfully synthesizing copolymers with sufficiently high molecular weight and target compositions and demonstrating that copolymerization of macromonomers with AN can lead to effective Tg depression. We were also able to successfully melt-spin a four-filament mini-tow with AN/VA copolymer. Plans are to build on this work in progressing towards a melt-spinnable 95/5 AN/MA system. The development of a melt processing scheme for the AN/MA copolymer system will require an intensive effort involving synthesis and rheology along with refinements of the processing scheme. The first phase of the project is to develop a correlation between the copolymer ratio and molecular weight. The molecular weight distribution and intrinsic viscosity of various copolymer systems will be determined using GPC and solution viscosity techniques, respectively. Although some of these resins will be provided by ORNL, others will be synthesized by the Virginia Tech group in order to find an acceptable AN/MA copolymer suitable for melt processing. In addition to molecular weight, the melting, and Tg temperatures will be determined via DSC.

The new resins after plasticization with water will then be evaluated rheologically using a specially designed rheometer capable of measuring viscosity of materials containing plasticizers such as water which require pressurization of the extruded material. These measurements will allow us to determine conditions (processing temperature, thermal stability, viscosity, spinning pressure) suitable for melt spinning a given composition (i.e. AN/MA ratio and molecular weight). Once these conditions are established, then suitable amounts of the composition will be synthesized and then spun into fibers.

In addition to the synthesis of AN/MA, copolymers will be synthesized for evaluation as well. Macromonomers containing methacrylate functionality and a side chain of poly(caprolactone) with molecular weights of 1,000 to 5,000 will be prepared and core-polymerized with AN and MA to assess whether they can improve melt processibility.

Once the desired composition (i.e. AN/MA ratio and molecular weight) is identified, the processing conditions are established, and sufficient quantities of polymer are synthesized, the resins will be spun using a specially designed spinning system being developed. The spinning system allows the extruded filaments to be spun into a pressurized environmental chamber which cools the filaments and suppresses foaming. The filaments leaving the chamber will then be drawn on heated draw rolls to remove water and impart orientation and increased tensile strength. The mechanical properties of the filaments will be measured to obtain the modulus and tensile strength.

ORNRL will characterize the fiber and conduct conversion trials on precursor filaments generated using its precursor evaluation system. The filaments at various steps of the conversion process will be fully characterized and the data used to commence optimization of precursor chemistry and the filament generation process. We expect to achieve carbon fiber tensile properties of 15 Msi elastic modulus and 150 ksi tensile strength with first generation filaments. We are targeting 18 Msi modulus and 200 ksi strength in second generation filaments.

FY 2010 Publications/Presentations


References

### 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 hydrogen in a controlled manner 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 Storage technical barriers of the Fuel Cell 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 specific 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 (known to be highly polluting) and electric bicycles.

The developed technology will likely not meet all DOE technical targets, but there has been a significant focus on customer attributes such as safe operation, fast starting, rapid restarting, low-pressure operation, and ease of use. While this work addresses many of the technical barrier topic areas as outlined in the Fuel Cell Technologies Program Plan, this work is focused on portable power applications that do not have defined DOE targets.

The current effort seeks to establish system technology using sodium silicide. Not only does sodium silicide enable systems that are low cost and reliable, sodium silicide has a high energy density of 3,267 Wh/kg (lower heating value, LHV). SiGNa anticipates the development of advanced silicides with comparable system control architectures which will further increase performance metrics and are capable of over 4,200 Wh/kg (LHV).

The cost of energy storage for portable power applications is expected to approach DOE targets compared to those for vehicle technologies as it is expected to reach $4.47/kWh. Further cost reductions may be realized through manufacturing scale up and other industrial usage demands of sodium silicide and the waste product, sodium silicate.

### Accomplishments

Significant progress has been made in the development hydrogen generation system technology for fuel cell applications. The work in this program includes the following accomplishments:

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**IV.H.1 NaSi and Na-SG Powder Hydrogen Fuel Cells**

**Michael Lefenfeld (Primary Contact), Andrew Wallace**

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530 East 76th Street 9E  
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Phone: (212) 933-4101  
E-mail: michael@signachem.com, apwallace@signachem.com

**DOE Technology Development Manager:** Grace Ordaz  
Phone: (202) 586-8350  
E-mail: Grace.Ordaz@ee.doe.gov

**DOE Project Officer:** Katie Randolph  
Phone: (303) 275-4901  
E-mail: Katie.Randolph@ee.doe.gov

**Contract Number:** DE-FG36-08G088108

**Subcontractors:**
- Trulite Inc., El Dorado Hills, CA
- University of Texas, Austin, TX

**Project Start Date:** August 1, 2008  
**Project End Date:** January 31, 2010

---
Fabricated and tested a laboratory system which demonstrated key performance attributes: 9.8 wt% hydrogen yield on a powder basis, multiple re-starts with up to one week of off time, and controlled generation (~3 slpm) at low pressures (~30 psi).

Successfully completed bench top testing and sustained operation of a 300 W fuel cell-powered electric bicycle.

Developed a hydrogen filtration system and verified results with gas chromatography verifying 99.99% hydrogen purity.

Completed construction of standalone hydrogen generation development unit capable of 4 slpm and a capacity of 1,000 liters of hydrogen.

Produced (via toll manufacturer) over 25 kg of sodium silicide.

Demonstrated combined water/powder energy density of 1,600 Wh/kg LHV (1,854 Wh/kg if 50% water recirculation is assumed).

SiGNa Chemistry, Inc. is developing a unique hydrogen storage mechanism utilizing SiGNa's air-stable sodium silicide powder derivatives (e.g., Na₄Si₄). SiGNa's stabilized powders have been shown to produce 9.8 wt% H₂. The primary goal of this work is to develop a prototype system including all balance-of-plant components which controllably generates hydrogen based on usage requirements. SiGNa Chemistry will initially target a 3 slpm (~250 W net output) hydrogen generation system. This flow rate 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
- other off-grid applications

While numerous hydrogen production chemistries have been explored for portable systems such as sodium borohydride or methanol reforming, 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, Na₄Si₄, rapidly react with water to form hydrogen and a benign, industrially useful, by-product, sodium silicate.

2 NaSi(s) + 5 H₂O(ℓ) → 5 H₂(g) + Na₂Si₂O₅(aq)

SiGNa has developed system 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 and water/alcohol mixtures, were also tested and verified to yield a controllable hydrogen flow rate with no impurities (as tested on an Agilent 6850 gas chromatograph). 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-mix and fully react large quantities of powder. To rapidly start a cold, partially reacted solution, the micro-spray system sprays water streams on un-reacted powder regions 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 was used to test the various control components and demonstrate core reaction characteristics. The results of these experiments have been incorporated to develop a standalone hydrogen generation system. Basic operation of the hydrogen generation system (Figure 2) has been verified with a Trulite 300 W fuel cell system (Figure 3) and then modified to fuel a hydrogen-fueled electric bicycle (Figure 4). During this project, material production has jumped from a 100 gram laboratory process to a >4 kg batch reactor. SiGNa is currently working with an established toll manufacturer with expertise in alkali metals to continue the scale-up of a next-generation manufacturing process.

### Results

#### Cartridge

A number of reaction vessels have been tested ranging from 30 to 1,200 ml. This work led to the development of a 1.2 liter cartridge fabricated using an impact extrusion process - similar to a paint can - for low-cost production. The cartridges have a quick-connect interface and are used in conjunction with both the Trulite 300 W fuel cell and a 300 W electric bicycle.

#### Reaction

The water feed and distribution system primarily consists of the pump and a micro-nozzle network. In practice, there are significant challenges in getting a far reaching spray at very low water flow rates (<1 ml/min).
The water distribution network is almost exclusively required for re-start conditions. Systems using this micro-nozzle manifold were shown to rapidly restart after storage at room temperature for seven days after first reacting 80% of powder.

**Control**

A predictive proportional-integral-derivative control system was developed to generate hydrogen at a near constant pressure even when using two canisters in parallel controlled via a single water...
pump. By using calibrated pump data in conjunction with a measurement of the change in pressure over time (dp/dt), the microcontroller estimates the actual hydrogen flow. The hydrogen generation system also indirectly measures hydrogen flow rate by monitoring the fuel cell electrical current. However, pump data and pressure measurements have proven sufficient to control the pressure to within approximately +/- 5 psi at a nominal pressure of 30 psi.

**Water Pump System**

In addition to active pump control, SiGNa has developed a passive, disposable, orientation-independent water pumping system and water reservoir within the hydrogen cartridge. This system has demonstrated a near constant hydrogen pressure of 3 psi for regulator-free, low-cost fuel cell operation. This has only been tested on a smaller cartridge with a capacity of 50 liters - although it is anticipated to be scalable to the 1.2 liter vessel, this will not be demonstrated in the project.

**Testing**

Hundreds of tests and thousands of hours of hydrogen generation have been performed over the course of the project. Hydrogen yield is reliably at or near the theoretical maximum of 9.8 wt%. A combined water/powder energy density of over 1,300 Wh/kg LHV was achieved. In addition, an advanced sodium silicide mixture was shown to yield over 1,600 Wh/kg LHV and over 1,854 Wh/kg when recirculating 50% of the fuel cell waste water.

**Conclusions and Future Directions**

Sodium silicide is capable of controlled hydrogen flow for a range of portable applications. A number of implementation issues that have plagued other hydrolysis systems – particularly 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:

- Final testing and verification of the hydrogen generation system.
- Continued testing on larger powder quantity runs to optimize control characteristics and minimize water usage.
- Continued testing and improvements on the hydrogen generation control system.
- Operation of the hydrogen generation system by a fuel cell system developer for independent performance verification.

**Special Recognitions & Awards/Patents Issued**


2. Received Commercial Development Contract for Micro-Fuel Cell Hydrogen Generation Cartridge.

**FY 2010 Publications/Presentations**


IV.H.2 Purdue Hydrogen Systems Laboratory: Hydrogen Storage*

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 Fuel Cell 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

Technical Targets

<table>
<thead>
<tr>
<th>On-board Storage</th>
<th>Units</th>
<th>2010/Ultimate</th>
<th>Purdue 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>H₂ wt%</td>
<td>4.5/7.5</td>
<td>11~15 (material)</td>
</tr>
<tr>
<td>Overall Efficiency of Off-Board Regeneration</td>
<td>%</td>
<td>&gt;60</td>
<td>The process is still being optimized</td>
</tr>
</tbody>
</table>

Accomplishments

- AB was prepared in kilogram-scale from sodium borohydride and ammonium sulfate in the presence of ammoniated tetrahydrofuran (THF) at room temperature in 92% yield and ≥98% purity.
- Trimethylborate was reduced using diethylsilane in the presence of N₁,N₁,N₂,N₂-tetramethylethane-1,2-diamine (TMEDA) to TMEDA-Bisborane complex.
- TMEDA-Bisborane complex was converted to AB via transamination in 80% yield.
- For the first time, characterized rheological properties of AB spent fuels.
- For the first time, captured the details of fast hydrogen evolution at the initial stage of the AB thermolysis process.
- Designed, constructed and tested a 10 g capacity batch reactor for neat AB thermolysis. Reactor capable of operating at up to 200°C and 8 bar.
- Investigated noncatalytic AB hydrothermolysis at near proton exchange membrane fuel cell (PEMFC) operating temperatures over a wide range of AB concentrations and pressure. The maximum hydrogen yield, obtained at 77 wt% AB and T<sub>reactor</sub> ~85°C along with rapid kinetics, was 11.6 and 14.3 wt% at pressure 14.7 and 200 psia, respectively.
- Using the neat AB thermolysis process, ~15 wt% H<sub>2</sub> yield was obtained at 14.7 psia and T<sub>reactor</sub> ~90°C with rapid kinetics also near the PEM fuel cell operating conditions.

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 Fuel Cell Technologies Program. Hydrogen production research of this project...
is reported in Purdue Hydrogen Systems Laboratory: Hydrogen Production.

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. To that end, a task is focused on finding energy efficient ways to recycle the ammonium borate to AB. The AB slurry dehydrogenation work was dedicated to 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. With the advantage of transportability of byproduct obtained from neat thermolysis of AB, a scaled AB dehydrogenation batch reactor capable of handling at least one gram AB per batch was designed. The lessons learned in designing, testing, and analyzing the data obtained with the neat AB reactor system are guiding the modeling and future design of a slurry-based reactor. A third task was devoted to developing a new approach to release hydrogen by noncatalytic hydrothermolysis of AB in aqueous solutions and slurries. It is known that the release of hydrogen from AB via both thermolysis and hydrolysis is exothermic. In AB hydrothermolysis process, it was found that the heat generated by hydrolysis initiates thermolysis near PEMFC operating temperature (85°C) along with rapid heat evolution. On the other hand, for neat AB thermolysis, the sharp evolution was not observed at 85°C, indicating that water (hydrolysis) drives the sharp heat evolution resulting in high H₂ yield. Nevertheless, since the release of hydrogen from AB via thermolysis (release of first and second H₂ moles) is exothermic, it was expected that with effective heat management, the sharp heat evolution could be observed near PEMFC operating temperatures during neat AB thermolysis as well.

**Approach**

The spent fuel, ammonium borate will be converted to triacyl- or trialkyl borates, which will provide molecules with the 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 lead to efficient ammonia borane regeneration.

To facilitate the design of thermal management and spent fuel removal, we investigated neat and ionic-liquid aided AB dehydrogenation kinetics, especially at the initial fast hydrogen evolution stage. A neat AB batch reactor module was designed and assembled at the Hydrogen Systems Laboratory. Made of stainless steel, the cylindrical reactor is designed to handle reactions with starting temperatures of about 155±5°C and a nominal batch reaction time of 10 minutes. On-going tests with batches of up to two grams AB are providing data and design guidance for the development of an AB-based reactor. We also developed a computational fluid dynamics (CFD) model to simulate the thermo-chemical process in an AB slurry reactor. In addition, we measured elastic stiffness and viscous damping of AB spent fuels from various reactions including hydrolysis, thermolysis and hydrothermolysis.

The AB hydrothermolysis method for H₂ generation was investigated over a wide range of AB concentration in water, pressure, and heating rate. The neat AB thermolysis was also studied near PEMFC operation temperatures. To better understand the reaction exothermicity (heat evolution), we developed a smaller size reactor (70 ml). Apart from the reactor temperature, the sample temperature (Tsample) was also measured by inserting a thermocouple inside the sample. In addition to mass spectrometry, ammonia was also measured by titration technique.

**Results**

AB was prepared in kilogram-scale from sodium borohydride and ammonium sulfate in the presence of ammoniated THF at room temperature in 92% yield and ≥98% purity. We have recycled ammonia borate to AB via conversion to trimethyl borate followed by the reduction using diethylsilane (Figure 1). We developed novel protocol for the reduction of trimethylborate in the presence of TMEDA using diethylsilane resulted in the formation of the diamine bisborane complex in very high yield (90%). The solid bisborane complex could be readily separated by filtration. The preparation of AB from this diamine bisborane complex was achieved in 80% yield by exchange with ammonia. We have initiated energy efficient schemes to convert NH₄B(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 measured the reaction kinetics of neat and 1-butyl-3-methylimidazolium chloride (bmimCl)-aided AB thermolysis under quasi-isothermal conditions in the

![FIGURE 1. AB recycling.](image-url)
The measured hydrogen storage capacity of the 80/20 AB/bmimCl mixture was 11.2 wt% at 120°C and foaming during AB thermolysis was partially suppressed by the ionic liquid. Hydrogen yield reduction caused by impurity and aging of bmimCl should be further addressed. bmimCl aided thermolysis should be implemented at sufficiently high temperature (>107°C) to achieve a noticeable gain in the hydrogen storage capacity when comparing to the neat AB thermolysis.

We also quantitatively revealed the visco-elastic differences between the spent fuels obtained from the various AB dehydrogenation methods. It was demonstrated that spent fuels obtained from AB neat thermolysis and hydrothermolysis are the most transportable, followed by its hydrolysis and ionic liquid-aided thermolysis, respectively. The spent fuels obtained at higher temperatures exhibit improved transportability.

A reactor system for neat AB thermolysis of up to two gram batches of AB was designed. The system is characterized by modularity and highly repeatable batch operation. It consists of an AB feeder, a reactor and a gas processing unit (Figure 2). Safety features such as remote operation and cooled AB reservoir make the operation very safe and reliable. Operation of the system was tested with AB batches weighing up to two grams. The average temperature for batch reactions was 160°C. Results of the batch tests are compared in Table 1 with those obtained with a bench top unit. In addition, we developed a CFD code to simulate an AB slurry reactor for on-board hydrogen storage. For 80/20 ammonia borane/ionic liquid slurry, a reactor was simulated at a H₂ release rate of 1.6 g/s with a reactor total weight of ~2.4 kg.

AB hydrothermolysis was investigated in a 70 ml stainless steel Parr reactor over a wide range of AB concentration, pressure, and heating rate. The maximum observed hydrogen storage capacity, obtained at 77 wt% AB concentration and T<sub>reactor</sub> ~ 85°C, was 11.6 and 14.3 wt% at pressure 14.7 and 200 psia, respectively (Figure 3). For 200 psia and heating rate 1°C/min, AB converted to NH₃ (NH₃/AB) in the gaseous product decreased with increasing AB concentration. It is worth noting that even for neat AB thermolysis (in absence of water), 2-4% of AB was converted to NH₃, which must be removed for use in PEMFC. With increasing

**TABLE 1.** Results Obtained During Bench Tests and Batch Reactions

<table>
<thead>
<tr>
<th>Type of reaction</th>
<th>Mass of AB (g)</th>
<th>Average Temperature (°C)</th>
<th>Yield of Hydrogen (mol of H₂ per mol of AB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Time (seconds)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Bench test</td>
<td>0.13</td>
<td>155</td>
<td>0.25</td>
</tr>
<tr>
<td>Batch #1</td>
<td>2.00</td>
<td>160</td>
<td>0.02</td>
</tr>
<tr>
<td>Batch #2</td>
<td>2.00</td>
<td>160</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**FIGURE 2.** Neat AB thermolysis batch reactor.

**FIGURE 3.** Hydrogen yield as a function of AB concentration, at different hydrothermolysis operating conditions.
Conclusions and Future Directions

We investigated the fundamental chemistry of AB recycling and achieved conversion of trimethyl borate to AB. 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 further optimized for the quantitative isolation of ammonia borane. Computations of the recycling of energy efficiency will be done.

We achieved 11.2 wt% (material) hydrogen storage capacity from the 80/20 AB/bmimCl mixture thermolysis, which is within the uncertainty limits of the highest ever reported in the literature. We measured the hydrogen yield and characterized the operation of a neat AB batch reactor. We obtained similar yield rates and chemical kinetics results for bench tests and batch reactions. However, the challenges associated with AB byproduct removal and transient mass flow rate measurement of gas yield need to be further addressed. We will apply the lessons learned with the neat AB batch reactor, the results of CFD simulations and overall engineering performance analyses to the design of the AB slurry reactor.

It was demonstrated that noncatalytic AB hydrothermolysis is a promising method for hydrogen storage. This process was studied over a wide range of AB concentrations, pressure, and heating rate. It was found that hydrogen yield, ammonia generation and thermal characteristics were influenced by these operating conditions. The maximum hydrogen storage capacity, obtained at 77 wt% AB and T\textsubscript{reactor} ~ 85°C along with rapid kinetics, was 11.6 and 14.5 wt% at pressure 14.7 and 200 psia, respectively. The kinetics of neat AB thermolysis under various operating conditions were also investigated. For neat AB thermolysis, ~15 wt% H\textsubscript{2} yield (2.3 H\textsubscript{2} molar equivalent) was obtained at 14.7 psia and T\textsubscript{reactor} 90°C with rapid kinetics under effective heat management. To our knowledge, this value is higher than by any other method using AB at near PEMFC operating temperatures.

**FY 2010 Publications/Presentations**

**Archival Papers**


**Conference Papers and Presentations**


Objectives

The ultimate vision of this project is to develop glass-based materials with structural properties that would make them promising candidates for use in H-storage: either as material for glass microspheres or for sponge-type storage.

- This is an extensive research project in physics and chemistry of glasses and of glass-based nano-crystalline materials.
- It will fill gaps in the current understanding of these very complex materials.
- It will shed more light on nucleation and crystallization phenomena in glass matrices, which could extend their technological applications.

Technical Barriers

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

(A) System Weight and Volume
(B) System Cost
(D) Durability/Operability

Technical Targets

This project is conducting studies of glasses and of glass-based nano-crystalline 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:

- Weight and Volume: 0.045 kg H₂/kg system; 0.028 kg H₂/L system
- Cost: $4/kWh net

Approach

The most desirable candidates for hydrogen storage are systems which do not interact chemically with hydrogen and possess high surface area to host substantial amounts of hydrogen. From this point of view, glasses built of a disordered network with ample void spaces, which are permeable to hydrogen and glass-derived nanocomposites, hybrids of glass and nanocrystals, appear to be promising candidates. Other essential advantages of glasses include simplicity of preparation, flexibility of composition, chemical durability, non-toxicity and mechanical strength, as well as low production costs and environmental friendliness.

This project will challenge to extend the concept of using glass-based materials as hydrogen storage media. The focus will be on research of specific glass compositions with emphasis on their fabrication process and characterization using multi-technique experimental approach. The endeavor is to show ways how to tailor the structure of disordered amorphous networks in selected glasses by taking advantage of controlled nucleation and crystallization phenomena and by transforming them into glass-crystal hybrid complex nanocomposites. The ultimate goal of this project is the successful development of glass-derived composite materials with structural properties that would make them promising candidates for potential use as hydrogen storage media: either as material for glass microspheres or for sponge-type storage. Moreover, this research will fill gaps in the current understanding of a very complex group of materials – glasses – and will shed more light on nucleation phenomena in glasses which will extend the existing variety of their technological applications.

Accomplishments

- Project begun in January 2010.
- This is a brand new project and requires the establishment of two new laboratories. The
execution of the project is conditioned by laboratory reconstruction/adaptation and by purchase of state-of-the-art experimental instrumentation.

- The project is composed of several experimental tasks which are sequential and depend on the completion of the new laboratories that is currently in its final phase.

**Future Directions**

Experimental work is scheduled to commence in September/October 2010.

**FY 2010 Publications/Presentations**

Objectives

- Investigation of maximum hydrogen storage capacity, adsorption/desorption kinetics, and catalyst effects in thin films and nanostructures of magnesium borohydride for hydrogen storage.
- Experimental investigation of methods to destabilize borohydrides in order to lower the temperature, and increase the rate of dehydrogenation/rehydrogenation.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Engineered Nanostructures

Successfully fabricated magnesium boride nanostructures at room temperature using GLAD.

System upgrades on our homemade quartz crystal microbalance (QCM) hydrogen storage measurement unit has been done and new measurement procedures has been introduced for accurate hydrogenation/dehydrogenation tests.

Performed material characterization and preliminary hydrogen storage experiments on GLAD magnesium boride nanostructures.

Introduction

After our previous studies on the model system nanostructured magnesium, we focused our studies on the fabrication and hydrogenation properties of nanostructured magnesium boride during past year. Magnesium borohydride Mg(BH₄)ₓ, which is the fully hydrogenated form of magnesium diboride (MgB₂), was the choice of material due to its promising properties for hydrogen storage applications with a high gravimetric (14.9 wt%) and volumetric density of hydrogen. Many theoretical and empirical studies state the reversibility of Mg(BH₄)ₓ is possible [1]. The chance of hydrogenating MgB₂ at reasonable pressure and temperatures has been shown in the LiH-MgB₂ systems [2]. The general
approach in the literature has been first starting with the synthesis of magnesium borohydride, dehydrogenate it, and trying to re-hydrogenate it back to magnesium borohydride. However, complete dehydration of \( \text{Mg(BH}_4\text{)}_2 \) was not possible at reasonable temperatures, making the following hydrogenation step even more difficult. It has been recently suggested that it may be easier to start hydrogenation process from the fully decomposed magnesium boride (\( \text{MgB}_2 \)) [3]. In addition, due to the reduced size and high surface/volume ratio of nanostructures, it is expected that kinetics of hydrogen adsorption/desorption can be further enhanced for nanostructured magnesium boride.

**Approach**

The GLAD [4] technique has been utilized for the growth of nanostructured magnesium boride coatings. For GLAD, a sputter/evaporation deposition system with a sample rotation and tilt control capability has been utilized. We used a new QCM gas chamber system that we developed for the hydrogen storage measurements on nanostructured magnesium boride.

**Results and Discussion**

After various experiments on optimizing the deposition parameters such as sputter power, deposition angle, deposition rate, and initial substrate patterning, the successful method for room temperature fabrication of nanostructured GLAD magnesium was determined to be placing the sample at 90° deposition angle from both sources of magnesium and boron. The sources were located across each other at 180° during the deposition where the sample was rotated around its surface normal axis. At the initial stages of growth, we introduced a formation of a few tens of nanometer long Mg nanoblades by a short Mg-only GLAD thermal deposition. This short pre-deposition was used as a template for the further enhancement of shadowing effect [4] during the following GLAD magnesium boride deposition. Figure 1(a) and (b) shows the top view scanning electron microscope (SEM) images of 270 nm (60 min deposition time) and 540 nm (120 min) thick columnar Mg+B nanostructures obtained from our GLAD experiments. Cross-sectional SEM images (not shown here) also confirm the isolated nanostructure formation. The columnar feature sizes are around 100 nm in diameter for 270 nm long magnesium boride nanostructures and it is about 200 nm for the 540 nm long nanostructures. In addition, Figure 2 shows the X-ray diffraction (XRD) profiles of these Mg+B samples as well as that of uncoated silicon substrate, XRD results indicates that we were able to form a nanostructured MgB\(_2\) coating. However, Figure 2 also shows relatively weak peaks of magnesium, which indicates that the some magnesium atoms couldn’t form a boride structure, possibly due to the lack of B or due to the low substrate temperature.
In addition, we deposited nanostructured magnesium boride onto QCM crystals in order to analyze its hydrogen absorption properties using our custom designed QCM chamber. Preliminary QCM results shown in Figure 3 indicate a ~2.9 wt% hydrogen absorption in nanostructured magnesium boride at 300°C under 30 bar hydrogen pressure. The SEM image in Figure 4(a) shows that morphology of the hydrogenated sample is significantly different than the initial product (Figure 3). Columnar features before the hydrogenation process disappeared and a cracked film with finer nano-scale features has formed, possibly due to the coalescence of the magnesium boride nanostructures and crack formation as a result of the volume expansion of the hydrogenated coating. The hydrogenated film did not delaminate from the substrate and was stable after the QCM experiment. XRD analysis on the hydrogenated magnesium boride sample (Figure 4(b)) shows the partial formation of Mg(BH₄)₂.

**Conclusions and Future Directions**

Our results show that we successfully fabricated magnesium diboride (MgB₂) nanostructures at room temperatures using the GLAD method. Preliminary QCM test indicate that we were able to partially hydrogenate MgB₂ at 300°C to form Mg(BH₄)₂ with about 2.9 wt% hydrogen storage. However, this storage value is still far below the theoretical maximum value of 14.9 wt%. Therefore we plan to investigate the fabrication of nanostructured magnesium boride with improved crystal and morphological properties and also study the effect of catalyst additives.

**Plan for Future Studies**

Fabrication of nanostructured GLAD MgB₂ at elevated substrate temperatures for enhanced crystallization, with catalyst additives for enhanced hydrogenation/dehydrogenation kinetics, and investigating their hydrogen storage properties.

**Borohydrides**

**Accomplishments**

- Examined the catalytic benefits on encapsulation of organic borohydrides in mesoporous silica. Surface chemistry was probed with neutron scattering showing involvement of the surface in decomposition.
- Tested the predicted thermal destabilization effects of the coupled decomposition of LiBH₄ and Ca(BH₄)₂.
- Performed a thorough investigation of a novel preparations for Ca(BH₄)₂ by solid state synthesis.

**Introduction**

**Borohydrides in Mesoporous Silicate**

The thermodynamic parameters obtained via ab initio studies predict that many borohydrides are theoretically capable of thermolysis at reasonably low temperatures [5,6]. In practice, much higher temperatures are required, and the rate of reaction is often sluggish except in the presence of a catalyst [7-9]. This implies that the limiting factors are associated with kinetics and the activation energy barrier. Fang et al. have shown that that dispersing LiBH₄ with a carbonaceous mesoporous network encourages thermal decomposition [10]. The nature of the interaction between the borohydride and its host network has not been thoroughly investigated as of yet. As a model system, we load organic borohydrides (R₄NBH₄) inside a mesoporous silicate MCM-48. MCM-48 was chosen because it has a regular structure that can easily be probed with XRD, whereas mesoporous carbons derived by templating have irregular pore ordering. Borohydrides with an organic cation provide high visibility of both the cation and anion to neutron scattering and better solvent options for loading the porous networks.

We conducted an additional study on mesoporous silicate loaded with inorganic molecular borohydride Zr(BH₄)₄. In addition to thermodynamic benefits, it was anticipated that the silicate will mitigate some of...
Calcium Borohydride Destabilization

Ca(BH₄)₂ is a promising candidate for a hydrogen storage material due to its rich hydrogen composition, and lower decomposition ΔH of ~41 kJ mol⁻¹ [1]. However, the decomposition of the neat material is sluggish. In practice, the temperatures required to decompose Ca(BH₄)₂ are also much higher than the thermodynamics imply [11]. This discrepancy may be due to kinetics. Both of these difficulties may be aided in part by destabilization by coupled decomposition. The following reaction was predicted by Ozolins et al. to have a slightly more attractive enthalpy of ~57 kJ mol⁻¹ and comparable hydrogen emission of bulk Ca(BH₄)₂ [12].

\[
5\text{Ca(BH}_4\text{)}_2 + 2\text{LiBH}_4 \rightarrow \text{Li}_2\text{B}_{12}\text{H}_{12} + 5\text{CaH}_2 + 13\text{H}_2
\]

Additional decomposition with the release of hydrogen is also predicted to be possible from the products by reaction of Li₂B₁₂H₁₂ with CaH₂; but the initial step above must occur first. No clear predictions were made regarding the kinetics or reversibility of this reaction, hence our interest in testing it experimentally.

Approach

Borohydrides in Mesoporous Silicate

Mesoporous silicate MCM-48 was synthesized in a pressure vessel by hydrothermal methods as described elsewhere [13]. Me₄NBH₄ and Et₄NBH₄ were prepared by wet chemical methods; purity was verified by Fourier transform infrared (FTIR) and XRD. Silicates were loaded with borohydride by incipient wetness methods (see 3rd quarter 2009 report for further preparation details). Loaded compounds were subsequently characterized by differential scanning calorimetry (DSC)/thermal gravimetric analysis (TGA) for thermal analyses, FTIR for general composition and validation, XRD for structural analyses, Brunauer-Emmett-Teller (BET) surface area determination, residual gas analysis to determine the gas product composition and inelastic neutron scattering (INS) to probe the chemical environment inside the pores. INS spectra were collected on the filter difference spectrometer at the Manuel Lujan, Jr. Neutron Scattering Center at Los Alamos National Laboratory.

Calcium Borohydride Destabilization

The theoretically predicted destabilization reaction between Ca(BH₄)₂ and LiBH₄ was investigated in solid state by ball milling of a stoichiometric mixture of commercially obtained calcium and lithium borohydrides and pressing a pellet of the mixture. DSC/TGA were performed on several pellet samples during heating. Volumetric analyses were also performed on larger samples (~300 mg) of loose ballmilled powder. The sample was heated in a sealed reactor of known volume which was purged by vacuum and backfilled with a small amount of Ar. All preparations were carried out in a helium glove box.

Results and Discussion

Borohydrides in Mesoporous Silicate

The combined results of XRD, FTIR and BET analyses revealed that Me₄NBH₄ and Et₄NBH₄ were...
each successfully loaded into mesoporous silicates in uniform fashion (see 3rd quarter 2009 report for further details). TGA analyses revealed that both Me₄NBH₄ and Et₄NBH₄ decompose at lower temperatures when loaded in MCM-48. Figures 5(a) and 5(b) show TGA data for pure R₄NBH₄ and R₄NBH₄ loaded in MCM-48 for R=Me and R=Et respectively. It should be noted that host MCM-48 (not shown) displays no measurable mass loss until temperatures well above 500°C. The thermal analyses in Figures 5(a) and 5(b) reveal that temperature for the onset of decomposition is lowered significantly for both borohydrides when loaded in MCM-48. Mass spectrometry reveals that the primary product of both decomposition reactions is hydrogen. However, the mass spectrum also indicates that a significant quantity of diborane is present in the decomposition gas stream of both R₄NBH₄ compounds. Diborane was present in the bulk decomposition products as well.

INS analyses indicated shifts in frequency and changes in intensity of the vibrational modes of both [R₄N⁺] and [BH₄⁻] ions after loading in MCM-48. These changes indicate that the ions are adsorbed onto the silica surface, and that the silica surface changes the chemical environment of these borohydrides slightly. Comparisons of the INS spectra of the bulk and loaded compounds of Me₄NBH₄ are shown in Figure 6(a). The spectra of Et₄NBH₄ and its porous silicate loaded counterpart are shown in Figure 6(b). Further evidence of surface interaction is indicated by the formation of surface hydride compounds which occur during vacuum decomposition of Me₄NBH₄. This surface compound was verified to contain a surface Si-H bond by comparison with the INS spectrum of amorphous silica gel with gaseous hydrogen. INS spectra of MCM-48 loaded

FIGURE 5. (a) TGA 5K/min. heating performed under light Ar flow [1]. Bulk Me₄NBH₄ [2]. MCM-48 loaded with Me₄NBH₄. (b) TGA 5K/min. heating performed under light Ar flow [1]. Bulk Et₄NBH₄ [2]. MCM-48 loaded with Et₄NBH₄.

FIGURE 6. (a) INS spectra of bulk Me₄NBH₄ and MCM-48 loaded with Me₄NBH₄. Adsorption is apparent from the shifts in frequency of numerous vibrational modes and broadening of spectral features, particularly at low frequencies. (b) INS spectra of bulk Et₄NBH₄ and MCM-48 loaded with Et₄NBH₄. Adsorption is apparent from the shifts in frequency of numerous vibrational modes and broadening of spectral features, particularly at low frequencies.
with Me$_4$NBH$_4$ after decomposition and the hydrogen exposed silica can be seen in Figure 7(a) and 7(b) respectively. It should be noted that this surface Si-H bond does not form on the decomposition of Et$_4$NBH$_4$ adsorbed on MCM-48 nor did it occur in samples of Me$_4$NBH$_4$ adsorbed on nickel-doped MCM-48.

Zr(BH$_4$)$_4$ also adsorbs on MCM-48 with alterations in its chemical environment as observed by INS spectroscopy. Several low frequency normal modes of Zr(BH$_4$)$_4$ were shifted by significant amounts; with higher frequency modes less affected. Currently Zr(BH$_4$)$_4$ has been essentially ruled out as a hydrogen storage medium because it becomes volatile upon melting at ~30°C, and decomposes in gas state at ~160°C [14]. This volatility renders the compound unusable in most hydrogen storage systems. TGA data reveal that the Zr(BH$_4$)$_4$ is retained by the MCM-48 during heating, mitigating the volatility issue. Zirconium was verified to be retained by comparison of the Si:Zr ratio as measured by XRF. The severe sensitivity to moisture of Zr(BH$_4$)$_4$ in MCM-48 is also apparently reduced somewhat from the bulk compound.

### Calcium Borohydride Destabilization

The TGA/DSC curves for the LiBH$_4$/Ca(BH$_4$)$_2$ mixture (heated under Ar flow) are shown in Figure 8(a). Two notable endothermic events occur during the heating of the mixture. The endothermic peak at ~115°C coincides with the structural phase transition in LiBH$_4$. The second endothermic peak in the DSC curve of Figure 4b (labeled with a '?') onsets around 200°C. The melting of LiBH$_4$ typically occurs at 285°C, and is greater in total enthalpy change than the structural phase transition at ~120°C and is thus non-consistent with this feature. No melting was evident in the sample upon visual inspection after heating. At higher temperatures, the melting of LiBH$_4$ is notably absent from the DSC curve. There is no such feature in the DSC curve of Ca(BH$_4$)$_2$, which only begins to decompose at ~350°C [15]. The pressure and temperature data from the volumetric analysis of the Ca(BH$_4$)$_2$/LiBH$_4$ mixture is plotted in Figure 8(b). A reaction releasing gas (presumably hydrogen) begins around 220°C. These data are consistent with a thermal destabilization effect from the ballmilling of Ca(BH$_4$)$_2$ and LiBH$_4$. However, it is unclear if the reaction proceeds as Ozolins et al. [5] predict. FTIR showed the resultant solid residue to be free of the Li$_2$B$_{12}$H$_{12}$ product which is the cause of the predicted thermal destabilization (see 4th quarter 2010 report for more details; residual BH$_4$ was clearly present as well). Also the observed reaction released only 39% of the expected gas emissions that would account for the theoretical reaction of Ozolins et al. This implies partial reaction, or a separate destabilization mechanism.
**Conclusions and Future Directions**

**Borohydrides in Mesoporous Silicate**

We have demonstrated that adsorption of the borohydrides within the MCM-48 pores provides various utilitarian effects. In Me$_x$NBH$_4$ and Et$_x$NBH$_4$ a significant reduction (>50°C decrease) in decomposition temperature was observed in TGA for each compound respectively. Rates of thermal decomposition are also improved in the adsorbed compound vs. bulk. Preliminary results indicate that MCM-48 adsorbed Zr(BH$_4$)$_4$ is retained by the MCM-48 during heating, mitigating the volatility issue. Additionally, the air sensitivity of Zr(BH$_4$)$_4$ is significantly reduced when adsorbed on MCM-48.

Inelastic neutron scattering has revealed that the surface chemically interacts with pore encapsulated borohydrides, and plays some role in decomposition of adsorbed borohydrides. We have also demonstrated that doping of this network with transition metals can alter the decomposition chemistry.

**Calcium Borohydride Destabilization**

We have verified a destabilization effect caused by mechanical mixing of LiBH$_4$ and Ca(BH$_4$)$_2$. The mechanism of this reaction does not appear thus far to be consistent with the theoretically reaction producing Li$_2$B$_{12}$H$_{12}$. However, we have not conclusively verified a separate mechanism, and subsequent reaction to decompose the Li$_2$B$_{12}$H$_{12}$ may occur. While the observed destabilization is an improvement versus either bulk Ca(BH$_4$)$_2$ or LiBH$_4$, the reaction temperature, hydrogen yield and kinetics of the observed destabilized decomposition reaction are still require further improvement to be directly usable in hydrogen storage.

**Plan for Future Studies**

- The effects of surface sites on dehydrogenation of borohydrides may prove useful to future researchers investigating borohydrides for hydrogen storage. The impact on storage capacity and reversibility associated with the use of hydride complexes in porous networks is yet unknown.
- The destabilization of CaBH$_4$ and LiBH$_4$ by solid state mixture has not yet been optimized, and may be viable if it can be further catalyzed by addition of dopants. The products and reversibility are yet unknown.

**FY 2010 Publications/Presentations**


References


IV.I.1 Standardized Testing Program for Solid-State Hydrogen Storage Technologies

Objectives

Overall

• Support DOE’s Hydrogen Storage sub-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 effects of piezo-induced charge on the sorption capacity of nano-porous carbon.

• Evaluate and validate hydrogen sorption capacity in polyether ether ketone (PEEK)-derived carbon material.

• Assess hydrogen spillover effects and kinetics in AuAl$_2$ and AuLi-intercalated isoreticular metal organic framework (IRMOF)-16.

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 Fuel Cell 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 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.
Accomplishments

- 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.

- Evaluated the effect of piezo-induced charge on hydrogen adsorption in nanoporous carbon at 77 and 298 K, using materials provided by Michigan Tech University, and observed that piezo-induced charge accumulation did not lead to a measurable increase in hydrogen uptake via hydrogen-charge binding interactions.
- Validated the hydrogen sorption capacity in PEEK-derived carbon at 77 and 298 K using material provided by Duke University. Experimental measurements showed:
  - Maximum excess concentration of 5.4 wt% at 77 K and 55 bar.
  - Absolute volumetric capacity approaching 30 g/L at 77 K and 70 bar.
- By leveraging SwRI’s parallel research activities, IRMOF-16 compounds entrapping nanoparticles of AuAl₂ and AuLi (i.e., metal intercalated IRMOF-16) were successfully synthesized and characterized. Experimental measurements showed:
  - Excess concentration of 1.1 wt% at 80 bar and room temperature for the AuAl₂-IRMOF-16 compound, which can be attributed to hydrogen spillover, with relatively fast kinetics (15 min for equilibration).
  - Total loading of intercalated AuAl₂ in IRMOF-16 sample was only 0.13 wt%.
  - Total loading of intercalated Ti in previously-reported Ti-IRMOF-16 compound (showing 1.3 wt% uptake at room temperature and 80 bar) was only 0.04 wt%.

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, nanoporous carbon materials [3,4], and silica nanosprings, 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 and the DOE. The most recent priorities for the laboratory have concentrated on evaluating piezo-induced charging effects on hydrogen binding interactions in nanoporous carbon, and hydrogen sorption in PEEK-derived nanoporous carbon. In addition to these DOE directives for validation, internally-sponsored materials development activities have been undertaken to evaluate whether chemisorptive strategies for hydrogen storage predicated on spillover can be elicited in AuAl₂ and AuLi-intercalated IRMOF-16 compounds. These efforts were principally motivated by the need to overcome the diffusion-limited kinetics associated with hydrogen spillover 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 Center of Excellence), 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 program provides a venue for the discovery of new materials and the elucidation of unknown mechanisms.

Results

Effects of Piezo-Induced Excess Charge on Hydrogen Binding

The results of our studies over the past year are highlighted in Table 1. An important directive this year was to independently determine whether or not hydrogen uptake could be enhanced by injecting excess charge into a conductive, porous sorbent, such as nanoporous carbon, and thereby provide the means by which the binding energy between dihydrogen and the localized charge on the sorbent could be increased. This idea, which was conceived at Michigan Technological University (MTU) [6], required that we design and construct a highly-modified sample vessel for low-temperature (77 K) sorption measurements. In this modified vessel, the sample was electrically isolated from the assembly via a thin-walled glass insert, while two piezoelectric elements of the lead magnesium niobate-lead titanate type were embedded in the sample at a fixed distance from each other. One pole (i.e., face) of each piezoelectric element was also electrically insulated so that the face of the conductive pole could emit a local excess-charge into the surrounding carbon sample as hydrogen gas pressure was increased.

While the premise of this concept would seem intuitively sound, our laboratory failed to demonstrate a measurable difference in hydrogen uptake between piezo-induced charge generation in nanoporous carbon and the same carbon sample in the uncharged state under identical analytical conditions of the volumetric technique (Table 1 and Figure 2). This difference between hydrogen-charge binding interactions in the charged and uncharged states, however, may have been so subtle due to the experimental conditions employed, such as a low ratio of total charge to sorbent surface area, that the desired effect could not be effectively realized. Indeed, other passive or active modalities of injecting excess charge into a conductive sorbent may be more effective in enhancing hydrogen uptake or increasing the sorption temperature, or both.

PEEK-Derived Carbon

High-pressure volumetric analysis of PEEK-derived carbon was encumbered by this material’s propensity to absorb helium, thus invalidating the use of a helium calibration for determining the skeletal density of the sample (or free volume of the system). To overcome this analytical challenge, the high-pressure gravimetric technique was employed to measure the hydrogen isotherm at room temperature. In this case, the simplified local density (SLD) model combined with the Bender equation of state were used in a fitting algorithm to derive the hydrogen skeletal density and the pore volume of the sample by treating these characteristic properties as fitting parameters [7].

TABLE 1. Overall Summary of Results for Various Classes of Storage Materials under Investigation

<table>
<thead>
<tr>
<th>Storage Material</th>
<th>Source</th>
<th>Gravimetric Excess and/or Absolute Volumetric Capacity (Conditions)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piezoelectric Transducer/Nanoporous Carbon</td>
<td>MTU</td>
<td>3.84 wt% (77 K, 29 bar)</td>
<td>Piezo-induced excess charge accumulation did not lead to measurable increase in hydrogen uptake compared with carbon alone.</td>
</tr>
<tr>
<td>Nanoporous Carbon</td>
<td>MTU</td>
<td>3.94 wt% (77 K, 24 bar)</td>
<td></td>
</tr>
<tr>
<td>PEEK-Derived Carbon</td>
<td>Duke Univ.</td>
<td>5.39 wt.% (77 K, 55 bar), 29.4 g/L (77 K, 70 bar)</td>
<td>Relatively fast kinetics, achieving steady-state within ~20 min.</td>
</tr>
<tr>
<td>AuAl2 -IRMOF-16</td>
<td>SwRI</td>
<td>1.10 wt% (298 K, 80 bar)</td>
<td>Fast spillover kinetics (~15 min steady-state); only 0.13 wt% catalyst loading.</td>
</tr>
<tr>
<td>AuLi-IRMOF-16</td>
<td>SwRI</td>
<td>0.30 wt% (298 K, 67 bar)</td>
<td>Fast spillover kinetics (~15 min steady-state); only 0.10 wt% catalyst loading.</td>
</tr>
</tbody>
</table>

LTDMS = laser induced thermal desorption mass spectrometry
The corrected hydrogen isotherms at 77 K measured by the volumetric technique are shown in Figure 3. Here the maximum excess concentration for hydrogen uptake was 5.39 wt% at 55 bar with no measureable hysteresis in the desorption path. Using the pore volume derived from the SLD model and fitting algorithm, the profile for absolute volumetric capacity was computed as shown in Figure 4. The absolute volumetric capacity for this material approached 30 g/L at 70 bar and, while this is a remarkable result, it is less than the current benchmark of 40 g/L at 70 bar for MOF-177.

Metal-Intercalated IRMOF-16

Storage materials predicated on hydrogen spillover effects are under intensive study in our laboratory. However, spillover materials exhibiting enhanced uptake at room temperature have been consistently plagued by exceedingly slow kinetics, principally because doping of these materials with a catalyst (and bridging compounds) has been limited to the surface of the porous receptor (e.g., carbon or MOF) [3-5]. A better than present strategy for engineering an “ideal” spillover material has been envisaged in which metal clusters are intercalated into (or rather encapsulated by) 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 and in close proximity to receptor sites for binding of atomic hydrogen following catalytic dissociation.

In pursuit of unique spillover motifs with improved kinetics, we have expanded our work on the synthesis and characterization of IRMOF-16 [Zn₄O(1,4-di(4-carboxyphenyl)benzene)] compounds entrapping nanoparticles of metal catalysts (i.e., metal intercalated IRMOF-16) by preparing the AuLi-IRMOF-16 and AuAl₂-IRMOF-16 intercalated compounds [8]. These were successfully synthesized using an ionic liquid (IL) as a co-solvent and in situ entrapment of the catalyst particles. The catalyst compounds used here were previously prepared in our laboratory by depositing each metal alloy into IL in vacuo under conditions of plasma magnetron sputtering. In each case, the gravimetric technique was employed to measure hydrogen isotherms at room temperature. The catalyst loading in each compound was also quantified using inductively coupled plasma mass spectrometry (ICP-MS).

The AuAl₂-IRMOF-16 intercalated compound demonstrated higher than expected hydrogen uptake at room temperature (1.1 wt% excess at 80 bar) (Figure 5), achieving steady-state conditions at each pressure point within 15 min (as compared with 600 min for surface-catalyzed spillover materials evaluated in our laboratory). Surprisingly, the AuLi-IRMOF-16 compound yielded only 0.5 wt% excess at 67 bar. In both cases, however, hydrogen uptake via spillover occurred with only 0.1 wt% loading of catalyst in the voids of the MOF as determined by the ICP-MS analysis.

Overall, we have demonstrated that structural motifs of this kind can dramatically improve the kinetics associated with hydrogen spillover effects by encapsulating catalyst particles within framework voids and distributed therein throughout the bulk framework. This close proximity of catalytic centers to the structural moieties of the receptor shortens the diffusion length associated with the transport of atomic hydrogen to chemisorptive binding sites on the receptor following dissociative spillover.
Conclusions and Future Directions

The passive (or active) injection of excess charge into a nanoporous carbon is in principle an attractive means of increasing physisorption binding interactions of dihydrogen for enhanced storage, which is deserving of exploration. However, our laboratory has failed thus far to observe experimentally meaningful differences in hydrogen uptake between carbon samples in contact with half-insulated piezoelectric elements for charge generation and the same material in its uncharged state. The lack of supporting results notwithstanding, future work in this area should first seek to calculate the ratio of the total charge theoretically generated by piezoelectric elements (or other means) to the surface area of the carbon material. Such rudimentary calculations would provide the information needed to effectively scale the experimental setup so that differences in hydrogen uptake between the charged- and uncharged states, if they occur, are most likely to fall within the known limits of detection of the sorption technique.

In the search for novel forms and sources of active carbon materials for physisorption storage, robust materials have emerged with remarkably high surface areas. Nanoporous carbon derived from PEEK exhibits promising characteristics for hydrogen storage in terms of specific surface area and chemical stability. We observed excess gravimetric and absolute volumetric capacities at 77 K that are approximately 70% of those values for the current benchmark, MOF-177 [1]. Further gains in performance are possible as processing methods for the source PEEK polymer are refined.

The potential for chemisorptive strategies via spillover in catalytically-doped nanostructures points to promising opportunities in meeting the DOE on-board storage targets. In expanding our work on 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 chemisorptive sites that lie in close proximity. As was intended, this arrangement manifests in a dramatic improvement in sorption kinetics at room temperature. Future work should concentrate on refining the structural purity of these sorts of structural motifs so that additional gains in room temperature uptake can be realized.

FY 2010 Publications/Presentations


References

V. FUEL CELLS
V.0 Fuel Cells Sub-Program Overview

Introduction

The Fuel Cells sub-program supports research, development, and demonstration of fuel cell technologies, focusing on the development of fuel cells and fuel cell systems for use in a variety of stationary, portable and transportation applications, with a primary focus on reducing cost and improving durability. Efforts are balanced to achieve a comprehensive approach to fuel cells for near-, mid-, and longer-term applications. Early market penetration is targeted through the development of fuel cell technologies and systems for portable-power applications, auxiliary power units (APUs), and specialty applications such as material handling equipment. Fuel cell technologies already provide sufficient performance and durability to be competitive with alternative technologies in some of these applications, while in others relatively modest improvements are required. The expansion of fuel cells into applications and markets that have more stringent technical and cost requirements is also being pursued. The sub-program pursues the development of fuel cell technologies and systems for distributed power generation—including combined heat and power (CHP) for residential and commercial applications—and for light-duty vehicles, in the longer-term, to allow fuel cell technologies to have significant economic, energy security, and environmental benefits on a national scale.

The sub-program’s portfolio of projects covers a broad range of technologies including polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cells, alkaline fuel cells, and solid oxide fuel cells (SOFCs). Efforts support research and development (R&D) of fuel cell stack components, fuel processors for stationary and off-road transportation applications, and system balance of plant (BOP) components. Along with ongoing efforts, funding allowed for nine new projects, following a 2008 solicitation/lab call, to be initiated in Fiscal Year (FY) 2010. These projects include R&D of catalysts and membrane electrode assembly (MEA) structures with reduced platinum group metal (PGM) content, PGM-free catalysts, portable power, as well as degradation and durability studies, and fuel cell mass transport studies. The DOE funding for these projects is approximately $33 million.

Goal

Develop and demonstrate fuel cell power system technologies for stationary, portable, and transportation applications.

Objectives

• Develop a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of $45/kW, by 2010; and at a cost of $30/kW, by 2015.\

• Develop a fuel cell system for consumer electronics (<50 W) with an energy density of 1,000 Wh/L, by 2010.\

• 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, by 2011.\

• Develop a fuel cell system for APUs with specific power of 40 W/kg and power density of 35 W/L, by 2015.\

FY 2010 Technology Status

Major challenges in the advancement of fuel cell technology are reduction of cost and improvement of durability. Air, thermal, and water management are also key issues for enhancing fuel cell performance. Fuel cells are approaching their targets for power density and specific power, but further progress is required to achieve system packaging requirements necessary for commercialization. Efforts continue to evaluate, understand, and mitigate degradation mechanisms through modeling and experimental validation by the national laboratories, universities, and fuel cell developers. While

[1] Objectives are from the Multi-Year Research, Development and Demonstration Plan, which is under review.
hydrogen is the fuel of choice for automotive applications, stationary applications would benefit from technology improvements permitting fuel flexibility.

The tasks in the *Multi-Year Research, Development and Demonstration Plan*, to be updated in 2010, are organized around components (membranes, electrodes, MEAs, gas diffusion layers, bipolar plates, seals, and BOP components), supporting analysis, and benchmarking and characterization activities. Task areas for fuel cell system and fuel processor sub-system development for stationary power generation applications are included, as are those for early market fuel cell applications, such as portable power, and for the development of innovative concepts for fuel cell systems.

The Fuel Cells sub-program maintains a portfolio of R&D projects specifically aimed at meeting technical and cost targets that will allow fuel cells to compete in the marketplace. With cost a prime driver, analysis of the cost status on an annual basis is required for progress to be gauged. As shown in Figure 1, the cost of a hydrogen-fueled 80-kW fuel cell power system projected for high volume production (500,000 units/year) has been estimated to be $51/kW (assuming 2010 technology), a $22/kW (30%) reduction from the 2008 cost of $73/kW and $10/kW (16%) reduction from the 2009 cost of $61/kW. Cost reductions resulted from simplified architecture and reduction in stack component costs through ongoing R&D efforts. The cost of the fuel cell stack has been estimated to be $25/kW.

**FY 2010 Accomplishments**

Continued progress was made toward meeting 2010 and 2015 technical and cost targets during FY 2010. Notable technological advances in several component areas have led to significant improvements in performance and durability, with decreased cost.

**Advanced Catalysts Enable Reduction in Precious Metal Loading**

The high cost of catalysts based on platinum (Pt) and other PGMs presents a major impediment to widespread commercialization of fuel cell technology. Reducing the loading of Pt and other PGMs, without compromising performance, is therefore a key path to decreasing system cost.

3M continues to develop advanced cathode catalysts based on nanostructured thin film (NSTF) technology. In late FY 2009, 3M reported results from testing of 400 cm² short stacks with NSTF-based PtCoMn catalysts with total PGM content as low as 0.19 gPGM/kW. In FY 2010, 3M increased PtCoMn mass activity 30%, reaching 0.24 A/mg₉₉ for Pt₃Ni, alloy with mass activity of 0.40 A/mg₉₉. 3M developed a post-fabrication treatment process that is roll-good compatible and increases oxygen reduction reaction mass activity up to 50% for PtCoMn and the Pt₃Ni alloy. Further

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work promises to yield even greater improvements, allowing NSTF catalysts to approach activity levels observed with idealized model catalysts.\(^3\)

3M operated a membrane over 5,000 hours with load cycling with an MEA based on a non-stabilized 20-μm membrane and catalyst loading of 0.15 mg\(_{\text{PGM}}\)/cm\(^2\), meeting the DOE 2010/2015 durability target of 5,000 hours. (The 7,300 hours reported previously was with a higher PGM loading.) With the use of chemical stabilizers in the membrane, 3M exceeded the 200-hour DOE target for stability under open-circuit voltage hold in H\(_2\)/air by more than 300%.\(^3\)

Development of novel core-shell catalysts at Brookhaven National Laboratory (BNL) has contributed to efforts to decrease PGM loading. In FY 2010, BNL improved its core-shell catalyst by using an interlayer of gold (Au) to separate the Pt shell from the PdCo core. Rotating disk electrode testing of the new catalyst has demonstrated mass activity as high as 1.10 A/mg\(_{\text{PGM}}\) and specific activity as high as 1,170 μA/cm\(^2\) at 0.9 V,\(^4\) suggesting a high probability of meeting DOE MEA-level and stack-level targets of 0.44 A/mg\(_{\text{PGM}}\) and 720 μA/cm\(^2\). Scale-up of core-shell catalysts has also been demonstrated, with production of a Pt/Pd core-shell catalyst in batches up to 20 g at Cabot Fuel Cells.

These and other advancements in PGM-based catalysts represent significant progress in FY 2010 toward improvement of fuel cell performance and reduction in fuel cell cost through minimization of PGM loading.

**Non-Precious Metal Catalysts Demonstrate Potential for High-Performance, Low-Cost Fuel Cells**

Continued work at Los Alamos National Laboratory (LANL) on PGM-free catalysts yielded significant performance improvements in FY 2010, with volumetric current density as high as 60 A/cm\(^3\) measured at 0.80 V (iR-free) during fuel cell testing with Fe-cyanamide-C catalyst, representing a 64x improvement over the past two years.\(^4\) Extrapolation to correct for mass-transport limitations suggests that current density as high as 165 A/cm\(^3\) is achievable with this catalyst, in excess of the DOE 2010 target of 130 A/cm\(^3\). Progress also continues on PGM-free polyaniline-based catalysts at LANL, with activity as high as 31 A/cm\(^3\) measured at 0.80 V, a 36x improvement over the past two years.\(^4\)

**Innovative Polymer Chemistry Produces New Membrane Materials for Hot and Dry Conditions**

3M developed new polymer electrolyte membranes with higher proton conductivity and improved durability under hotter and dryer conditions compared with previously produced membranes, as shown in Figure 2.\(^5\) The new multi-acid side-chain polymer membranes have better mechanical properties than conventional single acid side chain perfluorosulfonic acid (PFSA) membranes. In FY 2010, 3M developed innovative polymers in which side chains contain both sulfonic acid and sulfonamide groups. These new perfluoroimide acid (PFIA) polymers have higher tetrafluoroethylene backbone crystallinity than PFSA of the same equivalent weight, and thus have better mechanical properties, including lower swelling and lower water uptake.

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solubility. Efforts continue to produce PFIA membranes of lower equivalent weight and higher conductivity under dry conditions.

Degradation Studies Reveal Pathways to Increased Durability

Improvements in durability of fuel cell systems will facilitate user acceptance of fuel cells to replace conventional power generation technology. Argonne National Laboratory is investigating the role of electrocatalyst degradation in fuel cell durability, and has thus far highlighted the effect of catalyst particle size on degradation rates, revealing that performance of catalysts with small initial particle size moves toward that of larger particles during operation with cycling, as shown in Figure 3. Work at LANL has demonstrated the critical role of electrode processing on durability. Electrodes formed by an ink-painting technique are strongly sensitive to the nature of the solvent used in the ink. Electrodes prepared from glycerol-based inks demonstrated excellent durability (less than 30 mV loss at 0.8 A/cm² after 70,000 cycles, (exceeding the DOE target of 30,000 cycles), while electrodes prepared from water/alcohol-based inks suffer from severe degradation.

Metal Bipolar Plate Development Demonstrates Corrosion Resistance at Low Cost

Since bipolar plate corrosion and high cost have a negative impact on fuel cell stack cost and durability, sub-program activities support development of novel materials and fabrication methods for bipolar plates. TreadStone Technologies demonstrated coating approaches that allow for the development of low-cost, corrosion-resistant, metal bipolar plates, with an FY 2010 cost estimate well below $5/kW, achieving the FY 2010 target. The approach relies on the use of small, conductive, corrosion-resistant materials as conductive points to cover a small portion of metal surface, together with the use of non-conductive, corrosion-resistant materials to cover the majority of the surface of the metal plates.

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FIGURE 3. Cycling Degrades Performance of Catalysts with Small Initial Particle Size toward that of Larger Particles

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CHP Operation Demonstrates Capability for Energy and Cost Savings

DOE is developing distributed energy and CHP systems based on several technologies. Acumentrics Corporation is funded to develop micro-CHP systems based on tubular SOFC technology. In FY 2010, Acumentrics achieved a 24% increase in system power density, enabling a 33% reduction in stack volume and a 15% reduction in stack weight. A low degradation rate of 0.86%/1,000 hours during 1,500 hours of testing was demonstrated.9

Budget

The President’s FY 2011 budget request calls for approximately $67 million for the Fuel Cells sub-program, with emphasis on R&D of materials, fuel cell stack components, and system BOP components, targeting lower cost and enhanced durability for stationary, portable, and transportation applications. Further emphasis is placed on R&D for integrated fuel cell systems for distributed power, including CHP applications, where a ‘technology-neutral’ approach is pursued. The FY 2011 request also includes approximately $19.5 million for a potential solicitation, subject to approval and congressional appropriations. The figure below shows the budget breakdown by sub-program R&D area for the FY 2010 congressional appropriation and the FY 2011 budget request.

FY 2011 Plans

In FY 2011, the Fuel Cells sub-program will continue R&D efforts on fuel cells and fuel cell systems for several key applications, with a focus on further developing multiple fuel cell technologies using various fuels, which involves improving component properties. Support will continue for R&D that addresses critical issues with membranes, catalysts, electrodes, and modes of operation. The sub-program will continue to place emphasis on the science and engineering at the cell and stack level and, from a systems perspective, on integration and component interactions.

The sub-program will also place significant emphasis on BOP component R&D (such as water transport, sensors, and air compression) that can lead to lower cost and lower parasitic losses. Continued support of modeling will guide component R&D, to benchmark complete systems before

they are built and explore alternate system components and configurations. Cost analysis efforts will be expanded to include distributed power generation systems (including CHP) for a variety of fuel cell technologies.

FY 2011 will see the continuation of existing projects and of those awarded in FY 2010, as well as a new initiative. A planned solicitation, subject to approval and congressional appropriations, is expected to lead to the awarding of new projects in FY 2011.

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V.A.1 Fuel Cell Systems with Low Platinum Loadings

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Project Start Date:  October 1, 2003
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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost
(C) Performance
(E) System Thermal and Water Management
(F) Air Management
(G) Start-up and Shut-down 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

• Determined the performance of nanostructured thin film catalyst (NSTFC) stacks with 0.15 mg/cm² Pt loading and supported 20-µm membranes.
• Evaluated the performance of the Honeywell integrated compressor-expander-motor module (CEMM) for 1.5-atm operation.
• Analyzed the performance of parallel ejector-pump hybrids for fuel management.
• Constructed performance maps for planar membrane humidifiers.
• Collaborated with Honeywell to evaluate the performance of advanced microchannel automotive radiators.
• Conducted drive cycle simulations to determine the fuel economy of hybrid fuel cell vehicles for different rated-power efficiencies.

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.
In Fiscal Year (FY) 2010, we changed our reference FCS configuration (see Figure 1) to eliminate the anode humidifier, switched to a single stack (with metal bipolar plates) that produces the gross power required for 80-kW, net power, and expanded the system configurations to include the low-pressure option. We evaluated the performance of three systems: S1 – the reference pressurized FCS with 2.5-atm stack pressure at rated power, S2 – a low-pressure FCS with 1.5-atm stack inlet pressure at rated power, and S3, which is S2 without a cathode humidifier [1].

**Air Management**

We modeled the performance of the Honeywell CEMM originally designed for 2.5-atm peak pressure (S1 conditions). We determined the optimum operating points of the mixed axial flow compressor, variable area nozzle turbine, 3-phase brushless direct current motor, and the liquid-cooled motor controller. We found that the CEMM component efficiencies are quite comparable under S1 and S2 conditions. The main difference is that the peak shaft speed is 85,000 rpm under S2 conditions compared to 110,000 rpm under S1 conditions. Thus, it may be possible to improve the performance of the CEMM for S2 conditions by redesigning it for a higher speed at 1.5-atm and full flow.

Our analysis indicates that the maximum turndown may be limited by compressor surge for shaft speeds less than 45,000 rpm. We estimate that at rated power, the CEMM consumes ~10 kW, in S1 and <6 kW, in S2. At idling conditions, the estimated power consumption is 250–400 W, depending on the allowable minimum shaft.
speed. The minimum shaft speed, if lower than the lift speed, will affect the durability of the airfoil bearings.

Fuel Cell Stack

In FY 2009, we had developed a cell and stack model for 3M’s NSTFC-based membrane electrode assemblies (MEAs) using data for electrochemically active surface area, specific activity, short and crossover currents, high-frequency resistance and polarization curves over a wide range of temperatures and inlet relative humidities [2]. In FY 2010, we used the model to determine the optimum stack operating conditions for S1, S2 and S3 scenarios. With fixed air and fuel stoichiometry (50% oxygen and 50% per-pass hydrogen utilization) and rise in coolant temperature (10°C), at rated power, we calculated the optimum stack temperature (i.e., coolant exit temperature) and the inlet cathode and anode dew point temperatures as 85°C/64°C/59°C for S1, 75°C/61°C/53°C for S2, and 65°C/22°C/22°C for S3, respectively. These results clearly show the role of pressurization and air humidification in determining the optimum stack temperature.

Figure 2a shows a comparison of the power density and the Pt content of the FY 2009 (0.1(a)/0.15(c) mg-Pt/cm², 35-µm 850 equivalent weight [EW] membrane) and FY 2010 (0.05(a)/0.1(c) mg-Pt/cm², 20-µm 850 EW supported membrane) reference S1 systems. We estimate that the power density for the 2010 system is 20% lower at 50% system efficiency due to lower Pt loading (0.8-1 A/cm²) but is about 6% higher at 40% system efficiency because of the thinner membrane (>2 A/cm²). Lower Pt loading and thinner membrane combine to produce a 30-45% reduction in Pt content for the 2010 systems (0.12-0.30 g-Pt/kWe-net).

Figure 2b compares the performance of the FY 2010 S1 and S2 systems. The cell voltage in S1 is 25-35 mV higher to achieve the same system efficiency by compensating for the greater CEMM parasitic power. In spite of the higher cell voltage, S1 can have higher power density because of the positive effect of the system pressure on the current density. Depending on the system efficiency, we project up to 12% higher Pt content for the S2 scenario.

Fuel Management

We analyzed the performance of the parallel ejector-pump hybrid in the fuel management system. Figure 3 shows the entrainment by a supersonic ejector [3] in which the motive gas is pure hydrogen from the compressed gas tank and the suction gas is spent hydrogen at the stack outlet. We consider that the motive gas is available at pressure less than 15 atm (regarded as the empty tank pressure) and that the suction gas is saturated with water vapor (molecular weight of 3-7) at 1-1.15 atm (S2 scenario). The desired lift pressure is 3 psi at rated power and the recirculation ratio (suction to primary mass flow rate) is 2.5. In our terminology, entrainment expresses the ratio of the suction flow rate established by the ejector to the flow rate required for 50% hydrogen utilization.
Figure 3 shows the entrainment and the motive gas pressure as functions of the normalized stack power. A single ejector alone can recirculate hydrogen for stack power down to 43% of rated power (Figure 3a). Between 28 and 43% stack power, a blower is needed to assist in recirculating the hydrogen; below 28% stack power, the motive gas pressure is too low to achieve the required lift pressure and the blower alone recirculates hydrogen. The ejector-only portion of the operating map can be expanded by including a second ejector that is parallel to and smaller than the first ejector (Figure 3b); however, the blower is still needed for stack power less than 24%. Alternately, a variable throat-area ejector can be employed to expand the ejector-only operating window to 36-100% stack power (Figure 3c).

Our model indicates that, without an ejector, a 400-W (mechanical power) blower is needed to recirculate hydrogen in the S2 scenario. A single fixed-area ejector reduces the blower power by more than 90%. Although the blower power can be reduced considerably with a variable-geometry ejector (to 25 W) or a dual-ejector arrangement (to 10 W), additional complexity may be difficult to justify [4].

**Water Management**

We received and analyzed Honeywell and PermaPure data for full-scale, half-scale and one-tenth-scale membrane humidifiers [5]. We derived permeance for the units (aggregate, not local values) and showed that the permeance can be represented in terms of the operating temperatures and the relative humidity of the dry air exiting the humidifier. We also constructed a map for mass-transfer effectiveness factors that, together with the permeance chart, can be used as nomographs for sizing such membrane humidifiers.

We used the data to develop and validate a model to determine the heat and mass transfer between the counterflowing wet and dry streams separated by a Nafion® membrane. The model considers water uptake from the wet stream, diffusion through the Nafion® membrane, and desorption into the dry stream. Figure 4 shows the model results for mass flux of water from a saturated wet stream at 2.5 atm and 80°C to dry air at different inlet temperatures. The flux is a strong function of the dew-point approach temperatures ($T_{dp}$), the difference between the inlet wet-air $T_{dp}$ and the outlet dry-air $T_{dp}$. Figure 4 indicates the existence of an
optimum dry air inlet temperature ($T_{in}$) for maximum flux. The flux decreases for dry air inlet temperature ($T_{in}$) higher than $T_m$ because of the low water uptake in the membrane (too dry). The flux decreases for $T_d$ lower than $T_m$ because the humidified air approaches saturation. Also, $T_m$ is a function of the dew-point approach temperature. The lower the approach $T_{dp}$, the lower the $T_{sat}$ and the smaller is the maximum water flux.

Our simulations show that the water mass transfer flux is also a strong function of the membrane thickness, temperature of the wet air and the operating pressure. For a given approach $T_{dp}$, the flux increases if the membrane is made thinner, the pressure is increased, or the wet-air temperature (i.e., the stack temperature) is raised.

The results in Figure 4 confirm the importance of including the pre-cooler that lowers the temperature of the compressor discharge air to 55-60°C before entering the humidifier. Without the pre-cooler, the cathode humidifier will need five- to ten-times larger mass-transfer area.

Thermal Management

We received and analyzed the thermal and fluid mechanics data from Honeywell for 25 cm x 25 cm x 3.3 cm sub-scale and 70 cm x 45 cm x 5.5 cm full-scale radiators with 18 and 24 louver fins per inch (fpi) and 40 and 50 fpi plain microchannel fins. We derived the friction factor ($f$) and heat transfer ($j$) 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 40 fpi microchannel fins are superior to the 18 fpi louver fins in the full-scale design. We also concluded that the fuel cell powertrains may need to be derated for ambient temperatures higher than 40°C since the fan power doubles for every 5°C increase in ambient temperature.

We conducted a study to assess heat rejection in fuel cell vehicles as a function of the FCS efficiency and stack temperature. We considered that the air conditioning condenser (9 kW heat load) and the low-temperature radiator (13-17 kW heat load) are stacked in front of the high-temperature radiator that rejects waste heat generated in the fuel cell stack. Our results show that for a given fan power, the system S2 with 40% efficiency at rated power must be capable of operating at 5-10°C higher stack temperature than the same system with 50% efficiency. Also, from the standpoint of heat rejection, the 40%-efficiency FCS may be acceptable if it can be operated at stack temperatures exceeding 95°C.

We evaluated the prospect of raising the stack temperatures to 95°C under transient conditions (e.g., hill climbing at 55 mph) where high heat rejection may be required for several minutes. We determined that the maximum stack temperature is limited by the system pressure and the dew-point temperature of the cathode air at stack inlet. The CEMM motor power may limit the ability to pressurize adequately if the CEMM does not include an expander. Similarly, the stack temperature cannot be raised if the system does not include a humidifier. We concluded, therefore, that the S3 configuration may not be viable for transportation applications.

System Performance

We analyzed the part-load performance of the S2 system configurations and found that the system efficiencies peak at about 10% of the rated power. Reducing the rated power efficiency from 50% to 45% results in less than a 1% difference in peak efficiency. We also found an inverse relationship between the rated-power efficiency and the system efficiency for power less than 10%; because of hydrogen crossover, the efficiency is marginally higher for the system with 40% rated-power efficiency than the system with 50% rated-power efficiency. We conducted battery-FCS hybrid vehicle simulations to establish the relationship between the rated power efficiency and the system efficiency over drive cycles. The simulations were run for two modes of operation, one in which the FCS is operated primarily as a battery charger and the second in which it is operated in the load-following mode (LFM). The fuel economy is higher in the battery-charging mode (BCM) but the FCS durability may be an issue because of the excessive number of starts and stops. On the Urban Dynamometer Driving Schedule (UDDS), our battery power management strategy produces 58 fuel cell start-stops in BCM and only four in LFM. FCS start-stops can be eliminated altogether if the fuel cell is allowed to idle at low loads. Our LFM simulations indicate that reducing the rated-power efficiency from 50% to 40% results in just 2% difference in system efficiencies over the UDDS, <3% over the Highway Fuel Economy Test (HWFET) cycle, and >9% on the Los Angeles drive cycle (LA92). The corresponding differences in fuel economy are ~2% over the UDDS, <6% over the HWFET, >9% over the LA92, and <7% over the combined cycle used for fuel economy certification. We conclude that reducing the system efficiency at rated power from 50% to 40% results in >50% reduction in Pt content and >40% reduction in cost of stacks manufactured at high volumes while decreasing the peak efficiency by <1% and fuel economy by <7%.

Conclusions and Future Directions

- The variable-area nozzle turbine allows the CEMM to be adapted to different design pressures without significant losses in component efficiencies. The parasitic CEMM power can be reduced by 40% if the compressor discharge pressure is lowered from...
2.6 atm (S1 scenario) to 1.6 atm (S2 scenario) at the rated power design point.

- The Pt content can be potentially decreased by 30-45% by reducing the Pt loading from 0.25 mg/cm² (2009 status) to 0.15 mg/cm² (2010 status) and using a thinner supported membrane (20 µm vs. 35 µm). Depending on the system efficiency at the design point, we project the Pt content (2010 status) to be between 0.12 and 0.30 g/kWe (net), with the potential to meet the ultimate DOE target.

- Our analysis of the different arrangements of the fuel management system indicates that the recirculation blower power can be decreased by 90% by using a parallel ejector for metering the fuel and entraining the depleted hydrogen from stack outlet. The blower power can be further decreased with dual ejectors or a variable-geometry ejector, but the system complexity may be difficult to justify.

- A pre-cooler between the air compressor and the membrane humidifier can lead to a more than five-fold increase in mass transfer flux of water in the humidifier. Besides the dry air inlet temperature, the water flux is also a strong function of the membrane thickness, temperature of the wet air from the fuel cell stack and the operating pressure.

- From the standpoint of heat rejection, a lower efficiency FCS may be acceptable, provided that the stack temperature can be allowed to increase under certain transient conditions. The maximum stack temperature may be limited by the operating pressure and air humidification.

- In FY 2011, we will investigate the effects of alternative system configurations, rated power efficiency (Pt content) and system operating points on the high-volume manufacturing cost, dynamic drive-cycle performance and component durability.

**FY 2010 Publications/Presentations**


**References**


V.A.2 Mass-Production Cost Estimation for Automotive Fuel Cell Systems

Objectives

- Identify the lowest cost system design and manufacturing methods for an 80 kW, direct-H₂ automotive proton exchange membrane (PEM) fuel cell system based on three (now two) technology levels:
  - Current status
  - 2010 projected performance (replaced by “current status” for 2010 update)
  - 2015 projected performance
- 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
  - 150,000 vehicles per year
  - 500,000 vehicles per year
- 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

| DOE Targets/DTI Estimates in $/kWₑ (at 500,000 Systems/Year Manufacturing Rate) |
|-----------------|-------|------|------|------|
| Stack Cost
| 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  |
| DTI 2009 Estimate (Year 4) | -   | $26  | $24  | $22  |
| DTI 2010 Estimate (Year 5) | -   | $25  | $21  |
| System Cost
| 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  |
| DTI 2009 Estimate (Year 4) | -   | $61  | $56  | $51  |
| DTI 2010 Estimate (Year 5) | -   | $51  | $39  |

Accomplishments

- DTI 2009 Cost Estimate:
  - Improved existing conceptual design and component specification of complete fuel cell power systems at three technology levels (2009, 2010, and 2015).
  - Determined final 2009 cost status.


- 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.

**DTI 2010 Cost Estimate:**
- Improved existing conceptual design and component specification of complete fuel cell power systems at two technology levels (2010 and 2015).
- Determined final 2010 cost status.

**Introduction**

In this project, DTI has built on previous analyses to estimate the cost of 80 kWₑₓₚₜₑₜₜ 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 state-of-the-art PEM fuel cell technology and prepared system cost models to reflect 2006, 2010, and 2015 estimates. Each ensuing year, the cost model was updated to reflect advances in technology and the evolving cost analysis. During the most recent reporting period, an adjustment in funding led to a compression of the project timeline, and the 2010 update was completed earlier than originally scheduled. As such, this annual progress report covers the fourth year and part of the fifth year of the DTI project, reflecting updates and advances in technology from both 2009 and 2010. Since the current year is 2010, the “current” technology and the 2010 projected technology have merged, leaving only two technology levels to examine: the current status (2010) and the 2015 projection.

A Design for Manufacturing and Assembly (DFMA®) methodology is employed to obtain the fuel cell system cost estimates. DFMA® is a methodology created by Boothroyd Dewhurst, Inc. to systematically estimate the total manufacturing cost of a component or system and then to conduct a comparative cost analysis so as to allow a redesign to achieve the lowest system cost. Typically, a markup factor is applied to the costs of general and administrative, scrap, research and development (R&D), and profit and is applied to all manufacturing entities 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 2010 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 the different technology levels. 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. When it was unclear which approach was best, several different methods were analyzed, 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 between the two different technology levels (see Table 2) are driven primarily by expected improvements in stack power density (833 to 1,000 mW/cm²), operating pressure (1.69 to 1.5 atm), and peak stack temperature (90 to 99°C). Of these, increased power density is most responsible for stack cost reduction. Balance-of-plant (BOP) cost reductions stem primarily from system simplifications (i.e. reduced or eliminate components). For example, the current technology system uses a Nafion® membrane air humidification system with an air precooler, and the 2015 has no humidification system at all. Simplifications of the air, humidification and coolant systems yield the majority of technology improvement savings.

The stack cost decreases with advancing technology level due to both power density improvement and reduction of the parasitic electrical loads. 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) result in a reduction of cell active area and a corresponding decrease in material cost.

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 refined. Therefore, most of our analysis in previous years of the project has been focused on the stack, since it provided the most potential for cost improvement. Since the 2008 status update however, the focus has shifted towards the BOP. With the exception of the nanostructured thin-film (NSTF) catalyst application process, the changes to the stack analysis are mostly adjustments of operating parameters rather than the addition of new components or changes in design. Also, the number of stacks per system is cut from two to one based on suggestions from industry and the United States Council for Automotive Research Fuel Cell Technical Team (FCCT).

The NSTF catalyst application process is a major technological improvement on the previous VertiCoater die-slot application method, and facilitates large improvements in power density and catalyst loading while simultaneously improving durability. The previously-modeled VertiCoater method had the advantage of being one of the least-costly application techniques judged adequate for high production rates and reasonably high MEA performance. However, it became increasingly clear that further increases in power density with simultaneously lower Pt loading were probably not possible with this technique. Consequently, the switch was made to the NSTF method, which has shown remarkable recent improvements in power density and durability at low Pt loadings. Developed at 3M, the NSTF deposition process begins with the sublimation of a layer of crystalline finger-like projections, or “whiskers”, that create a high surface area substrate on which the active catalysts may be deposited. Next, vapor deposition methods are utilized to deposit a very thin layer of a ternary catalyst alloy coating onto the whiskers in a very precise and even manner. The resulting catalyst-coated whiskers can then be hot pressed into the fuel cell membrane to form a porous mat electrode intimately bonded to the membrane. 3M has

<table>
<thead>
<tr>
<th>TABLE 2. System Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Power Density (mW/cm²)</strong></td>
</tr>
<tr>
<td><strong>Total Pt loading (mgPt/cm²)</strong></td>
</tr>
<tr>
<td><strong>Stack Power (kWpeak)</strong></td>
</tr>
<tr>
<td><strong>Operating Pressure (atm)</strong></td>
</tr>
<tr>
<td><strong>Peak Stack Temp. (°C)</strong></td>
</tr>
<tr>
<td><strong>Membrane Material</strong></td>
</tr>
<tr>
<td><strong>Radiators/Cooling System</strong></td>
</tr>
<tr>
<td><strong>Bipolar Plates</strong></td>
</tr>
<tr>
<td><strong>Air Compression</strong></td>
</tr>
<tr>
<td><strong>Gas Diffusion Layers</strong></td>
</tr>
<tr>
<td><strong>Catalyst Application</strong></td>
</tr>
<tr>
<td><strong>Air Humidification</strong></td>
</tr>
<tr>
<td><strong>H₂ Humidification</strong></td>
</tr>
<tr>
<td><strong>Exhaust Water Recovery</strong></td>
</tr>
<tr>
<td><strong>MEA Containment</strong></td>
</tr>
<tr>
<td><strong>Coolant &amp; End Gaskets</strong></td>
</tr>
<tr>
<td><strong>Freeze Protection</strong></td>
</tr>
<tr>
<td><strong>H₂ Sensors</strong></td>
</tr>
<tr>
<td><strong>End Plates/Compression System</strong></td>
</tr>
</tbody>
</table>
recently demonstrated significant improvements in the durability and the power-density-to-catalyst-loading ratio that surpass the 2010 DOE performance targets.

When compared to the previous method of catalyst application considered (die-slot application based on the Coatema VertiCoater), the total NSTF catalyst system and application is only slightly more expensive for a given power density and catalyst loading. However, the NSTF method facilitates a lower catalyst loading and improved power density that cannot be otherwise achieved. Consequently, taking power density and catalyst loading into consideration, a net savings of $10.28/kW_{net} is obtained by switching from a die-slot catalyst application to the NSTF catalyst system.

A central theme of the past year’s work has been the integration of performance-parameter-based scaling into the cost model. Although the previous cost model included performance parameters, we have enhanced the level of detail and interaction to better reflect the actual performance. Integration between all of the components (in both the stack and the BOP) has been greatly increased, such that geometries and costs now scale dynamically based on a variety of parameters (e.g. operating pressure, air mass flow, and cooling and power requirements).

In past years of the analysis, the power density and catalyst loading values used in the model were specified by the DOE and the FCTT, and reflected the average performance of several different technologies. Now that the NSTF process has been implemented in the model, the power density and catalyst loading values are based on experimental data polarization curves that correspond to NSTF MEAs under specified operating conditions. Interpolation between polarization curves is used to determine power density at the model-specified operating pressure.

Almost all of the BOP components were re-examined in greater detail, with extra emphasis on those with the largest contribution to cost. The system schematics were refined, and components were added and subtracted. Detailed analyses were conducted of the wiring and piping/tubing requirements, with consideration for flow rates, cooling and power requirements, and the physical distances between components.

The most substantial cost analysis improvement relates to the new compressor/expander motor (CEM) analysis, for which an all-new cost estimate was conducted in collaboration with Honeywell. It is a bottom-up cost analysis based directly on the blueprints from an existing Honeywell design, utilizing a combination of DFMA® methodology and price quotes from established Honeywell vendors. Current and future CEM designs were analyzed, and a detailed model was developed to scale the size, cost, and power draw of the CEM based on rotational speed, air mass flow, pressure ratio, and the inclusion or exclusion of an expander. For current technology, the CEM cost shrinks from $8.51/kW_{net} in 2008 to $8.07/kW_{net} in 2010. For 2015 technology, it increases from $5.37/kW_{net} to $6.31/kW_{net}.

Numerous other small changes were made to the fuel cell system cost model, the result of which yields a small cumulative net savings. While their net effect is comparatively small, the improvements enhance 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 $25/kW_{net} and $21/kW_{net}, for the 2010 and 2015 technology year cost projections respectively (see Figure 1). 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 $51/kW_{net} and $39/kW_{net} for 2010 and 2015, respectively (see Figure 2).
Conclusions and Future Directions

Key conclusions from the past year of the project include:

- 2010 stack cost estimate (at 500,000 systems/year) meets the DOE target of $25/kW_{net}, and 2015 cost is predicted to be $6/kW higher than DOE target for 2015.
- The 2010 and 2015 system cost estimates (at 500,000 systems/year) are $6/kW and $9/kW higher than DOE targets, respectively.
- Significant technical breakthroughs will be required in order to achieve the 2015 DOE system cost targets.
- NSTF catalyst application method represents current state-of-the-art, shows great promise.
- Switch from die-slot catalyst coating to the NSTF method yielded savings of $10.28/kW_{net}, due primarily to enhanced power density made possible by NSTF MEA.
- Though not as dominating as in previous years, catalyst cost (especially Pt) remains largest single stack cost contributor.
- Pt catalyst reduction remains a potential pathway to appreciable cost savings.
- Although detailed new CEM cost analysis resulted in only minor cost changes, new estimate is much more robust, scales with system performance parameters.
- 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 component costs are comparable to stack costs, so R&D to reduce, simplify, or eliminate BOP components is needed for significant overall system cost reduction.

When compared to the DOE’s 2005 status values and our estimates from the previous four years, it’s clear that the significant technology advances of the last several years have resulted in substantial cost reductions (see Figure 3). Still, there is a substantial predicted overage in meeting 2015 targets: $6/kW on the stack and $9/kW for the total system. Further R&D or system configuration advances are needed to close these gaps.

During the coming year, DTI will address the following topics:

- Documentation of the 2010 update in the Year 5 annual report update.
- Updating of the 2010 technology system to reflect 2011 technology.
- Identification of capital equipment and R&D needs.
- Optimization study of stack operating pressure.
- Lifecycle cost analysis.

FY 2010 Publications/Presentations

1. July 15th, 2009 - Hartford, CT: HTAC Open Meeting
2. August 12th, 2009 - Detroit, MI: Presentation to Fuel Cell Tech Team
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 (2009-2010) objectives were:

- Estimate the bottom-up manufactured cost of the 2009 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 2009 PEMFC system.
- Update the bottom-up manufactured cost for the PEMFC system based on updated stack performance assumptions and system configuration for 2010 – preliminary costs reported.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the

V.A.3 Cost Analyses of Fuel Cell Stacks/Systems

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>System¹</td>
<td>$/kWe</td>
<td>45 / 30</td>
<td>60 / 45</td>
<td>55.2 / 52.4</td>
</tr>
<tr>
<td>Stack²</td>
<td>$/kWe</td>
<td>25 / 15</td>
<td>/ 25</td>
<td>22.3 / 22.3</td>
</tr>
<tr>
<td>Compressor</td>
<td>$/unit</td>
<td>400 / 200</td>
<td>982 / 832</td>
<td></td>
</tr>
<tr>
<td>Expander Motor</td>
<td>(CEM)³</td>
<td>$/unit</td>
<td>20 / 20</td>
<td>11.4 / 18.7</td>
</tr>
<tr>
<td>Membrane²</td>
<td>$/m²</td>
<td>20 / 20</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>Electrocatalyst²</td>
<td>$/kWe</td>
<td>5 / 3</td>
<td>10.6 / 8.0</td>
<td></td>
</tr>
<tr>
<td>MEA²</td>
<td>$/kWe</td>
<td>10 / 5</td>
<td>16.5 / 13.7</td>
<td></td>
</tr>
<tr>
<td>Bipolar Plates²</td>
<td>$/kWe</td>
<td>5 / 3</td>
<td>2.9 / 6.2</td>
<td></td>
</tr>
</tbody>
</table>

¹ Based on bottom-up high-volume manufacturing cost and an assumed 15% markup to the automotive original equipment manufacturer (OEM) for all major balance-of-plant (BOP) components.
² Assumes a vertically integrated stack manufacturing process by the OEM based on bottom-up, high-volume manufacturing cost and assumes no markup for all major stack components.

Accomplishments

- Updated the bottom-up manufacturing cost for the 2009 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 2010 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/kWe for the technology to be competitive with automotive internal combustion engine power plants, which currently cost about $25-35/kWe.

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 PEM fuel cells for transportation since 1999, analyzing reformate-based systems through 2004, followed by direct-hydrogen systems from 2005 through 2010.

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 and BOP components. TIAX has developed a proprietary, bottom-up, technology-based cost model which is used in conjunction with the Boothroyd-Dewhurst Design for Manufacturing and Assembly (DFMA®) software.

The approach starts with a technology assessment of the system configuration and components. Argonne National Laboratory (ANL) develops a fuel cell stack/system configuration and performance models that would represent the state-of-the-art for fuel cell vehicle technology in the current year. 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 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 2009, we updated the PEMFC system configuration, materials, processes, performance assumptions and component specifications [1,2]. Figure 1 shows the ANL 2009 PEMFC system configuration chosen for costing [1-3]. Table 2 is a summary of the stack performance assumptions and resultant high-volume manufactured cost of the 2009 PEMFC stack cost for six different scenarios modeled by ANL [3,4]. We assumed a baseline Pt cost of $1,100/tr.oz., and captured the impact of variability in Pt cost through the sensitivity analyses.

The high-volume 2009 PEMFC stack cost for six scenarios ranges from $19/kWe to $40/kWe [4]. Using S5 as the 2009 baseline scenario, the updated assumptions lowered the stack cost from $29/kWe in 2008 to $22.3/kWe in 2009. The low Pt loading with high power density is attributed to novel catalyst and support structure (i.e. NSTFC on organic whisker support). We based our cost assessment on ANL’s single-cell modeling which is calibrated using data from an NSTFC-based short stack. The electrodes, primarily due to the Pt material, represent ~48% of the ~$22/kWe fuel cell stack manufactured cost in 2009.

We developed bottom-up manufacturing costs for the cathode and anode planar membrane humidifier, high-temperature (HT) and low-temperature (LT) radiators, hydrogen blower and CEM based on ANL specifications [3] and other patents [1,4]. We scaled vendor/catalog quotes for the air precooler, radiator fan, HT and LT coolant pumps, hydrogen demister, air demister, solenoid valves, flow orifice, and air/H₂ mixer. Table 3 is a summary of the projected high-volume OEM cost for the 2009 BOP subsystems and individual components [4].

Figure 2 shows the component/subsystem cost breakout for the 2009 PEMFC stack and system. BOP,
**FIGURE 1. ANL 2009 PEMFC System Configuration** [1-4]

**TABLE 2. 2009 PEMFC Stack Scenarios and Costs** [3,4]

<table>
<thead>
<tr>
<th>Key Cost Assumptions</th>
<th>2009 PEMFC Stack Scenarios$^1$ [3,4]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1</td>
</tr>
<tr>
<td>System net power</td>
<td>kW</td>
</tr>
<tr>
<td>Stack gross power [3]</td>
<td>kW</td>
</tr>
<tr>
<td>Cell voltage (rated power) [3]</td>
<td>V</td>
</tr>
<tr>
<td>Stack gross power density [3]</td>
<td>mW/cm$^2$</td>
</tr>
<tr>
<td>Pt loading (total) [3]</td>
<td>mg/cm$^2$</td>
</tr>
<tr>
<td>Stack Pt content</td>
<td>g/kW$_{gross}$</td>
</tr>
<tr>
<td>System Pt content</td>
<td>g/kW$_{net}$</td>
</tr>
<tr>
<td>Stack efficiency (rated power) [3]</td>
<td>% LHV</td>
</tr>
<tr>
<td>System efficiency (rated power) [3]</td>
<td>% LHV</td>
</tr>
<tr>
<td>System voltage (rated power)</td>
<td>V</td>
</tr>
<tr>
<td>System active area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>Stack cost$^2$</td>
<td>$$/kW_{net}$</td>
</tr>
</tbody>
</table>

$^1$ All 2009 scenarios assume a Pt cost of $1,100/tr.oz., NSTFC-based MEA, 20 µm PFSA membrane, and stack operating conditions of 90°C and 2.5 atm.

$^2$ Assumes a vertically integrated stack manufacturing process by the OEM-based on bottom-up, high-volume manufacturing cost and assumes no markup for all major stack components.

$^3$ High-volume manufactured cost based on an 80 kW$_{net}$ net power PEMFC system; does not represent how costs would scale with power (kW$_{net}$).

LHV = lower heating value
### TABLE 3. High-Volume OEM Cost\(^1\) of the 2009 BOP Subsystems [4]

<table>
<thead>
<tr>
<th>BOP Subsystem</th>
<th>Component</th>
<th>Technology / Cost Basis</th>
<th>Factory Cost(^2), $</th>
<th>OEM Cost(^1), $</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Management</td>
<td>Cathode planar membrane humidifier (for air)</td>
<td>ANL</td>
<td>96</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>Anode planar membrane humidifier (for H(_2))</td>
<td>ANL</td>
<td>52</td>
<td>59</td>
</tr>
<tr>
<td>Thermal Management</td>
<td>HT automotive tube-fin radiator</td>
<td>Modine</td>
<td>83</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>LT automotive tube-fin radiator</td>
<td>Modine</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Air precooler</td>
<td>Bell Intercooler</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>HT/LT radiator fan</td>
<td>McMaster-Carr</td>
<td>-</td>
<td>75</td>
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<tr>
<td></td>
<td>HT coolant pump</td>
<td>McMaster-Carr</td>
<td>-</td>
<td>150</td>
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<tr>
<td></td>
<td>LT/Air precooler coolant pump</td>
<td>Aweco</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Other (two temperature sensors)</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Fuel Management</td>
<td>(\text{H}_2) blower</td>
<td>Parker Hannifin</td>
<td>219</td>
<td>252</td>
</tr>
<tr>
<td></td>
<td>(\text{H}_2) ejectors</td>
<td>-</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>(\text{H}_2) demister</td>
<td>Parker Hannifin</td>
<td>-</td>
<td>61</td>
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<tr>
<td></td>
<td>Solenoid valves</td>
<td>McMaster-Carr</td>
<td>-</td>
<td>46</td>
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<tr>
<td></td>
<td>Purge valve</td>
<td>DFMA</td>
<td>13</td>
<td>15</td>
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<tr>
<td></td>
<td>Check valve</td>
<td>DFMA</td>
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<td>Air demister</td>
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<td>Air/(\text{H}_2) mixer</td>
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<td>Flow orifice</td>
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<td>Air filter</td>
<td>-</td>
<td>-</td>
<td>4</td>
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<tr>
<td></td>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>1,815</strong></td>
<td><strong>1,991</strong></td>
</tr>
</tbody>
</table>

\(^1\) Based on bottom-up high-volume manufacturing cost and an assumed 15% markup to the automotive OEM for all major BOP components.

\(^2\) Assumes a vertically integrated stack manufacturing process by the OEM-based on bottom-up, high-volume manufacturing cost and assumes no markup for all major stack components.

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![FIGURE 2. TIAX 2009 PEMFC Stack and System Cost [4]](image-url)
balance of system, and system assembly costs together represent ~60% of the PEMFC system cost in 2009, compared to ~38% in 2005. The projected high-volume OEM cost of the CEM at $790/unit (~$10/kWe) is the largest contributor to the combined BOP and assembly cost of $33/kWe in 2009.

We performed single- and multi-variable sensitivity analyses to examine the impact of major stack and BOP parameters on the high-volume 2009 PEMFC system cost. As seen in Figure 3, 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 4; the high-volume 2009 PEMFC system OEM cost ranges between $45/kWe and $97/kWe (± 2σ), with the mean of the distribution being $71/kWe.

We are currently working on updating our cost projections to the ANL 2010 PEMFC system configuration, stack performance assumptions, and stack and BOP component specifications. Figure 5 shows a preliminary layout of the 2010 PEMFC system [4,5]. The key features are: NSTFC MEA with 20 μm reinforced PFSA membrane, thermal nitrided metal bipolar plates, non-woven carbon paper gas diffusion layer (GDL), pleated planar membrane humidifier for cathode air humidification, and no anode fuel humidifier.

Table 4 is a summary of the stack performance assumptions and resultant high-volume manufactured cost of the 2010 PEMFC stack cost for six different scenarios modeled by ANL [4,5]. Our preliminary estimates show that the high-volume 2010 PEMFC stack cost for six scenarios ranges between $17/kWe, and $33/kWe [4]. These initial estimates will be finalized by the next reporting period.

Table 5 is a summary of the high-volume system OEM cost of the 2010 PEMFC system for six different scenarios modeled by ANL [4,5]. The preliminary 2010 PEMFC system OEM cost is estimated to range from $49/kWe, to $65/kWe [4]. These initial estimates will be finalized by the next reporting period.

**Conclusions and Future Directions**

- The 2009 PEMFC stack cost was estimated to range between $19/kWe and $40/kWe over six different scenarios.
- The PEMFC stack and system costs were estimated to be $22/kWe and $55/kWe, respectively for the 2009 baseline scenario.
- BOP, balance of system and system assembly costs together represented ~60% of the projected PEMFC system cost, for the 2009 baseline scenario.
Monte Carlo analysis shows that the 2009 PEMFC system OEM cost ranges between $45/kWe and $97/kWe (± 2σ), with a mean cost of $71/kWe. Preliminary estimates for the manufactured cost of the 2010 PEMFC stack range between $17/kWe and $33/kWe, while preliminary estimates for the OEM cost of the 2010 PEMFC system range from $49/kWe to $65/kWe over six different scenarios.

The projected high-volume OEM cost of the CEM at $790/unit (~$10/kWe) is the largest contributor to the combined BOP and assembly cost of $33/kWe in 2009.

Platinum loading, power density, platinum cost, membrane cost and CEM cost are the top five drivers of the PEMFC system cost in 2009.

Monte Carlo analysis shows that the 2009 PEMFC system OEM cost ranges between $45/kWe and $97/kWe (± 2σ), with a mean cost of $71/kWe.

Preliminary estimates for the manufactured cost of the 2010 PEMFC stack range between $17/kWe and $33/kWe, while preliminary estimates for the OEM cost of the 2010 PEMFC system range from $49/kWe to $65/kWe over six different scenarios.
TABLE 4. Preliminary 2010 PEMFC Stack Scenarios and Costs [4,5]

<table>
<thead>
<tr>
<th>Key Cost Assumptions</th>
<th>2010 PEMFC Stack Scenarios [1,2,4,5]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1-1</td>
</tr>
<tr>
<td>System net power</td>
<td>kW net</td>
</tr>
<tr>
<td>Stack gross power</td>
<td>kW gross</td>
</tr>
<tr>
<td>Cell voltage (rated power)</td>
<td>V</td>
</tr>
<tr>
<td>Stack gross power density</td>
<td>mW/cm²</td>
</tr>
<tr>
<td>Pt loading (total)</td>
<td>mg/cm²</td>
</tr>
<tr>
<td>Stack Pt content</td>
<td>g/kW gross</td>
</tr>
<tr>
<td>System Pt content</td>
<td>g/kW net</td>
</tr>
<tr>
<td>Stack efficiency (rated power)</td>
<td>% LHV</td>
</tr>
<tr>
<td>System efficiency (rated power)</td>
<td>% LHV</td>
</tr>
<tr>
<td>System voltage (rated power)</td>
<td>V</td>
</tr>
<tr>
<td>System active area</td>
<td>m²</td>
</tr>
<tr>
<td>Stack cost3,4</td>
<td>$/kW net</td>
</tr>
</tbody>
</table>

1 All 2010 scenarios assume a Pt cost of $1,100/tr.oz., NSTFC-based MEA, and 20 µm reinforced PFSA membrane.
2 S1: 2.5 atm, 85 °C; S2: 1.5 atm, 75 °C
3 Assumes a vertically integrated stack manufacturing process by the OEM-based on bottom-up, high-volume manufacturing cost and assumes no markup for all major stack components.
4 High-volume manufactured cost based on an 80 kW net power PEMFC system; does not represent how costs would scale with power (kW).

TABLE 5. TIAX 2010 PEMFC System Cost Scenarios [4]

<table>
<thead>
<tr>
<th>PEMFC System Cost1 ($/kW)</th>
<th>2009 OEM Cost4,5</th>
<th>2010 Stack Scenarios1,2,3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1-1</td>
<td>S1-2</td>
</tr>
<tr>
<td>Stack4</td>
<td>22.3</td>
<td>33.0</td>
</tr>
<tr>
<td>Water Management5,6,7</td>
<td>2.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Thermal Management5,7</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Fuel Management5,7</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Air Management5,6,7</td>
<td>12.3</td>
<td>12.2</td>
</tr>
<tr>
<td>Balance of System5,7</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>System Assembly</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Total System5,6,7</td>
<td>55.2</td>
<td>65.0</td>
</tr>
</tbody>
</table>

1 All scenarios assume a Pt cost of $1,100/tr.oz., NSTFC-based MEA, and 20 µm reinforced PFSA membrane.
2 S1: 2.5 atm, 85 °C; S2: 1.5 atm, 75 °C
4 High-volume manufactured cost based on an 80 kW net power PEMFC system. Does not represent how costs would scale with power (kW).
5 Assumes 15% markup to the automotive OEM for BOP components
6 Water Management in 2010 preliminarily assumes cathode planar membrane humidifier and no anode humidifier
7 Using 2009 cost numbers for BOP subsystems’ preliminary cost; all BOP costs pending ANL input, are planned to be updated in 2010
8 CEM motor controller cost varies based on preliminary modeling by ANL, of CEM parasitic power, for different scenarios

These initial estimates will be finalized by the next reporting period.

Our next steps are outlined below:
- Finalize baseline scenario for 2010 PEMFC system and develop BOP cost estimates.
- Develop bottom-up cost projection for stack conditioning.
- Perform single-variable and Monte Carlo sensitivity analyses on stack and system costs.

DOE Hydrogen Program
FY 2010 Publications/Presentations


References


V.A.4 Characterization of Fuel Cell Materials

Objectives

- Develop new, innovative microanalysis and imaging techniques to characterize fuel cell 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 fuel cell component developers and manufacturers, university researchers, and other national laboratories, to evaluate materials using electron microscopy and complimentary microstructural/compositional analysis techniques; provide feedback for optimization.

Technical Targets

This project is focused on conducting fundamental characterization studies on the stability of individual constituents comprising fuel cell 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, proton exchange (or polymer electrolyte) membrane fuel cell (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 PEM fuel cells. Insights gained will be applied toward the design and manufacture of fuel cell materials that meet the following DOE 2015 MEA targets:

- Cost: ≤$5/kW
- Durability with cycling: ≤80°C – 5,000 h; >80°C – 5,000 h
- Operating temperatures: ≤120°C
- Total catalyst loading (for both electrodes): 0.2 g/kW (rated)
- Extent of performance degradation over lifetime: 5%

Accomplishments

- Investigated microstructural and compositional contributions to cathode carbon-support corrosion mechanisms in electrochemically-aged MEAs.
- Conducted detailed microstructural studies of Pt migration as a function of changing aging protocols.
- Applied advanced statistical analysis techniques to evaluate Å-scale elemental and compositional analyses and segregation within catalyst nanoparticles (multivariate statistical analysis – principal component analysis).
- Continued ‘proof-of-principle’ testing of ORNL’s 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).
- Established several new research collaborations in FY 2010 with industry (3M, UTC Power), other laboratories (Naval Research Laboratory, Jet Propulsion Laboratory) and universities (University of Texas at Austin, Brown University).
- Supported a full-time graduate student from Rensselaer Polytechnic Institute working on microstructural characterization of PA-PBI.
membranes (Kelly Perry received her Ph.D. from Rensselaer Polytechnic Institute in December 2009 and now works at ORNL on fuel cell characterization).

- Continued extensive alloy catalyst nanoparticle characterization studies using sub-Å resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM).

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 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.

The techniques developed as part of this “baseline” research project are also being applied to other fuel cell systems.

Approach

The microstructural characterization task utilizes advanced electron microscopy analysis techniques to characterize the individual material components comprising PEMFCs, before and after incorporation into an MEA and after electrochemical aging. Our approach is focused on identifying and optimizing novel high-resolution imaging and compositional/chemical analysis techniques, and developing unique specimen preparation methodologies, for the mm-Å-scale characterization of the material constituents of fuel cells (electrocatalyst, support, membrane, etc.). ORNL applies these advanced analytical and imaging techniques for the evaluation of the microstructural and microchemical changes of each material constituent and correlating these observations with fuel cell performance (aging studies are conducted at collaborators laboratories). These studies are designed to elucidate the microstructure-related degradation mechanisms contributing to fuel cell performance loss. Most importantly, ORNL is making the techniques and expertise available to fuel cell researchers outside of ORNL via several mechanisms – (1) Work for others (proprietary) research, (2) ORNL User Facilities (Shared Research Equipment, Center for Nanophase Materials Science, and High Temperature Materials Laboratory), and (3) collaborative non-proprietary research via the Microstructural Characterization Project that is in line with ORNL’s “baseline” research activities.

The research effort in FY 2010 was focused on establishing two primary characterization focus areas for the evaluation of the degradation of fuel cell materials as a function of aging protocol; (1) understanding the mechanisms of cathode carbon support corrosion and (2) performing the in-depth characterization of Pt migration and re-precipitation during PEMFC aging. In addition, the application of statistical data analysis techniques, in particular multivariate statistical analysis and principal component analysis to the compositional analysis (energy dispersive spectroscopy and electron energy loss spectroscopy spectrum imaging) of nanoparticles (bi- and ternary-alloy catalysts) has been optimized (not discussed). Significant progress has been made in each of these focus areas.

Results

Carbon Corrosion

Carbon support corrosion is a well-recognized degradation problem during the operation of PEM fuel cells, and is particularly problematic at the cathode. While the rate of carbon corrosion is relatively low during “normal” fuel cell operation, the oxidation of the carbon support is severe during fuel (H₂) starvation and under open circuit voltage conditions experienced during start-up/shut-down cycling (cathode potentials >1.2 V). There are several recent studies that have focused on the kinetics of carbon support corrosion under adverse fuel cell operating conditions [1-5] and several mechanisms for electrochemical carbon oxidation have been postulated. At the center of these mechanisms is the permanent loss of carbon in the cathode layers due to oxidation via the reaction:

\[
C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- 
\]

This mechanism has been confirmed (at least to some degree) by the direct observation of collapsed cathode layers and the measurement of the CO₂ (and
CO) evolution during operation. Carbon loss at the cathode has been associated with decreased catalyst utilization in the cathode due to Pt agglomeration and Pt detachment from the carbon support, thereby decreasing the electrochemically active surface area (EASA). While it is clear that there is increased carbon corrosion during fuel cell operation under high potential-cycling conditions, the actual structural reasons for, and mechanism of, carbon corrosion have yet to be unambiguously identified.

Recently, several electrochemically-aged MEAs that have experienced significant cathode corrosion (most of these MEAs are at end-of-life, EOL), have been evaluated using high-resolution electron microscopy imaging and analysis techniques to elucidate the microstructural and compositional factors that play a role in (1) the observed structural collapse/compression of the cathode layer(s) and (2) changes/growth of Pt cathode catalyst nanoparticles contributing to loss of EASA. For example, a “typical” thinned/compressed cathode (composed of Pt-supported on Vulcan XC72) observed after 1,500 0.1-1.2 V (10 mV/sec) cycles is shown in Figure 1. The high-resolution (HR)-TEM images shown in Figure 2 compare the structure of the as-processed (Pt loaded) Vulcan XC72 carbon support (2a) and the same material after potential cycling (2b) in an MEA. There was a significant amount of carbon remaining in the cathode structure after aging, however, the crystalline structure of the Vulcan changed dramatically during potential cycling. The graphitic nature of the starting Vulcan support (2a) was completely amorphous after aging (2b) and these amorphous (glassy) carbon particles were tightly bound (sintered) and densified together, resulting in extensive densification (compression) of the cathode. This graphitic-to-amorphous transformation was confirmed by electron energy loss spectroscopy, as shown in

![Figure 1: Typical Cross-Section of a “Collapsed” EOL Cathode](image1)

![Figure 2: TEM images of (a) Pt nanoparticles on Vulcan XC72 carbon particle and (b) Pt nanoparticles on Vulcan carbon particle after aging.](image2)
Figure 3, which also indicated relatively high oxygen contents within the amorphous carbon regions. The Pt particles clearly coalesce during potential cycling, but this phenomenon is exacerbated by the enhanced carbon oxidation due to the presence of Pt and the sintering together of the carbon particles. The Pt particles do not become detached from the carbon support (as previously reported by other research groups), but experience significant growth and remain attached to a non-conductive, amorphous, O-enriched carbon support structure. The combination of these major degradation events will have a detrimental impact on fuel cell life.

These results are typical of the types of structures found in compressed/collapsed cathodes after electrochemical aging – in FY 2011, additional (and systematically aged using different aging protocols) examples will be analyzed to establish carbon-corrosion mechanisms and to directly correlate microstructural degradation with durability (extent of performance loss).

Pt Migration

The migration of Pt\textsuperscript{2+} from the cathode layer into the membrane during fuel cell operation, and the consequent re-precipitation of Pt nanoparticles at different locations in the membrane (related directly to H\textsubscript{2} and O\textsubscript{2} gas cross-over), which is relatively easy to observe/image in a microscope (optical of scanning electron microscope, SEM) at low magnifications. However, extensive evaluation of aged MEAs during the past year has shown that the re-precipitation of Pt at the cathode/membrane interface AND within the membrane is significantly more complicated than the formation of a simple Pt-band.

To understand the Pt migration as a function of aging protocol, numerous aged cross-sectioned (intact) MEAs have been characterized via TEM/STEM in terms of size, crystalline nature, and distribution (distance from cathode layer) within the membrane (from cathode/membrane interface to anode/membrane interface), the results of which will be directly correlated with performance loss. In addition, the amount of Pt loss from the cathode layer will be quantified. These analyses will be extended to include Pt-alloy catalysts to determine leaching effects and the stability of alloy catalysts during aging.

Figure 4 shows an example of the measurements being made via TEM/STEM, where the MEAs evaluated (Pt loaded on both cathode and anode layers) were subjected to a low number (4-5) of freeze-thaw cycles. In this case, the only differences between the cells evaluated (cell #1 and cell #2) were the type of membrane used (Nafion\textsuperscript{®} 111 vs. 211) and the type of gas diffusion layer (GDL) used (paper vs. cloth). Figure 4(a) shows a cross-section SEM image of a typical Pt-band. Figure 4(b) shows the typical size and morphology of the Pt-nanoparticles from two separate areas of the membrane; within the Pt-band (single-crystal cuboctahedron-shaped Pt particles ranging in size from ~30-70 nm) and away from the Pt-band (closer to the anode, single-crystal Pt particles ranging in size from ~3-10 nm). The Pt particle distribution profiles were completely different, as shown in Figure 4(c), where cell #2 (Nafion\textsuperscript{®} 211 membrane and cloth GDL) exhibited significantly larger (and fewer) Pt particles distributed across the entire membrane and a well-defined Pt-band at a distance between 15-30 µm from the cathode, and cell #1 (Nafion\textsuperscript{®} 111 membrane and paper GDL) exhibited a linear decrease in Pt nanoparticle size from the cathode side (from 15 nm to 5 nm, cathode to anode) and a less distinct Pt-band at a distance between 30-40 µm from the cathode layer. The reasons for such dramatic differences in Pt migration are not fully understood, but additional data from other aged MEAs will permit the correlation of such behavior with performance. This work will continue in FY 2011.

Conclusions and Future Directions

- 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).
We will continue to establish new collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of unique capabilities. We will also continue to support new DOE fuel cell projects with microstructural characterization and advanced characterization techniques.

- Progress to date to develop in situ liquid TEM/STEM as a viable technique to monitor the degradation of fuel cell materials has been hampered in FY 2010 for one primary reason – while we have been able to meet all program milestones for FY 2010 regarding optimizing the holder design and windows/chips, we are still delayed because of unreliable delivery of “working” windows/chips for the cell. Addressing this issue will be a priority in FY 2011.

- Initiated microstructural and microchemical characterization of EOL PEMFC MEAs to assess cathode carbon-support degradation mechanisms. Several collaborations have recently been pursued (General Motors and UTC Power) to systematically evaluate the progression of carbon corrosion as a function of aging conditions (via durability studies) rather than using EOL MEAs, which will be a primary focus of research in FY 2011.

- The migration and re-precipitation of Pt into and within has been studied in greater detail. Detailed studies to evaluate the amount, particle shape, size distributions, etc. of Pt from the cathode and into the membrane are being correlated with EASA losses and extent of carbon corrosion to fully interpret degradation behavior as a specific function of aging protocol. These correlative studies will be continued in FY 2011.

**FY 2010 Publications/Presentations**


References


V.A.5 Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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Contract Number: DE-AI-01-01EE50660
Project Start Date: Fiscal Year (FY) 2001
Project End Date: Project continuation and direction determined annually by DOE

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 a 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) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) Durability
(C) Performance
(D) Water Transport within the Stack

2015 System Targets
- Unassisted start from low temperature: -40°C
- Durability with cycling at operating temperature of ≤80°C: 5,000 h
- System energy density: 650 W/L
- System specific power: 650 Watt/kg

- Energy efficiency: 65% at 25% rated power, 55% at 100% rated power
- Cost: $35/kW
- Start-up time to 50% power: 50 seconds from -20°C, 5 seconds from 20°C
- Freeze start operation: unassisted start from -40°C
- Durability with cycling: 5,000 hrs

Accomplishments
- Improve spatial resolution of the measurement of the through-plane water content of an operating proton exchange membrane fuel cell (PEMFC). Develop stable, high resolution charge-coupled device (CCD)-scintillator detector system.
  - New high resolution neutron imaging system deployed and in use.
  - Measured spatial resolution is 13 μm.
  - High resolution system using scintillator coupled to CCD achieves sub 20 μm spatial resolution
- Measure fundamental through-plane transport properties of diffusion media (DM) and membranes that incorporates improved measurement uncertainty analysis. Transfer new data analysis suite to fuel cell industry and national labs. Prepare for publication in a peer reviewed journal article demonstrated use of new analysis tools with established models and data.
  - Measured gas diffusion in DM as a function of saturation and electroosmotic drag in hydrogen pumping experiments.
  - In collaboration with Los Alamos National Laboratory (LANL), have studied a range of membrane histories and compositions; results and analysis are being prepared for publication.
  - The measured water content in the DM has been compared to models of the saturation using NIST-developed analysis tools.
- Search for systematic errors in neutron radiography:
  - Determined systematic underestimation of water content due to unaccounted residual water in dry membrane images and beam hardening.
  - Developed experimental method to overcome this systematic undercounting of water.
- Improvements to the Neutron Imaging Facility and fuel cell support infrastructure:
  - Improved the facility fuel cell test stand humidification system allowing for more
accurate humidification of fuel cells designed for high resolution testing.
- Improved the high resolution freeze testing capabilities of the facility.

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 length scales of interest in a PEMFC are: channels approximately 1 mm wide and 1 mm deep, the DM 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 2 cm² to 500 cm². Thus, to nondestructively study in situ the water and hydrogen transport in PEMFCs while in operation we will develop new facilities and improve existing capability for obtaining high spatial and temporal resolution neutron images. 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, academia, and national laboratories 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

We have worked in close collaboration with LANL to develop a fundamental understanding of the water uptake by the membrane, a critical materials characterization for modeling the through-plane water transport in PEMFCs. This collaborative effort explored multiple sources of measurement uncertainty, both in the neutron imaging system and in the fuel cell operation and assembly; a full journal article is in preparation that will detail the effort summarized here. The most important advancement impacting these measurements has been the recent introduction of the new high resolution microchannel plate detector, with a measured spatial resolution of about 13 μm. The impact of this detector on the measurement of PEMFC through-plane water content can be seen in Figure 1, where images of a test section viewed edge on are imaged at three different spatial resolutions. The right-most image shows the current detector spatial resolution, which is a factor of 20 improvement over the spatial resolution at the start of this project.

Another important refinement that was recently made to the neutron image analysis is the proper accounting of the residual water content of the membrane (both in the active area and under the gaskets) in the dry reference image. For the new detector, the measured neutron attenuation is not linear in water thickness, a known effect called beam hardening. Beam hardening can be modeled by a quadratic function allowing the water content to be accurately estimated from the radiographs. Accounting for the beam hardening effect and the residual water in the membrane modifies the calibration of neutron intensity versus water thickness. Shown in Figure 2a is a comparison of the membrane hydration with and without incorporating the residual water. This
The neutron imaging facility staff facilitates and collaborates with a broad group of neutron imaging users with experiments that support the DOE Hydrogen Program. In the past year, neutron imaging data from this unique facility has been used by researchers from six companies, eight universities, three national laboratories, and has been a part of the thesis research of 12 graduate students. Among these projects researchers from General Motors, Rochester Institute of Technology, and the Michigan Technological University used the imaging facility to study a wide range of purge conditions and the impacts of varying thermal properties of the DM on water management. These studies are critical to develop a fuel cell robust enough to withstand the stresses of freeze and achieve the DOE cold start targets. A cell was designed for this work that closely parallels publicly known details of automotive fuel cell designs. This allows the cell to be more representative of commercial automotive designs yet the details of cell operation can be publicly shared. Coupled with neutron imaging measurement of the water content, the design incorporates in situ current, temperature, and high frequency impedance distribution measurements, enabling precise, local correlations between water mass, current density, temperature and high frequency resistance (HFR) (Figure 3a). While HFR measurements probe the state of hydration of the fuel cell membrane, they are not capable of determining the actual amount of water in the fuel cell membrane. Using neutron imaging, which allows quantification of the water content, a correlation between the local HFR and local water content in the fuel cell during a purge can be made (Figure 3b). Here the sensitivity of neutron imaging to water is clearly shown to be as low as 4 micrometers corresponding to a water mass of about $6.5 \times 10^{-8}$ g per pixel. The correlation clearly shows a marked change in HFR when the amount of water in the cell is roughly equal to the membrane thickness. With this information, accurate models of the dry purge can be derived that aim to reduce the amount of input energy needed to purge the fuel cell stack at shutdown and still start under freeze conditions.

In addition to studying the effects of purge on cold-start, this cell was used to study the effects of varying the properties of the DM on water management, in particular the thermal conductivity. During operation of the cell, the waste heat from the cathode reaction results in a temperature gradient between the membrane and the flow fields, with the membrane at a higher temperature; thus the water saturation pressure at the membrane is higher than at the flow fields. Changing the temperature profile can therefore reduce or increase the amount of water that condenses in the DM. As shown in Figure 4, by raising the thermal conductivity of the DM the temperature gradient decreases, resulting in more condensed water in the DM. Conversely by lowering the thermal conductivity of the DM the temperature gradient increases, resulting in less condensed water in the DM. Overall more condensed water was observed in diffusion media with higher thermal conductivity than ones with lower thermal conductivity. From this data, one can create structured DM, shown in Figure 4d, to optimize the water transport along the length of the active area seen in Figure 4e.
FIGURE 3. Shown here in a) is the fuel cell with representative images of the separate in situ characterizations that were performed at once. The second image from the top shows the neutron image and how it correlates to all the other in situ measurements. Here the water distribution is peaked where the current peaks along with the minimized HFR and a maximum in temperature due to waste heat from the chemical reaction. In b) the local HFR is shown as a function of water mass measured using neutron imaging. The neutron method is capable of measuring the local water content with 4 micrometer uncertainty.

FIGURE 4. Shown in a) are the neutron images of the water distribution of a DM with low thermal conductivity for various current densities and b) a DM with high thermal conductivity. The amount of retained water is plotted in c) for the various current densities for the DMs of varying thermal conductivity. A graded DM is shown in d) where high thermal conductivity DMs are used near the dry inlets to improve membrane hydration seen in e), while low thermally conductive DMs are used in the middle wetter region to reduce flooding in the DM.
Researchers from Pennsylvania State University used the NIST high-resolution detector to image a cell from the edge and varied the hydrophobicity of the flow fields to determine where the retained water was between the anode and cathode [1]. A previous study of the in-plane water distribution showed the surprising result that the cell retains more water with hydrophobic flow fields at lower current densities [2]. The present study observed that the hydrophobic lands result in small unconnected droplets, preventing the capillary wicking that occurs with the laminar sheets formed on hydrophilic surfaces. Therefore less water was pulled out of the DM into the channel, and more water was present on the anode due to increased back diffusion. This excess water in the DM formed large, connected regions under the flow channels, increasing the likelihood of flooding in the channels, and could have adverse affects on the cell operation during shutdown and startup under sub-zero conditions.

Conclusions

- High-resolution imaging is playing a key role in understanding the through-plane water transport in fuel cells:
  - Current resolution of 13 μm represents a factor of 20 improvement in spatial resolution over a four year period.
  - Fundamental water transport measurements in the DM provide:
    - Understanding of transport in fuel cells with hydrophobic channels.
    - Understanding of the role of phase change induced flow.
  - In situ membrane hydration measurements are critical for accurate models of water transport:
    - Worked with LANL in understanding the hydration of membranes as a function of water activity, membrane compression, and protonation.
    - Determined an experimental method to account for undercounting of water and eliminate this systematic from neutron imaging.
    - Combined results from thermo gravimetric analysis and neutron imaging to correctly analyze data.
- Neutron user program successfully provides users with unique access to neutrons:
  - In the past year, neutron imaging data from this unique facility has been used by researchers from six companies, eight universities, three national laboratories, and has been a part of the thesis research of 12 graduate students.

Future Directions

- Study transport and dynamics in four cell stacks designed for neutron radiography.
- Study water transport in the microporous layer and compare with realistic models of the microporous layer.
- Work with modelers to correlate models and experimental data in an operating fuel cell.
- Develop large area detectors (10 cm by 10 cm) with spatial resolution of less than 15 μm.
- Investigate neutron optical techniques to improve the spatial resolution to less than 10 μm.

FY 2010 Publications/Presentations


References

Objectives

The overarching objectives of the project are to assist the DOE in developing fuel cell systems by analyzing the technical, economic, and market drivers of direct hydrogen polymer electrolyte membrane fuel cell (H-PEMFC) adoption.

In 2010, Battelle’s major task focused on developing a manufacturing cost analysis and associated technical targets for a 5 kW backup power fuel cell system operating on direct hydrogen. The cost analysis was performed at three technology levels and production volumes:

- Current Status (2,000 Units)
- 2012 (10,000 Units)
- 2015 (100,000 Units)

Preliminary analysis of the manufacturing costs is presented in this report. Final review and refinement are expected to be complete after the deadline for submission of this report.
in fuel cell technology. This information was used to determine the preliminary design of the H-PEMFC stack and system for the years of interest (2010, 2012, and 2015). The overall system design was used to design the main components of the system, like the membrane electrode assembly, bipolar plate etc. The system design and configuration was then iterated multiple times based on further input from industry and insights provided by the simultaneous cost analysis. Manufacturing methods were then selected based on the industry practices and considerations for achieving desired durability and costs. These methods were further refined based on feedback from industry and based on cost modeling. Once the system configuration was defined, the system cost was determined. The system cost is comprised of capital equipment, stack production, balance of plant (BOP), and assembly/test costs. Capital equipment and BOP costs are determined using estimates and quotations from vendors of suitable hardware. Whenever possible, multiple vendors were solicited for pricing information to gain confidence in the validity of the costs used in the analysis. The cost of production of the stack and the system assembly and testing was estimated using models developed from the manufacturing process definitions, implemented in the Boothroyd-Dewhurst DFMA™ software.

**System Design and Assumptions**

An air-cooled system was chosen for the analysis. This is reflective of many commercially available H-PEMFC systems for backup power applications. Compared to a water-cooled system, an air-cooled system offers a reduction in BOP components and advantages in reliability, transport, and durability. An air-cooled system is generally operated at a lower current density than a water-cooled system which in turn requires more membrane active area. Due to equipment limitations, an air-cooled system also is limited on the stack size. The system schematic is shown in Figure 1.

The operational characteristics for the system are listed in Table 1. Stack construction details are summarized in Table 2. Primary changes considered for systems in 2012 and 2015 are an increase in current density, an increase in the membrane utilization, and a decrease in the number of bipolar plates. The increase in current density is expected to come from research advances in membranes and catalysts. The increase in membrane utilization is attributed to improvements in the design and manufacturing capabilities. The reduction in bipolar plates is realized by combining the cathode air and cooling air process streams into a single process air flow and thereby eliminating the need for separate cooling air channels.


<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2012</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net Power Output</td>
<td>5,000</td>
<td>5,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Gross Power Output (W)</td>
<td>7,000</td>
<td>7,000</td>
<td>7,000</td>
</tr>
<tr>
<td>Nominal Operating Voltage (VDC)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Stack Temperature (C)</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Power Density (W/cm²)</td>
<td>0.455</td>
<td>0.52</td>
<td>0.65</td>
</tr>
<tr>
<td>Current Density (A/cm²)</td>
<td>0.7</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Cell Voltage (VDC)</td>
<td>0.65</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Active Area Per Cell (cm²)</td>
<td>200</td>
<td>175</td>
<td>140</td>
</tr>
<tr>
<td>Overall Membrane Dimensions (cm)</td>
<td>33 x 10</td>
<td>31 x 8.3</td>
<td>25 x 7.1</td>
</tr>
<tr>
<td>Overall Membrane Area (cm²)</td>
<td>330</td>
<td>257</td>
<td>178</td>
</tr>
<tr>
<td>Membrane Utilization (Active Area/Total Area)</td>
<td>0.606</td>
<td>0.680</td>
<td>0.789</td>
</tr>
</tbody>
</table>

Battelle approached manufacturing by defining a business model where the fuel cell stack components, stack assembly, system assembly, and test and conditioning are all performed in-house. Doing so means acquiring and operating all necessary machinery as well as buildings and associated infrastructure such as electric distribution, heating and cooling, cleanliness control, lifting and transportation of materials, and storage. System components falling outside the defined core will be purchased or outsourced. As a result, no equipment or facilities are included for production of commercially available off-the-shelf items, such as blowers and pressure regulators, nor are any resources allocated to commercially common processes like metal machining or plastic molding.

Since a transition to high production volumes was anticipated well before the lifetime of the manufacturing equipment, high-volume equipment was identified and used at the outset. The manufacturing processes utilize roll-to-roll style processing (instead of batch processing). This approach results in excess manufacturing capacity initially, but as production volumes increase over time...
the capacity is eventually exceeded. More equipment is bought as those limits are reached, phasing the cost of manufacturing capital expenditures.

Cost estimates were developed for each piece of machinery in the manufacturing process. Quotes were gathered from vendors when possible, from published pricing information, resale listings, internet searches, and by engineering estimate when necessary. The same price was used across the various manufacturing line itemizations if a machine appears in multiple process lines.

Any capital expenditures are amortized over a 20-year period and the annual amortized cost is distributed over production volume for that year. For example, if total capital financing costs in year 1 are $2,000,000 with a production volume of 10,000 units, each unit’s price will reflect $200 of capital cost. This approach results in capital costs representing a diminishing portion of the fuel cell system cost with increasing production volume. In all three of the forecast years, manufacturing capital costs are a minority contributor to the overall cost of a fuel cell system.

The cost of production was estimated using models developed from the manufacturing process definitions, implemented in the Boothroyd-Dewhurst DFMA™ software. Standard models for processes or machinery existing in the software were used whenever possible. A custom model was programmed, using fundamental mechanical principles and published machinery specifications or data gathered from vendors.
when a standard model was not available. Basic cost assumptions are detailed in Table 3.

### TABLE 3. Production Process Assumptions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA Manufacturing Process</td>
<td>Roll-to-roll</td>
</tr>
<tr>
<td>Process line speeds:</td>
<td></td>
</tr>
<tr>
<td>Catalyst application</td>
<td>10 m/min</td>
</tr>
<tr>
<td>GDL fabrication</td>
<td>5 m/min</td>
</tr>
<tr>
<td>MEA hot pressing</td>
<td>0.5 m/min</td>
</tr>
<tr>
<td>Roll length</td>
<td>1,000 ft</td>
</tr>
<tr>
<td>Membrane roll width</td>
<td>1 m</td>
</tr>
<tr>
<td>Carbon cloth width</td>
<td>1 m</td>
</tr>
<tr>
<td>Overall plant efficiency</td>
<td>85%</td>
</tr>
<tr>
<td>Inspection steps included in processing</td>
<td>None</td>
</tr>
<tr>
<td>Labor cost</td>
<td>$45/hr</td>
</tr>
<tr>
<td>Machine cost</td>
<td>$25/hr</td>
</tr>
<tr>
<td>Energy cost</td>
<td>$0.07/kW-h</td>
</tr>
<tr>
<td>Setup operations per roll</td>
<td>1</td>
</tr>
<tr>
<td>Operators on membrane line</td>
<td>3</td>
</tr>
<tr>
<td>Operators on all other lines</td>
<td>1</td>
</tr>
</tbody>
</table>

Assumptions were developed from previously published information, discussions with vendors, using standard values defined in the software, and by engineering estimates.

Scrap rates for the stack manufacturing processes vary and in some cases represent a tangible portion of the process’s cost. As with the manufacturing process definition itself, much of this information is considered proprietary in industry. The values used for the Battelle analysis are representative of ranges documented in previously published information. When such data was not available, engineering estimates were made based on Battelle’s manufacturing knowledge. Table 4 delineates the scrap rates, which were held constant over all the forecasted years. These rates capture not only scrap resulting from initial production of material, but also excess material consumed during stack rework as part of test and conditioning.

The remainder of the fuel cell system components, including BOP and structure (frame) and enclosure, are purchased or outsourced. The assembly, integration, testing, and conditioning of all these items are done in-house. Stack assembly and test costs are included in the stack estimate while the cost of system assembly and test is included at that level.

### Results

The system cost breakdown and total system costs are shown in Table 5. According to the Battelle analysis, in 2010 with an annual production volume of 2,000 units, cost of a 5 kW H-PEMFC system is $6,986 or $1,379 per kW. This cost declines by 26% to $5,084 or $1,017 per kW in 2012, and by 39% to $4,221 or $844 per kW in 2015. Approximately 60% of the reduction to $844/kW in 2015 is achieved through reduction in costs of the stack components, particularly the bipolar plates and the MEA. The remaining 40% is equally split between reductions in the BOP component cost and the lower assessment of capital costs on a per unit basis. The modest decrease in BOP costs is due to many of them already being produced in high quantities with limited margin for cost reduction. Approximately 50% of the source for reduction in cost for both the 2012 and 2015 cases is due to technology advances while the other half is due to increased production volume.

In general, materials represent the most significant cost of fuel cell stack production, evident in Figure 2. In the case of the bipolar plates; production cost is split more uniformly across all three of tooling, processing, and raw materials. The cost production breakdown is similar for 2012 and 2015.

At initial and low volume production, much of the capacity of the manufacturing equipment goes unused. In some cases, the entire year’s worth of production can be run in a few calendar days. However, by business model definition, the equipment purchase at the beginning is justified by the rapidly increasing production quantities over the five year period of study. Despite much of the machinery’s production capacity potentially going unused in the first few years, the unused capacity represents, by way of capital costs allocated to each unit, a small portion of the system cost.

Considering line utilization is useful for identifying process bottlenecks. Battelle defined line utilization as a percentage calculated as the number of machine hours necessary to produce the annual quantity divided by the total number of annual machine hours available.
The annual machine hours available are the number of machines times 24 hours (3, 8-hour shifts) in a day. The results of this are tabulated in Table 6.

The bottlenecks in production are identified by these tables and include the bipolar plate forming, stack assembly, and test and conditioning. Despite having limitations to productivity, the system cost impact of these bottlenecks is mostly low since raw material costs are the predominant expense in stack production. Of the group, eliminating the bipolar plate forming bottleneck will have the most impact on stack cost. The elimination of the bipolar plate bottleneck can be achieved by emerging technologies, like flat/unformed sheet metal or foils. Industry expects test and conditioning time to decrease significantly over the next five years, providing a modest opportunity for cost reduction.

**Conclusions and Future Directions**

System costs and stack costs are expected to decline to $847 per kW and $203 per kW, respectively with annual volumes of 100,000 units. Major contributors to the system cost are the bipolar plates, MEA, and the DC/DC converter. The main drivers to MEA cost are the raw materials, most specifically catalyst. Additional research in alternative material-based bipolar plates and lower-catalyst MEAs could reduce these costs. The lack of a suitable off-the-shelf DC/DC converter is a significant obstacle. Further work to understand the
application requirements and the drivers for DC/DC converter cost is recommended.

Next steps on the project are to complete a sensitivity analysis of the cost drivers likely to most impact the cost of the system and incorporate the feedback from industry and the peer reviewers and publish final results.

**FY 2010 Publications/Presentations**

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 Fuel Cell 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 Fuel Cell 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)
  - 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.

Accomplishments

- Characterized two 5-kW complete systems.
- Characterized one 12-kW complete system.
- Began characterization of a 2-kW stack which contains bipolar plates designed for high-temperature operation.
- Participated in and made technical presentations at meetings of the International Organization for Standardization Working Group 11 under Technical Committee 105 of the International Electrotechnical Commission, held on February 8-9, 2010, in Milan, Italy. The goal of this international group is to draft the technical specification of a single-cell test protocol. Representatives from six countries attended. The technical specification has been published.
- Initiated collaborative effort to compare the test protocols developed by the European Fuel Cell Testing and Standardization Network (FCTESTNET)/fuel cell testing, safety, and quality assurance (FCTESQA) and by DOE to characterize and age fuel cell stacks. The objective of the effort is to determine if the results depend on the protocol used or if the results are protocol-independent.

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 standardized fuel cell testing procedures to aid in the evaluation of different stack technologies on a common basis. The procedures and methods used at the Argonne Fuel Cell Test Facility do not depend on the technology being tested, that is, they 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 room-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 crossover), 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 fuel cell 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 two 5-kW, direct hydrogen fuel cell systems 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 (1,000 DST cycles) of this accelerated aging protocol, the DST cycling was interrupted and the stack performance was characterized by measuring a sequential polarization curve.

The performance and aging characteristics of the two 5-kW stacks were very similar; the results from one will be used in the following discussion. 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 ~1,200 h of the accelerated aging under the DST cycling conditions. After that, however,
there was a significant decrease in the measured performance of the stack.

The power vs. current density curves were calculated from these data (see Figure 3). As expected, very little change in these curves was seen during the first ~1,200 h of DST aging.

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 FCTESQA program in a number of EU laboratories.

As part of our collaboration with FCTESQA, we compared the performance of a previously-tested, hydrogen-fueled, 15-kW stack using the sequential polarization protocols developed by FCTESTNET and by DOE. The major differences between the two polarization protocols are the sequence of currents used and the portion of the polarization experiment that is reported as the resulting data. Figure 4 shows that the DOE protocol starts at open circuit, and then increases and decreases the stack current in turn. The FCTESTNET protocol, on the other hand, can start at almost any current setting. In the example shown in Figure 4, the test protocol starts at about 50% of the rated current; the current then increases, decreases, and finally increases again. The DOE protocol reports data from both the current-increasing and the current-decreasing sections; for the FCTESTNET protocol, only the results from the current-decreasing portion are reported. Figure 5 shows the current-decreasing portion of the polarization curves obtained from the 15-kW stack using the two protocols; there was no significant difference between the two curves.

Based on the genesis of the protocols, differences in the levels and profiles of stress placed on the fuel cell or stack may be expected to affect how the cell or stack ages during a durability test. The U.S. durability protocol was based on the accelerated testing of automotive-class traction batteries (Figure 1). Those used by the EU were based on different assumptions, such as a smooth power increase followed by power off (Figure 6a) or on-off cycling (Figure 6b). Aging experiments were conducted to measure the relative stress imposed by the test profile. Here, the DST and FCTESTNET Profile B were used to age the stack; each aging test lasted about 75 h. The change in performance of the stack with aging profile was gauged by polarization curves (see Figure 7). As can be seen from Figure 7, the DST profile produced a 7.4% decrease in performance at the maximum current density. The FCTESTNET Profile B produced an additional 2.0% decrease in performance. Thus, the DST profile seems to age the stack faster. FCTESTNET Profile A will be used next to complete the study as well.
as to investigate whether the order in which the tests are performed affects the results (path dependency).

**Conclusions and Future Directions**

- We have characterized the performance of two identical 5-kW systems, a 12-kW system, and a 2-kW stack, the last containing bipolar plates designed for high-temperature operation.
- The performance of the two 5-kW stacks was observed to be essentially identical and representative of this particular fuel cell technology.
- Testing of the stacks under an accelerated aging regime of current and potential cycling showed little change in performance over the first ~1,200 h (12,000 DST cycles); however, the stack performance degraded rapidly after 1,200 h.
- We are collaborating with the EU’s FCTESTNET program to compare and validate the fuel cell test protocols being developed by the EU and the DOE. Preliminary results from the testing of a 15-kW stack of circa 2002 technology showed that there was no significant difference between the polarization curves obtained under these two different protocols. More detailed work is still needed to confirm these early results for the state-of-the-art fuel cell technology, and to evaluate the effects of accelerated aging schedules under the two testing protocols.
- In future work we will continue to characterize DOE fuel cell contract deliverables, as well as benchmark other fuel cell technologies.
- We will continue to collaborate with other fuel cell testing laboratories, such as the Institute for Energy (Netherlands), and we will begin the maintenance of the technical specification that Working Group 11 has produced (single-cell test protocol).

![FIGURE 6a. A Dynamic Test Profile Proposed by FCTESTNET](image)

![FIGURE 6b. Another Dynamic Test Profile Proposed by FCTESTNET](image)

![FIGURE 7. Polarization curves comparing of the aging effects of the DST profile with that of the FCTESTNET Profile B. Each test lasted ~75 h.](image)
V.A.8 Technical Assistance to Developers

Objectives

- Assist technically, as directed by DOE, fuel cell component and system developers.
- Test materials and components and provide feedback to customers.
- Support the development and testing of durability protocols with the US Fuel Cell Council (USFCC).
- Provide support to the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE Freedom Cooperative Automotive Research (FreedomCAR) Fuel Cell Technical Team.
- 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 (3.4.2) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP), however it principally addresses:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

In this particular task, any of the technical targets in the MYRDDP Table 3.4.4 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 continued testing insight and advice to DOE principal investigators.
- Testing of materials and participation in the further development and validation of durability test protocols with the USFCC.
- Offering technical assistance to USCAR and the USCAR/FreedomCAR Fuel Cell Technical Team.
- Participating in working groups and review meetings.

Approach

Our approach has consistently focused on collaborative-type interactions as guided by DOE. A large portion of this effort goes unpublished, for proprietary reasons. However in this fiscal year, we have continued to provide testing support and actively participated in developing test protocols. In addition, LANL has provided hands-on short courses on several fuel cell topics.

Accomplishments

- Honored several invited presentations.
- Hosted numerous visitors to LANL.
- Collaborated with multiple industrial, university, or laboratory partners.
- Provided test insight and/or results to several DOE principal investigators.
- Participated in the review and development of USFCC durability protocols.
- Held Hands-On Fuel Cell Short Course.

Highlights

Figures 1-5 show some highlights of the technical assistance task for the 2010 Fiscal Year.
FIGURE 1. Hardware designed at LANL, to provide National Institute of Standards and Technology (NIST) beam line scientists (Hussey and Jacobson) support in conducting beam hardening experiments.

FIGURE 2. Los Alamos measured water profiles and performance of dead-ended anode to help University of Michigan develop and validate simple control oriented models and simulate the dynamics of large fuel cell stack systems operating with a dead-ended anode, which do not rely on anode humidification or re-circulation systems.

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.

FIGURE 4. Impedance spectra runs on an operating fuel cell measured by LANL for the NIST Metrology group.
FY 2010 Publications/Presentations


FIGURE 5. LANL's fuel cell testing capabilities as a function of relative humidity (RH) are highlighted in the voltage-current curve.
### V.B.1 Water Transport Exploratory Studies

<table>
<thead>
<tr>
<th>Rod Borup¹ (Primary Contact), Rangachary Mukundan¹, John Davey¹, Roger Lujan¹, Jacob Spenkelov¹, Joe Fairweather¹, Dusan Spernjak¹, Tom Springer¹, Muhammad Arif², David Jacobson², Daniel Hussey², Ken Chen³, Karren More⁴, David Wood⁴, Partha Mukherjee⁴, Peter Wilde⁵, Ruediger-Bernd Schweiss⁵, Tom Zawodzinski⁶, Peter Olapade⁷, Jeremy Meyers⁷, Adam Weber⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹Los Alamos National Laboratory MS D429, P.O. Box 1663 Los Alamos, NM 87545 Phone: (505) 667-2823 E-mail: <a href="mailto:Borup@lanl.gov">Borup@lanl.gov</a></td>
</tr>
<tr>
<td>DOE Technology Development Manager: Nancy Garland Phone: (202) 586-5673 E-mail: <a href="mailto:Nancy.Garland@ee.doe.gov">Nancy.Garland@ee.doe.gov</a></td>
</tr>
<tr>
<td>Subcontractors:</td>
</tr>
<tr>
<td>² National Institute of Standards and Technology (NIST), Gaithersburg, MD</td>
</tr>
<tr>
<td>³ Sandia National Laboratories, Albuquerque, NM</td>
</tr>
<tr>
<td>⁴ Oak Ridge National Laboratory, Oak Ridge TN</td>
</tr>
<tr>
<td>⁵ SGL Technologies GmbH, 86405 Meitingen/Germany</td>
</tr>
<tr>
<td>⁶ Univeristy of Tennessee, Knoxville TN</td>
</tr>
<tr>
<td>⁷ University of Texas at Austin, Austin, TX</td>
</tr>
<tr>
<td>⁸ Lawrence Berkeley National Laboratory, Berkeley, CA</td>
</tr>
<tr>
<td>Start Date: March 2007 Project End Date: 2011</td>
</tr>
</tbody>
</table>

**Objectives**

- Develop understanding of water transport in polymer electrolyte membrane (PEM) fuel cells.
- Evaluate properties of materials affecting water transport and fuel cell performance.
- Develop (enable) new components and operating methods.
- Accurately model water transport within the fuel cell.
- Develop a better understanding of freeze/thaw cycles and sub-freezing operation.

**Technical Barriers**

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

<table>
<thead>
<tr>
<th>(D) Water Transport within the Stack</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel Cell Stack Technical Targets</strong></td>
</tr>
<tr>
<td>- Energy efficiency (65% at 25% rated power, 55% at 100% rated power)</td>
</tr>
<tr>
<td>- Power density (2,000 Watt/Liter)</td>
</tr>
<tr>
<td>- Specific power (2,000 Watt/kg)</td>
</tr>
<tr>
<td>- Cost ($25/kWe)</td>
</tr>
<tr>
<td>- Start-up time to 50% power (30 seconds from -20°C, 5 seconds from 20°C)</td>
</tr>
<tr>
<td>- Freeze-start operation (Unassisted start from -40°C)</td>
</tr>
</tbody>
</table>

**Accomplishments**

**Gas Diffusion Layer (GDL) Materials**

- Demonstrated better water removal characteristics with modified microporous layer (MPL) properties.
- Demonstrated performance improvement by optimizing GDL properties and in-plane GDL type in relation to its flow-field position.

**Membrane Water Content Measurements (by Neutron Imaging)**

- Measured compression effect on water content in membranes.
- Made reversible in situ measurements of membrane water content to examine Schroeder’s paradox.

**Freeze**

- Measured durability of various cell configurations and the location of frozen water (ice) for various operating conditions.

**Modeling**

- Created modeling simulations of oxygen partial pressure in the cathode catalyst layer as a function of channel liquid pressure for various types of GDLs.
- Modeled the dynamic behavior of water in response to various step-changes in current density.

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**Introduction**

Ineffective control of water distribution can be a major impediment to implementation of PEM fuel cells (PEMFCs). Several important 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 PEMs 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. 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.

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.

Results

Effect of Hydrophilic Treatment of Microporous Layer on Fuel Cell Performance

The GDL in a PEMFC is the component primarily responsible for effective water management under a wide variety of conditions. Optimal GDL performance is obtained when the MPL has enough hydrophobic pores for gas access and enough hydrophilic pores for water wicking [1]. To optimize the water transport properties of the GDL, SGL Technologies has developed new GDLs that incorporate aluminosilicate fibers to create hydrophilic pathways in the MPL to facilitate liquid water removal from the cathode catalyst layer [2]. Figure 1a shows the performance of fuel cells using the GDL with the hydrophilic fibers in the MPL (25BL) is significantly better than the baseline hydrophobic GDL (25BC). The cell with the 25BL GDL shows a 150 mV improvement in the voltage at a current density of 2 A cm\(^{-2}\). However when the cathode gas was changed to HelOx, the performance of the two cells were almost identical. This indicates that the improvement in the performance is primarily due to better mass transport characteristics of the 25BL GDL with the hydrophilic fibers in the MPL.

The improvement in mass transport was verified with alternating current impedance spectra of the two cells which confirms the better mass transport for the 25BL GDL and is illustrated in Figure 1b. The high frequency resistance (HFR) of both these cells is the same (≈0.04 Ω cm\(^{-2}\)), however, the low frequency (0.1 Hz) resistance of the cell with the 25BL GDL is ≈40% lower. Moreover, the impedance spectra in HelOx of these two cells is identical, indicating that the improved performance of the 25BL GDL is due to better water removal resulting in improved oxygen diffusion kinetics. The decreased mass transport resistance in HelOx when compared to air is directly attributed to the 3.7 times better diffusion of O\(_2\) in He vs N\(_2\) [3].
Neutron Imaging of MEA Water Profiles

In order to further investigate the origin of the mass transport improvement, the water profiles of two cells with 24BC and 25BL GDLs were obtained via neutron radiography with the newly installed 13 µm resolution detector at NIST. The 25BC cell is expected to behave similar to the 24BC one (based on the performance data). Figure 2 shows the water profiles obtained in the cross-section view of these cells. The baseline GDL (24BC) shows a typical profile where a peak in water content is seen close to the location of the cathode catalyst layer. Moreover the MPL (≈50 µm thick) exhibits low liquid water content as illustrated by the steep drop in water content as one moves away from the membrane electrode assembly (MEA). In contrast, the cell with the 25BL GDL shows significant liquid water in the MPL region as evidenced by the steady water content profile as one moves across the MPL. This figure also indicates that the liquid water saturation in the cathode catalyst layer is lower when using the 25BL GDL. Both GDLs show significant water accumulation in the substrate with the 25BL GDL having greater water saturation. The water content indicates a maximum saturation of only 15% in the GDL substrate for the 25BL GDL. Although the absolute water content in the thin catalyst layers and membranes is difficult to obtain due to the smearing of the water content based on the 13 mm detector resolution, these results indicate that the mass transport losses are predominantly due to liquid water in the catalyst layer pores.

Modeling of GDL Properties Effect

Modeling simulations examined various GDL properties to evaluate the mass-transfer limiting current as a function of inlet water flux. Results show that there are high limiting currents and the water flux is flat in the practical fuel cell operating range. The modeling results agree with the experimental results, showing that bulk transport (convection) does not lead to mass-transfer limitations because the effective permeability remains too high. These results indicate that once a water pathway is established, it can sustain practical liquid-water fluxes. The effect of variations in GDL properties on mass transport can be summarized in Figure 3, which shows the oxygen partial pressure as a function of the channel water pressure. At high channel water pressures, the GDL with hydrophilic pores retains the highest oxygen partial pressures at the catalyst layer.

Neutron Imaging of Membrane Water Content

Water transport in the Nafion® ionomic membrane has profound influence on the performance of the polymer electrolyte fuel cell, in terms of internal resistance and overall water balance. We conducted high resolution neutron imaging of Nafion® membranes in order to measure water content in situ with varied compression on the membrane. Figure 4 shows the measured membrane water content ($\lambda = \# \text{ water molecules per sulfonic acid group}$) for various cell compressions, including a restricted membrane (low membrane compression, <140 psi) and a highly compressed membrane (>400 psi). Restricted and compressed membranes have identical water content with the exception of when the membrane was in contact with liquid H$_2$O. In contact with liquid water, the highly compressed membrane had substantially less water ($\lambda = 17.5$) than the membrane that had lower compressions ($\lambda = 21.5$), indicated that compression can limit the membrane water uptake, but only at high water contents. When comparing the constrained
and compressed cases, it is interesting that additional membrane compression did not cause significant reduction in water uptake. A possible explanation may be that the compression of the GDL mitigates the pressure exerted on the membrane itself. The in situ measurement ability of neutron imaging was also used to examine Schroeder’s paradox, which addresses the inconsistency between the measured membrane water content at 100% RH and in contact with liquid water, which is inconsistent with thermodynamics because the chemical potential of saturated water vapor is equal to that of liquid water at the same temperature. For this measurement, the membrane RH was increased from 50% RH to 100% RH to liquid, then reversed. The membrane water content at 100% RH was identical in the forward and reverse directions at $\lambda = 10$, compared with the liquid $\lambda = 21.5$, thus proving the validity of Schroeder’s paradox.

**Conclusions**

**GDL Materials**
- Modified MPL properties show better water removal characteristics and performance.
- Performance improvement can be realized by varying the in-plane GDL type in relation to its flow-field position.
- Mass transport losses are predominantly due to liquid water in the catalyst layer pores, not due to water saturation levels in the GDL substrate.

**Membrane Water Content Measurements by Neutron Imaging**
- Cell compression influences membrane water content at high levels of water.
- Reversible in situ measurements of membrane water content verified existence of Schroeder’s paradox in Nafion® fuel cell MEAs.

**Freeze**
- Membrane hydration due to the generated current and back diffusion is dominant at sub-freezing temperatures.
- Freeze operation/cycling can result in loss of catalyst surface area, increase in porosity of catalyst layer and mass transfer limitations.
- High Teflon® content in the MPL results in better durability during freeze/thaw cycling and operation.
- Ice formation location depends on temperature, current density, cell configuration.

**Future Directions**

**Experimental and Characterization**
- Segmented cell measurements of new optimized GDL materials (25BL).
- Pneumatic pressure control to change in situ GDL compression and measure GDL compression effect on water transport.
- X-ray radiography/tomography of GDLs measuring water movement through pores.

**Modeling**
- Modeling of through-plane water distribution and transport in MEA-GDL regions by simulating water profile measurements with varying conditions and GDL hydrophobicity.

**Transport Projects**
- Support new transport projects and distribute measurements to 2008-funded projects.

**FY 2010 Publications/Presentations**


References


V.B.2 Water Transport in PEM Fuel Cells: Advanced Modeling, Material Selection, Testing, and Design Optimization

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• Techverse, Cary, NC
• SGL Carbon, Meitingen, Germany
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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 Fuel Cell 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

• Generated flow regime map from experimental studies of droplet emergence at a gas diffusion layer (GDL)-channel interface studies; demonstrated improved model agreement with the transition from film flow to droplet regime;
• Implemented experimental setup for collecting wet pressure drop and transient pressure signatures in two-phase flows in channels and cells; improved agreement of model predictions and observed wet pressure drop;
• Integrated electrochemistry, heat transfer, and phase change with the computational fluid dynamics (CFD) two-phase flow models and demonstrated improvement in current density distribution for initial validation test case; and
• Identified materials and design modifications to focus on for improved water management.

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Introduction

Water management in PEM fuel cells is challenging because of the inherent conflicts among the needs for: (1) supplying adequate water to establish and maintain the membrane electrical conductivity, (2) removing the water produced by the electrochemical reactions at the cathode, and (3) 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 the 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 progressed from water and two-phase (water and air) fluid transport properties of GDL materials, to analysis of water transport in non-operational and operational fuel cells. The related modeling studies have followed a similar progression, with initial emphasis on microscale simulations of single fluid and two-phase transport within GDL materials. The knowledge gained from the materials characterization and microscale simulations was 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, is in progress and 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 third year of research, the emphasis has been on completing experimental studies and model evaluation for water transport in fuel cell components such as GDLs and channels, and on completing integration of the water transport models with electrochemistry and heat transfer for modeling of operational cells. We have also begun to apply the gathered data and developed models to screening concepts for improving fuel cell performance through better water management.

Ex situ studies completed this year included two-phase, i.e. liquid water and air, experiments in fuel cell microchannels and channel-GDL assemblies. A flow regime map for the two-phase system arising from liquid water injection into microchannels was generated from controlled experiments designed to model water emergence phenomena in a PEM fuel cell cathode gas microchannel. The microchannel was 250 μm square in cross-section, with a single 50 μm square opening in the bottom for water injection. In general, higher air flow velocities resulted in decreased contact angle hysteresis so that the leading and trailing edges of the droplets had similar contact angles. Higher air flows also promoted droplet detachment in surface tension controlled regimes, as shown in Figure 1. The Weber number scales on the top and right axes of Figure 1 correspond to the relative values of the droplet inertial forces and surface tension forces. With increasing water velocity, the region corresponding to droplet flow regime becomes smaller. At some point, while increasing the superficial water velocity, the slug and film regime will intersect and thus the flow pattern might turn into an intermittent quasi single-phase liquid flow. The desirable operating states are expected to be at the higher air flows within the droplet regime. In this operating region, droplets are formed and more easily removed from the GDL surface, as opposed to the water forming liquid films that would prevent reactants from reaching the fuel cell catalyst or the water accumulating in slugs that would large pressure drops and pressure variations along the channels.

The capabilities of the developed two-phase flow models to predict trends from the droplet injection in microchannel experiments have been improved by
refining the treatment of surface tension. Simulations of experiments such as these are typically performed using the volume of fluid approach, VOF, which provides better resolution of liquid-vapor interface movement and better captures surface tension effects but assumes a no-slip interface at the liquid-vapor surface. The principal disadvantage of the VOF technique is the computational time requirement, since it is inherently a transient technique requiring limited time steps and a relatively fine computational grid to capture surface tension effects accurately. The computation of surface tension forces for liquid-vapor interfaces in channels has recently been improved in the developed two-fluid, two momentum equation solution approach, and initial tests indicate that this new algorithm improves the ability to identify the onset of droplet formation and surface-tension dominated flows. Although the two-phase multiplier is still slightly underestimated for ‘wet’ to dry pressure drop ratios, the improved surface tension algorithm does result in droplet and slug formation for steady state simulations enabling faster screening of design concepts.

Techverse experimentally studied two-phase flow regimes in the cathode channels of a non-operational cell as a function of air flow rates, water flow rates, and cell orientation to analyze transport in channel-GDL assemblies. The apparatus was prepared by using a GDL to separate a liquid water reservoir from transparent serpentine cathode channels. Visualization and image analysis were used to identify the flow regimes, and pressure drop measurements were performed. In general, a horizontal cell with water entering from above the flow channels exhibited the least two-phase flow pressure drop, while a vertical cell with air flowing up had the largest pressure drop for the same air and water flow rates. Analysis of photographs at steady operation indicated that a horizontal cell orientation with water flowing up into the channels, and a vertical cell orientation with air flowing up, were most likely to form water films blocking open GDL surface area. Several operating points from the experiments for the vertical orientation of the channels, Figure 2, were simulated using the developed two-fluid models for water transport through porous GDL materials and in the channels. The model predictions were qualitatively consistent with the experimental observation of film formation at these conditions, and the predicted variation in channel pressure drop with water flow rate was in good agreement with the experimental measurements.

The integration of two-phase flow models with the key effects necessary for simulation of an operational cell at typical conditions of temperature, pressure, and inlet states has continued. Initial testing and validation simulations were for the Ballard MK902 cell. This cell and operating conditions were selected for the detailed diagnostic data and past modeling results available for comparison [1,2]. The simulation utilized two-phase flow in the channels and porous media, electrochemistry, and heat transfer. The coupling between gas phase chemical species transport and liquid water formation was primarily through the treatment of the oxygen reduction reaction. For this reaction, the water product is formed as either vapor or liquid phase water based on the local thermodynamic state. The resulting liquid water fraction distribution at the level of the cathode GDL for an average current density of 0.85 A/cm² indicated that liquid water is predominantly under the lands. The predicted current density distribution, Figure 3, is below the experimental...
curve because we were unable to obtain a converged solution at the desired 1 A/cm² average current. The two-phase model does show improved agreement with the experimentally measured trends compared to simpler models, particularly near the inlet where the current density starts low and rapidly increases in the single phase solution. During these tests, improvement of the numerical stability and accuracy of the heat transfer solution was identified as the highest priority for further model improvements.

Two main thrusts have emerged for concepts to improve cell performance, GDL materials modification and channel design. In the area of GDL material properties, during the second year of this project BCS Fuel Cells demonstrated improved performance in a self-humidified cell operated under dead-end conditions for an intermediate loading of poly-tetrafluoroethylene (PTFE) in the microporous layer. Within the last year, these results have been confirmed, and the initial interpretation of the basis for improved performance has been supported by improved diagnostics using impedance spectroscopy. The best performance is observed at the intermediate PTFE loading because less hydrophilic GDL materials do not maintain adequate membrane ionomer hydration, while additional loading blocks pores and introduces mass transfer limitations for the gaseous reactants between the channels and the catalyst. For channel designs, the specific objectives are to minimize the pressure drop variation between ‘wet’ and ‘dry’ operation and the amplitude of pressure drop transients caused by liquid water in the cells while maintaining or improving cell power density. Initial experiments at Ballard have identified wicking channel designs, in conjunction with channel surface treatments to control the water contact angle, as promising approaches to meet these objectives. In those experiments, several channel design concepts either achieved the wet pressure drop performance improvements, or had promising CFD output, but none met both objectives.

### Conclusions and Future Directions

In the past year, we have identified advantageous operating regimes while completing the planned characterization of two-phase transport in cell components and assemblies. The predictive capabilities of the cell-scale CFD models for two-phase flow in fuel cell microchannels, and in porous components such as GDLs and catalyst layers, have been improved and are integrated with electrochemistry and heat transfer to enable analysis of operational cells. Specific accomplishments for the past year include:

- Generated flow regime map from experimental studies of droplet emergence at a GDL-channel interface studies; demonstrated improved model agreement with the transition from film flow to droplet regime;
- Implemented experimental setup for collecting wet pressure drop and transient pressure signatures in two-phase flows in channels and cells; improved agreement of model predictions and observed wet pressure drop;
- Integrated electrochemistry, heat transfer, and phase change with the CFD two-phase flow models and demonstrated improvement in current density distribution for initial validation test case; and
- Identified materials and design modifications to focus on for improved water management.

Key activities planned for the coming year include:

- Improve numerical stability of electrochemistry, heat transfer and phase change models integrated with the two-phase CFD models; test and validate the developed integrated models using operational cell-scale steady and transient data.
- Apply validated measurements and simulation tools to the identified optimization strategies: channel design, surface finish, and GDL design for effective water removal with low pressure drop and minimal transients; GDL design and treatment for improved cell performance.

Future work will consist primarily of testing and improving the developed models, while applying validated capabilities to support the development and demonstration of improved water management approaches.

### FY 2010 Publications/Presentations


References


V.B.3 Visualization of Fuel Cell Water Transport and Performance Characterization under Freezing Conditions

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Project Start Date: March 1, 2007
Project End Date: February 28, 2010

Objectives

• Improve fundamental understanding of the water transport processes in 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 Fuel Cell Technologies (FCT) 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 FCT Multi-Year RD&D Plan:

• Unassisted start from low temperature: -40°C
• Durability with cycling at operating temperature of ≤80°C: 5,000 h
• Energy density: 2 kW/L

Accomplishments

In this project, Rochester Institute of Technology (RIT), General Motors (GM) and Michigan Technological University (MTU) have focused on fundamental studies that address water transport, accumulation and mitigation processes in the GDL and flow field channels of the bipolar plate. These studies have been conducted with a particular emphasis on understanding the key transport phenomena which control fuel cell operation under freezing conditions. 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.
• Identified two-phase flow patterns (slug, film and mist flow) in flow field channel, established the features of each pattern, and created a flow pattern map to characterize the two-phase flow in GDL/channel combination.
• Implemented changes to the baseline channel surface energy and GDL materials and evaluated their performance with the ex situ multi-channel experiments. It was found that the hydrophilic channel (contact angle \( \theta \sim 10^\circ \)) facilitates the removal of liquid water by capillary effects and by reducing water accumulation at the channel exit. It was also found that a GDL without a microporous layer (MPL) promotes film flow and shifts the slug-to-film flow transition to lower air flow rates, compared with the case of GDL with MPL.

• Identified a new mechanism of water transport through GDLs based on Haines jump mechanism. The breakdown and redevelopment of the water paths in GDLs lead to an intermittent water drainage behavior, which is characterized by dynamic capillary pressure and changing of breakthrough location. MPL was found to not only limit the number of water entry locations into the GDL (thus drastically reducing water saturation), but also stabilizes the water paths (or morphology).

• Simultaneously visualized the water transport on cathode and anode channels of an operating fuel cell. It was found that under relatively 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 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 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 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.

• Determined the effect of surface wettability and channel cross section and bend dihedral on liquid holdup in fuel cell flow channels.

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**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:

1. Two-phase (water and gas) transport in the fuel cell stack, including the GDL, flow channels, and their interfaces.
2. Structural and surface properties of materials and how they change during operational events, such as freeze/thaw.
3. 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 were 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**

Previous studies under this project have identified the most important GDL material properties that affect the water accumulation within GDLs are thermal conductivity and thickness. Decreased thermal conductivity effectively increases the MEA temperature and thus, the saturation pressure gradient that drives water vapor from the electrode to the channel, resulting in lower steady-state liquid water accumulation within GDLs. Thinner GDLs simply hold less water. To minimize the quantity of water that accumulates within the GDLs, the effects of variations in GDL thickness and thermal conductivity have been evaluated by GM for optimized water removal at various shutdown conditions. A series of experiments were conducted with Toray 030 and 090 (nominal thicknesses of 100 and 300 \( \mu \text{m} \), respectively) diffusion media, which are more thermally conductive than the baseline GDL, that
combined different combinations on the anode and cathode (MPL used in all cases). As shown in Figure 1, the steady-state water content with fully humidified inlet reactant streams was greatest when a thick cathode GDL was used; this impact is also observed in the significantly higher mass transport loss at high current density. By contrast, the thickness of the anode GDL had a relatively small effect on both water content and fuel cell performance.

Water removal during shutdown purge is critical for a robust freeze start. Conversely, the ionomer must not become over dried during purge because poor proton conductivity at sub-freezing start conditions will occur. In order to investigate the relationship between ionomer drying (as indicated by high frequency resistance, HFR) and water removal, GM employed the distributed current and temperature measurement tool with simultaneous neutron radiography [1]. The results in Figure 2 demonstrate that there is a very strong correlation between HFR and effective water thickness, and that a significant increase in local HFR due to ionomer drying does not occur until water in the GDL substrate has been removed. For the purge condition in Figure 2, this transition occurs at a measured water thickness of about 20 μm. The results indicate that purge time is constrained by GDL saturation properties.

Water accumulation in the through-plane dimension was directly measured with high resolution neutron imaging instruments at the National Institute of Standards and Technology. These measurements were executed with the baseline material set and same operating conditions that have been previously reported. When preconditioned and purged at 55°C, the majority of water accumulation was observed to occur within the anode GDL layer. This result directly confirms the previously inferred water accumulation location in the through-plane dimension. The data clearly demonstrates that the water removal rate during shutdown purge for freeze is constrained by water transfer through the membrane.

Various changes to the baseline GDL-channel systems, including channel surface treatment (hydrophobic or hydrophilic), channel geometries (sinusoidal, trapezoidal or rectangular), GDL Teflon® (poly-tetrafluoroethylene, PTFE) content and GDL thickness, were implemented in order to obtain the combination of GDL materials and flow channel design which give out the optimal ex situ performance. The channel surface energy displays significant impact on channel two-phase flow. The hydrophilic channel (contact angle, \( \theta \approx 10^\circ \)) was found to facilitate the removal of liquid water and decrease the slug formation tendency compared to the case of non-treated channels (\( \theta \approx 60^\circ \)), while the hydrophobic channel (\( \theta \approx 105^\circ \)) displays a large number of stationary water droplets or small slugs. The effects of different channel geometries, including sinusoidal geometry representing the stamped metal bipolar plate and trapezoidal geometry representing the molded carbon composite bipolar plate, on the two-phase flow in channels, were compared to the rectangular geometry (maintaining same hydraulic diameter) and no significant impact was found in terms of the two-phase flow pattern map. This confirms the validity of the selection of the baseline rectangular channel design. The effects of GDL PTFE content and thickness on channel two-phase flow were carried out
using Toray GDL with different thickness (190 μm for TGP-H-060 and 380 μm for TGP-H-120) and different PTFE contents (0-40 wt%). While GDL thickness shows little influence on the ex situ two-phase flow, the PTFE content shows remarkable impact on the flow pattern map. Plain GDL (non-PTFE treated) was shown to be completely wetted by water and a continuous water film was developed on GDL surface. In contrast, PTFE treatment promotes the formation of water slugs and films along the channel walls and little water resides on the GDL surface due to its hydrophobicity. As PTFE content increases, the transition from slug to film flow shifted to higher superficial air velocity, and no significant difference in flow pattern was found with further increasing hydrophobicity at PTFE content above 20 wt%.

Water breakthrough dynamics, characterized by the capillary pressure and water saturation, were determined ex situ with baseline and single gas layer GDLs with and without MPL. The water breakthrough in GDLs has been found to occur at a few preferential locations in both baseline and single gas layer GDLs, with the dynamic characteristics of this process having been observed. The dynamic behavior was reflected in two aspects: dynamic capillary pressure (or recurrent breakthroughs) and dynamic breakthrough locations (or changing of breakthrough locations with time). Generally small water saturations (less than 10%) were observed for GDLs at breakthrough and MPL was found to further reduce the water saturation in GDL. No changing of water breakthrough locations was observed in GDLs with MPL. This result suggests that MPL play a role in stabilizing the preferential water pathways.

Based on these observations, we have proposed a new water transport mechanism to account for the water breakthrough in GDLs (Figure 3). This mechanism is based on Haines jump dynamics [2,3]. Water drainage through a GDL occurs in a step-wise process. The water in GDLs remains unmoved until the point at which the pressure in water increases above the capillary pressure at the largest restriction and, at this point, the invading water suddenly moves into the adjacent pores. In the case of water breakthrough on the GDL surface, the bursting droplet grows fast as it carries away water from adjacent GDL pores. However, the supply of water is often not sufficient for the droplet to fill the gas channel. This “choke off” effect leads to empty pores in the GDL, which break down the continuous water paths. These emptied pores are refilled afterwards as water is constantly injected and the bursting process occurs again, leading to the recurrent breakthrough behavior. As the “choke offs” break down the original water paths and water spontaneously readjusts its interfaces inside GDL pores. This water/air interface relaxation process may lead to a new preferential pathway in the GDL and result in a new breakthrough location.

The pseudo-Hele-Shaw experiment was conducted to determine the water distribution inside the fuel cell and to quantify the amount of water held in the GDL. The two measurements derived from the experiment, wetted area and percolation pressure, were combined into a single variable by defining a new scaling for water percolation in porous media. The scaling is based on the ratio between the energy required to inject the water and the energy dissipated due to the viscous stress. When this energy ratio (Ce) is plotted against the non-dimensional time (t*) a simple logarithmic dependence was observed.

A series of two dimensional numerical simulations using a network model approach were conducted to study the effect the most significant variables affecting the water percolation within the GDL. The numerical model consists of the cross-sectional portion of GDL under a single gas channel. The impacts of the morphological and wetting properties of the GDL on the water transport were studied. The impact of the morphology was analyzed by varying the pore size distribution. These distributions were generated by defining pore size histograms using the Weibull distribution function. Even though the water percolates, forming a different array of fingers for different pore size distributions, it was found that the percolation pressure is the same for GDLs having the same pore size histogram. The effects of wetting properties were studied by varying the contact angle. In contrast to the morphology properties, varying the contact angle only modifies the percolation pressure while water moves through the same set of pores. Additionally, three different GDL scenarios were investigated corresponding to GDL without MPL, GDL with MPL and GDL with an MPL have defects. It was found that the overall water content in the GDL was reduced by the addition of the MPL between the GDL and the catalyst layer. This effect was enhanced when considering the addition of a perforation or defect in the MPL.

**FIGURE 3.** Schematic of water drainage in a GDL (a) without MPL, displaying a large number of water entry points into the GDL; and (b) with MPL, restricting water entry into GDL only at the crack/defect locations in the MPL.
The two-dimensional network model was extended to a three-dimensional version and a series of numerical simulation were performed imitating the conditions occurring in a pseudo-Hele-Saw experiment. The wetted area and percolation pressure were extracted from the simulations. The energy ratio was calculated and compared with experimental data. The comparison between the numerical and the experimental pseudo-Hele-Shaw experiments are plotted in Figure 4. An effective internal contact angle of 135 degrees collapsed the numerical simulation onto the experimental data. Thus, the behavior of liquid water in GDLs can be effectively characterized experimentally and can be captured in a simple computational tool.

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.

Conclusions and Future Directions

A major driving force for this research project has been the development of an optimal combination of materials, design features and cell operating conditions that achieve a water management strategy which facilitates fuel cell operation under freezing conditions. Based on our various findings, we have made the final recommendation relative to GDL materials, bipolar design and surface properties, and the combination of materials, design features and operating conditions:

- GDL materials: use lower thermal conductivity cathode GDL and decrease the anode GDL thickness.
- Bipolar plate design: use a channel geometry that can be produced using a high-speed manufacturing process, with a hydrophilic coating.
- Shutdown and gas purge protocol: incorporate above findings in developing cost effective and energy efficient shutdown purge protocol.

It should be noted that a comprehensive fuel cell operating strategy must consider the entire range of operating conditions under which the system needs to perform. Although the recommendations above will benefit fuel cell performance under conditions where liquid water is expected to be present, they must also be fully assessed to understand their impact under relatively dry conditions.

FY 2010 Publications/Presentations

Book Chapters


Journal Publications


References


V.C.1 Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

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Project Start Date: October, 2007
Project End Date: March, 2011

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

(B) Cost: the cost of fuel cells limits their use:
- Fuel and air impurity removal systems increase cost, weight and complexity.
- Higher platinum group metal loading required for maintaining performance, in the presence of impurities, increases cost.

(A) Durability: Durability may decrease in the presence of impurities.

(C) Performance: Fuel cell performance is degraded by impurity effects.

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 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)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2005 Status</th>
<th>Stack Targets</th>
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<tbody>
<tr>
<td>Platinum group metal (PGM) total content (both electrodes)</td>
<td>g/kW (rated)</td>
<td>0.6 1.1 0.3 0.2</td>
<td></td>
</tr>
<tr>
<td>PGM total loading</td>
<td>mg PGM/cm² electrode area</td>
<td>0.45 0.8 0.3 0.2</td>
<td></td>
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</table>

Accomplishments

• H₂S anode poisoning/durability test completed with current generation membrane electrode assemblies (MEAs) (milestone).
• SO₂ long-term testing was completed (milestone).
• Long-term NOₓ fuel cell poisoning was characterized (milestone).
• NH₃ effect on oxygen reduction on Pt/C was studied by rotating disk electrode voltammetry.
• Iridium oxide solid state pH sensors were developed for local proton activity measurements in polymer electrolyte membrane fuel cells.
• Neutron imaging at the National Institute of Standards and Technology (NIST) showed some cationic impurities change local water concentration in fuel cells (milestone)
**Introduction**

Fuel cells efficiently convert flows of chemical fuel and oxygen to electrical power. Fuel cell performance may 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 impurities may be generated by the fuel synthesis process or be present as ambient air impurities. The platinum metal catalyst surfaces may be deactivated by strongly adsorbing species such as sulfur containing molecules and carbon monoxide. The strongly bound 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 carry out fuel cell performance measurements in the presence of known quantities of introduced impurities and then study the impurity interactions with fuel cell components using electrochemical diagnostic methods such as adsorbate stripping voltammetry and alternating current impedance spectroscopy. Sometimes the experiments are performed in neutron imaging systems to visualize the effect of the impurity upon the water content and transport properties of fuel cell components. Post-experimental analysis includes trace level chemical analysis of fuel cell components and effluent water, electron microscopy and X-ray diffraction of the solid materials. We also experimentally determine impurity thermodynamic behavior (ion-exchange, proton 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. Last year we completed a long-term drive cycle test with hydrogen spiked with 10 ppb hydrogen sulfide. The degradation rate was the same as the control cell. However, both cells were using experimental membrane electrode assemblies that exhibited a higher performance loss than desirable. We obtained second generation fuel cell membrane assemblies from commercial suppliers and repeated the tests. An anode loading of 0.10 mg Pt/cm², cathode-0.20 mg Pt/cm², cycled in constant voltage mode between 0.85 V-0.6 V. After a pre-exposure run of 100 hours, the test cell received 10 ppb H₂S, for 1,000 hours.

Figures 1a, 1b, and 1c respectively show the baseline fuel cell performance at differing time intervals, the performance of an identical fuel cell with 10 ppb hydrogen sulfide and the electrochemical surface area of the electrodes after ~1,000 hours of operation. There was no significant difference in performance loss or electrochemical surface area loss between the control sample and the fuel cell fed with contaminated hydrogen thus supporting the earlier results.

The most prevalent sulfur containing air species is sulfur dioxide from fossil fuel combustion. The Fuel Cells sub-program targets call for a decrease in anode and cathode Pt loading. We evaluated the response of two 50 cm² fuel cells: a LANL-prepared Nafion® 212 fuel cell and a commercial fuel cell membrane with anode/cathode loading: 0.1/0.2 mg Pt/cm², to 100 ppb SO₂ in air (2.0 stoichiometry) injection at the cathode inlet past the humidification system (100% saturation). The fuel cell tests were performed at constant current 1 A/cm² for 500 hr. The fuel cell operating voltages at constant current decreased rapidly with approximately 200 mV of loss for both cells after sulfur dioxide injection was terminated. Unfortunately air concentrations of >100 ppb of sulfur dioxide are still common in industrial areas of the developing world.

Another common class of emission species from fossil fuel combustion systems is 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 long-term effects of 5 ppm NO₂ into an operating fuel cell similar to the one used for the sulfur dioxide experiments. Figure 2 illustrates the results of an over a 350-hour test. NO₂ reduces the fuel cell voltage by ~150 mV but reaches steady-state after about 50 hours of operation. The NO₂ is probably being reduced by hydrogen to ammonium cations; their concentration may be controlled by the ammonium ion-aqua ammonia equilibrium reaction.
Ammonia is also 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. A decrease in membrane acidity shifts fuel cell open circuit potential, decreases fuel cell electrocatalytic rates and reduces proton conductivity. We completed a rotating ring disk electrode (RRDE) study of the effect of ammonium ions on oxygen reduction on Pt-C catalysts. The study was carried out by measuring the oxygen reduction reaction (ORR) on carbon-supported platinum in 0.1 mol dm$^{-3}$ HClO$_4$ solutions containing different quantities of ammonium perchlorate. ORR current losses and increases in hydrogen peroxide generation were seen in two distinct potential regions, namely at $E > 0.7$ V vs reference hydrogen electrode (RHE) and at $E < 0.4$ V vs RHE. In order to better understand the observed effects, similar experiments were performed with solutions containing different concentrations of sodium perchlorate. Qualitatively similar, but different in magnitude effects were observed. It appears that the electrochemical oxidation of ammonia is responsible for the more significant effects of ammonium in the range of higher potentials, whereas the losses in the range of less positive potentials are mostly due to the coadsorption of ammonium and ClO$_4^-$.

A concentrated solution theory model was previously developed by us to describe the one-dimensional cation 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 cell. Increasing the current density deceases the proton concentration in the cathode leading to decreased proton transport to the oxygen reduction inhibiting fuel cell performance. However our cation poisoning experiments show impacts to performance in both electrokinetic and mass transport segments of the fuel cell polarization curve. We suspected that foreign cations might also changing the water concentration in the electrode layer. We verified these results by studying cation contaminated fuel cell membranes at the NIST neutron imaging beam line. Figure 3 shows the presence of cesium ions significantly changes the local water concentration.

The most likely effects of the impurities on the ORR kinetics are associated with changes in pH and water activity, which both depend on the cell operating conditions. Consequently, there is a need for a quantitative evaluation of these effects in situ.
Iridium oxide-coated electrodes have been used as pH sensors in various environments due to their chemical inertness and fast response and offer promise for pH measurements and indirect determination of cationic impurities in Nafion®. Iridium oxide (IrOx) can be deposited on a variety of substrates using three different techniques: electrochemical, sputtering, and high temperature oxidation. Gold and platinum were selected as substrates for the electrochemical deposition of the oxide. Gold was selected because of its inertness in a wide potential range and a common use as a substrate for iridium oxide-based pH sensors. On the other hand, platinum was tested to determine the viability of platinum interdigitated array electrodes for use in experiments aimed at monitoring local pH changes during oxygen reduction on Nafion®-coated platinum.

Iridium oxide layers were grown electrochemically employing various electrodes, including standard disk electrodes (1 mm diameter), ultramicroelectrodes (100 μm diameter), interdigitated electrodes (5 μm interdigitated bands separated by 5 μm gaps), and wire electrodes (1 mm diameter). The deposition was performed using a solution containing 4 mmol dm⁻³ IrCl₄⁻ and 40 mmol dm⁻³ H₂C₂O₄. The pH of the solution was adjusted to ~10.5 using solid K₂CO₃. The electrode potential was cycled at a rate of 100 mV s⁻¹ between +0.6 V and -0.75 V vs. Ag/AgCl (3 M NaCl) reference electrode. The rate of growth of iridium oxide under such conditions was equivalent to ~3 monolayers per 100 potential cycles.

The films grown electrochemically on platinum exhibited approximately linear potential (E) vs. pH characteristics between pH = 1 and pH = 3.7. The slopes of E vs. pH plots were lower than 60 mV per 1 pH unit and the response time was very short, in a sub-second to a few seconds range. While the fast response of the sensors utilizing electrochemically grown films made them an excellent choice for real time monitoring pH changes during oxygen reduction on platinum interdigitated electrodes, their other characteristics made them unsuitable for this application. Specifically, the films were very permeable which could lead to the participation of platinum in electrochemical equilibrium and, consequently, to a mixed potential. Despite the interference of redox agents with the electrochemical equilibrium of electrochemically grown IrOx films, iridium oxide sensors offer a great promise for the determination of cationic impurities in polymer electrolyte fuel cells.

In pursuit of ways to mitigate the problem of sensitivity of the sensors to oxygen, we employed chemical oxidation of iridium metal in molten lithium...
carbonate. The process produces thick and compact layer of black iridium oxide. The initial response of the sensor prepared this way upon immersion in acidic aqueous medium is relatively slow most likely because the equilibration is associated with a slow penetration of the initially dry film by water. Upon film hydration, the potential of the sensor was found to be virtually insensitive to oxygen and hydrogen in solution. Moreover, the response time of the hydrated film was significantly improved. The potential vs. pH dependence for the hydrated film is described by an excellent linear relationship with a slope of 42 mV as shown in Figure 4. Optimized sensors of this type will be used to monitor changes in pH (and concentration of cationic impurities) inside the membrane of an operating fuel cell.

Conclusions and Future Directions

- Low concentrations 10 ppb hydrogen sulfide do not appear to affect durability of current generation fuel cell MEAs.
- 100 ppb of SO$_2$ in air substantially decreases fuel cell performance of low-loading thin-ionomer polymer electrolyte fuel cells.
- NO$_2$ in air decreases fuel cell performance:
  - Fuel cells reach a steady-state equilibrium at constant concentration exposure.
- NH$_4^+$ ions hamper oxygen reduction on Pt-C catalysts in acid environments.
- The impurity cation species type is important in determining local water of hydration concentrations.

**FY 2010 Publications**

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

- It was confirmed that the effects of CO₂, C₂-C₇ paraffins, HCOOH and N₂ on Nafion® conductivity and on Pt for H₂ activation are insignificant.
- A simple acid catalyzed reaction (esterification) was used to quantitatively predict conductivity of a contaminated membrane and/or catalyst layer under typical fuel cell conditions and the predicted values agree well with experimental data.
- The effects of ammonium distribution on the conductivity of Nafion® membrane in the liquid and gas phase were studied. In the gas phase, the conductivities of uniformly poisoned membranes considerably differed from those of non-uniformly poisoned membranes having equivalent ammonium concentrations.
- The surface concentration of hydrogen on Nfn-Pt/C (Nafion®-loaded Pt/C) under fuel cell operation conditions was obtained using H₂/D₂ switching and it was found that:
  - Hydrogen activation occurred only on Pt.
  - Transport of protons between the sulfonic sites of Nafion® and the Pt particles was extremely fast.
- Humidity has been determined to have a minimal effect on the apparent activation energy of H₂ activation on Pt/C under typical fuel cell conditions. However, the humidity significantly influences the degree of CO poisoning on Nfn-Pt/C and the final rate of H₂ activation.
PEM fuel cell studies on the effects of 18 ppm tetrahydrofuran (THF) found ~40% loss in performance and full recovery once THF was removed from the fuel stream.

Investigation of long-term NH₃ poisoning at 0.1 ppm (maximum International Organization for Standardization [ISO] specified level) found no appreciable degradation at 60°C and 80°C.

CO poisoning experiments were performed to study the performance decay at ISO limits. Even a small concentration of CO (0.2 ppm) led to 10% performance decay in a few hours, but this could be recovered by electrochemical oxidation.

CO poisoning experiments were also performed to correlate and compare results from PEM fuel cell tests at SRNL to the results from H₂ activation on Nfn-Pt/C experiments at Clemson. The results match well.

**Results**

The investigation of the effects of H₂O on the surface hydrogen coverage and dissociation on Pt/C under fuel cell operation conditions suggests that:

1) in the absence of a poison like CO, equilibrium is still reached for H₂ activation on Nfn-Pt/C at 80°C in the presence of water vapor; 2) humidity has minimal effect on E_r for H₂ activation on Nfn-Pt/C in 10 ppm of CO at typical fuel cell conditions; 3) however, the humidity significantly influences the degree of poisoning by CO of Nfn-Pt/C and the final rate of H₂ activation.

Esterification was used as a diagnostic tool to investigate the proton availability of Nafion® components of a PEM fuel cell. It was found that a simple acid catalyzed reaction (esterification) can be used to quantitatively investigate the number of proton sites in a Nafion® membrane and can be further used to predict conductivity of a contaminated membrane under typical fuel cell conditions, as shown in Figure 1. In addition, this methodology can be used to determine the effects of impurities on the number of proton sites in a catalyst layer of a PEM fuel cell, which can be further used to predict the conductivity of the catalyst layer.

With respect to the effects of impurities on the ionic conductivities of Nafion® membranes, the effects of NH₄⁺ distribution in the liquid and gas phase were studied using physically assembled membranes with known ammonium compositions. Under typical fuel cell operations, the conductivities of non-uniformly poisoned membranes were ca. 1.07–1.86 times larger than those of uniformly poisoned membranes, depending on humidity, contamination level, and ammonium ion distribution.

The effect of Nafion® on H₂ activation on Pt was studied. It was found that while the impregnation of...
30 wt% Nafion® on Pt/C has dramatic effects on the physical characteristics of Pt/C, such as a reduction in Brunauer-Emmett-Teller surface area from 170 m² (g.cat)⁻¹ to 37 m² (g.cat)⁻¹, the overall effect of the Nafion® on the adsorption capability of hydrogen and CO by Pt is small. However, a clear blocking of cyclopropane from reacting during cyclopropane hydrogenolysis, a structure sensitive reaction, on a large portion of surface Pt sites by the Nafion® can be observed. This inhibition of cyclopropane by Nafion® appears to be due, mainly, to steric hindrance rather than the direct blocking of significant numbers of surface Pt atoms.

The DOE provided conditions for desired experiments at low levels of NH₃ and wanted 1,000-hour tests to be completed as soon as possible. SRNL worked on the required ammonia tests with the provided GORE membrane electrode assemblies. A baseline and 0.1 ppm poisoning at 60°C or 80°C and 50/50 percent relative humidity (RH) with an Ion Power MEA to determine the impact of NH₃ at the ISO limit were performed. As shown in Figure 2, no appreciable degradation from the introduction of NH₃ at the ISO specified level was observed over 800 hr.

THF was used to characterize the performance effects that hydrocarbons can have on fuel cell performance since THF is a popular solvent used in many chemical synthesis which include hydrogen storage materials. Approximately 40% loss in performance was observed within 1 h after 18 ppm THF was injected to the feed as indicated in Figure 3. It also can be seen that full recovery was observed as soon as THF was removed from the fuel stream.

SRNL is finishing the runs with CO poisoning experiments at the ISO limits and suggested new lower limits. It was found that even a small concentration of CO (0.2 ppm) led to 10% performance decay in a few hours (Figure 4a). Electrochemical oxidation after CO poisoning was able to successfully remove all traces of CO and the MEA performance was recovered (Figure 4b).

CO poisoning experiments were also performed under similar conditions at SRNL and Clemson to correlate and compare results from PEM fuel cell tests at SRNL to the results from H₂ activation on Nfn-Pt/C experiments at Clemson. The cyclic voltammetry data before and after PEM poisoning runs with CO were analyzed to characterize the number of electrocatalyst active sites poisoned. It was found that the electroactive surface areas of Pt obtained with the CO desorption peak matches closely with those obtained with the hydrogen desorption peaks. Also, the electroactive surface area of Pt was reduced with CO poisoning at 60°C and 80°C. However, after the cell was left at open circuit and 25°C with 8 ppm CO the electroactive area was recovered.

![Figure 2](image-url)

**Figure 2.** H₂/Air potentiostatic polarization baseline (a) without NH₃ and (b) in the presence of 0.1 ppm NH₃ for a GORE MEA with 0.1/0.4 mg/cm² catalyst loadings at 80°C and 50%/50% RH.

### Conclusions and Mitigation Strategies

Major conclusions are covered in the Accomplishments section.

To date, the following preliminary impurity mitigation strategies can be proposed based on the findings of this project:

- Fuel cells can tolerate up to 0.1 ppm of NH₃ (maximum ISO specified level) for long periods of time.
- Use of higher percent RH results in a smaller decrease in conductivity with NH₃ poisoning. Thus, a higher percent RH is recommended for fuel cell operation to increase the performance and lifetime when trace amounts of NH₃ are present in the fuel.
- Since during CO poisoning, CO does not fully cover all the Pt sites regardless of CO concentration, in order to maintain better fuel cell performance, the use of higher loadings of Pt is recommended if better CO-resistant catalysts are not available.
- Preliminary data suggest that in the presence of CO, lower humidity appears to decrease the effect.
Obviously, the actual materials and operational conditions chosen for use in a fuel cell must be determined by an optimization of material properties, operation conditions, possible mitigation strategies to minimize the effect of impurities, and desired fuel cell performance.

The project is on track for completion of the major objectives of this research in 2011.

**FY 2010 Publications/Presentations**

**Publications**


2. “Esterification as a Diagnostic Tool to Predict Proton Conductivity Affected by Impurities on Nafion Components for PEMFCs,” *Journal of Power Sources* 195 (2010) 3416-3424 (Kitiya Hongsirikarn, Xunhua Mo, and James G. Goodwin, Jr.).


**Presentations**


Objectives

- Identify the specific impurities and impurity families and their concentrations present in the fuel.
- Develop analytical chemistry protocols to detect the fate of contaminating species within fuel cells.
- Determine through controlled laboratory experiments and literature the main drivers for decay.
- Develop 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 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

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, 5,000 hours based on a test protocol issued by DOE in 2007.
- By 2015, 5,000 hours based on a test protocol issued by DOE in 2007.

Accomplishments

Hydrocarbon Testing

- Completed testing of the most critical hydrocarbon species likely to be present in hydrogen fuel streams including: formic acid, formaldehyde, methane, ethane, ethylene and acetaldehyde.
- Developed analytical procedures and mixing protocols for evaluating concentrations of acetaldehyde, formic acid, and formaldehyde in the fuel stream.

Other Impurities

- Evaluated the effects of several likely concentrations of ammonia on polymer electrolyte fuel cells (PEFCs) and characterized its effects on membrane integrity in the ammonium form.
- Characterized the effects of methyl chloride on PEFC performance.

Introduction

PEFCs 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 membrane electrode assemblies (MEAs). One of the causes for this is the introduction of impurities into the fuel stream that impacts the functionality of ion exchange groups within the electrolyte, degrades catalyst activity, and function causing voltage to degrade.
The technical issues addressed center around the identification of impurity 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 and procedures for contaminant testing of PEFCs. These studies provide the background and basis for the initiation of our research.

**Approach**

This project is focused on the experimental determination of the effects of key impurities on the performance of PEFCs. Experimental data collected from test protocols will be leveraged to create mathematical models that predict performance of PEFCs exposed to specific impurities. These models will be validated through laboratory experimentation and will be utilized to develop novel technologies for mitigating the effects of impurities on fuel cell performance. The effects of cationic impurities on the fundamental physio-chemical properties of perfluoroionomer membranes are also being evaluated. Results will be publicly disseminated through papers, conference presentations, and other means.

**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. We have focused our efforts on the evaluation of 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. Studies have focused on the evaluation of gaseous impurities, volatile liquids and less volatile liquids. Testing of many of the less volatile liquids requires the use of a saturator apparatus (Figure 1) that we developed specifically for these experiments.

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 I. 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.

**Acetaldehyde** - The effect of acetaldehyde (CH₃CHO) on cell performance was investigated at an impurity concentration of 30 ppm. Cell performance immediately dropped with 30 ppm acetaldehyde in the fuel stream. At the conclusion of the contaminant test, recovery was attempted using pure H₂ as fuel to run the fuel cell, and cell performance was restored to pre-contaminant injection performance. Figure 2a provides these test results. Our conclusion is that a

![FIGURE 1. Gas Mixing Set-Up for Liquid Hydrocarbons](image)

**TABLE 1. Test Cell Definition**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Early</th>
<th>Intermediate</th>
<th>Recent</th>
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</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Nafion² 212</td>
<td>Nafion² 212</td>
<td>Gore PRIMEA²</td>
</tr>
<tr>
<td>Pt Loading (mg/cm²)</td>
<td>0.4/0.2</td>
<td>0.4/0.4</td>
<td>0.1/0.4</td>
</tr>
<tr>
<td>Anode Type</td>
<td>50% Pt on C</td>
<td>50% Pt on C</td>
<td>50% Pt on C</td>
</tr>
<tr>
<td>Cathode Type</td>
<td>50% Pt on C</td>
<td>50% Pt on C</td>
<td>50% Pt on C</td>
</tr>
<tr>
<td>MEA Manufacturer</td>
<td>Ion Power</td>
<td>Ion Power</td>
<td>Gore</td>
</tr>
<tr>
<td>GDL</td>
<td>SGL 10BB</td>
<td>SGL 10BB</td>
<td>SGL 25BC</td>
</tr>
<tr>
<td>Cell Active Area (cm²)</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardware Manufacturer</td>
<td>Fuel Cell Technologies</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A - anode; C - cathode; GDL - gas diffusion layer

**TABLE 2. Definition of Major Test Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>i</th>
<th>ii</th>
<th>iii</th>
<th>iv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry (A/C)</td>
<td>1.3/2.0</td>
<td>2.0/2.0</td>
<td>2.0/2.0</td>
<td>1.2/2.0</td>
</tr>
<tr>
<td>Back Pressure (A/C₂ psig)</td>
<td>25/25</td>
<td>25/25</td>
<td>25/25</td>
<td>7/7</td>
</tr>
<tr>
<td>RH (A/C, %)</td>
<td>100/100</td>
<td>100/100</td>
<td>100/75</td>
<td>75/25</td>
</tr>
<tr>
<td>Cell Temperature (°C)</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Flow Rate (A/C)</td>
<td>Commensurate with current density</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RH - relative humidity
A moderate effect on cell performance was found during this impurity test. Further tests are being conducted to determine the mechanism.

**Formaldehyde** - Testing of the effect of formaldehyde (HCHO) on cell performance was investigated at impurity concentrations of 1 ppm and 5 ppm. No significant influence on cell performance was found during these lower concentration impurity tests (Figures 2b and 2c).

**Ethylene** - Testing of the effect of ethylene (C₂H₄) on cell performance was investigated at impurity concentrations of 5%. No significant effect on cell performance was observed (Figure 2d).

**Formic Acid** - Testing of the effect of formic acid (HCOOH) on cell performance was investigated at impurity concentrations of 2 ppm and 100 ppm. No significant effect on cell performance was found during the 5 ppm impurity tests (Figure 2e). Some degradation was found in the 100 ppm formic acid test (Figure 2f). Cyclic voltammetry (CV) scans performed at 20 mV/sec before and after the impurity tests showed that electrochemical area of the cathode decreased, signifying that HCOOH has a negative effect on the cathode catalyst. Similar scans were also performed every 20 hours (Figure 3a) during contamination and recovery periods to provide detail of the mechanism for contamination on the cathode. Pure nitrogen was
fed to the cathode at 250 sccm, while HCOOH/H\textsubscript{2} was fed to the anode at 250 sccm. The CV scans indicate a decrease in H\textsubscript{2} absorption peaks and an oxidation peak at 0.6 V which could be caused by absorbents on Pt surface. An individual CV scan is shown in Figure 3b. Each scan consists of four cycles. In the first CV cycle, the hydrogen absorption peak nearly disappeared. The Pt surface seems to be covered by absorbents (peaks at 0.4 V and 0.6 V that are not seen with pure H\textsubscript{2}). Absorbents are oxidized around 0.4 V and 0.6 V in the 1st cycle. In the next three cycles, recovery of H\textsubscript{2} absorption peak is observed, but evidence of surface coverage still exists. Mechanistic studies to evaluate the specific effect of formic acid on cell components using analytical tools, rotating disk electrodes and hydrogen pump experiments are underway.

**Methyl Chloride** - Testing of the effect of methyl chloride (CH\textsubscript{3}Cl) on cell performance was investigated at impurity concentrations of 1 ppm and 19 ppm. No significant effect on cell performance was found during these impurity tests (Figures 2g and 2h).

Testing is summarized in Table 3. Testing has indicated little effect of simple hydrocarbon species on fuel cell performance; however, more complex species do seem to affect performance.

**Cationic Impurities** - The effect of ammonia contamination on PEFCs was investigated with pseudo-reversible hydrogen electrodes. It was found that NH\textsubscript{4}\textsuperscript{+} affects the anode causing an increase in the overpotential in a hydrogen pump cell. Figure 4a shows the overpotential variations of the anode and the cathode respectively during contamination and recovery. 50 ppm NH\textsubscript{3} in H\textsubscript{2} can significantly affect the electrochemical kinetics on the electrodes. The initial drop of the overpotential is due to the poisoning effect of NH\textsubscript{4}\textsuperscript{+} on pseudo-reversible hydrogen electrodes. In a fuel cell, NH\textsubscript{4}\textsuperscript{+} was also found to affect the anode, however, the anode performance loss was less than on the cathode (Figure 4b).

**Conclusions and Future Directions**

**Conclusions**

- Simple hydrocarbons including methane, ethane, ethylene and acetaldehyde, particularly in low concentrations do not significantly affect fuel cell performance.
- Simple halogenates such as methyl chloride in low concentrations do not affect performance
- Acetaldehyde impurities show some effect on performance at higher concentrations.
- Formic acid impurities affect performance at higher concentrations likely due to adsorption on the electrode surface as well as the formation of reaction byproducts such as CO.
- Testing has shown both anode and cathode performance impacts of ammonia.

**Future Directions**

- Mechanistic evaluation of formic acid and acetaldehyde to support International Organization for Standardization standard development.
- Finalizing testing on aromatic hydrocarbons.
- Study the impact of catalyst ageing on sensitivity to hydrocarbon contamination.
- Finalizing modeling of impurity effects.
- Developing mitigation techniques for key impurities that show an impact on cell performance.

**FY 2010 Publications/Presentations**

TABLE 3. Compilation of Test Data from Impurity Tests

<table>
<thead>
<tr>
<th>#</th>
<th>Contaminant</th>
<th>I mA/cm²</th>
<th>RH (%) (A/C)</th>
<th>Pressure (psig) (A/C)</th>
<th>Stoich (A/C)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 ppm CH₄</td>
<td>200</td>
<td>100 / 100</td>
<td>25 / 25</td>
<td>1.3 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>2</td>
<td>100 ppm CH₄</td>
<td>600</td>
<td>100 / 100</td>
<td>25 / 25</td>
<td>1.3 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>3</td>
<td>5% CH₄ or 5% N₂</td>
<td>600</td>
<td>100 / 100</td>
<td>25 / 25</td>
<td>1.3 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>4</td>
<td>100 ppm CH₄</td>
<td>800</td>
<td>100 / 100</td>
<td>25 / 25</td>
<td>1.3 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>5</td>
<td>5% C₂H₆</td>
<td>600</td>
<td>100 / 100</td>
<td>25 / 25</td>
<td>1.3 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>6</td>
<td>5% C₂H₂</td>
<td>800</td>
<td>100 / 100</td>
<td>25 / 25</td>
<td>1.3 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>7</td>
<td>30 ppm CH₃CHO</td>
<td>800</td>
<td>100 / 100</td>
<td>25 / 25</td>
<td>1.3 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>8</td>
<td>100 ppm CH₃CHO</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>9</td>
<td>100 ppm HCOOH</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>Significant degradation</td>
</tr>
<tr>
<td>10</td>
<td>50 ppm HCOOH</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>Some degradation</td>
</tr>
<tr>
<td>11</td>
<td>2 ppm HCOOH</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>12</td>
<td>50 ppm HCOOH</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>Some degradation</td>
</tr>
<tr>
<td>13</td>
<td>2 ppm HCOOH</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>14</td>
<td>1 ppm HCHO</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>15</td>
<td>1 ppm HCHO</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>16</td>
<td>2 ppm HCOOH</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>17</td>
<td>1 ppm CH₃Cl</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>18</td>
<td>19 ppm CH₃Cl</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>Some degradation</td>
</tr>
<tr>
<td>19</td>
<td>5 ppm HCHO</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>20</td>
<td>5 ppm HCHO</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>21</td>
<td>5% C₂H₆</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>No significant degradation</td>
</tr>
<tr>
<td>22</td>
<td>30 ppm CH₃CHO</td>
<td>800</td>
<td>100 / 75</td>
<td>25 / 25</td>
<td>2.0 / 2.0</td>
<td>Degradation at beginning</td>
</tr>
<tr>
<td>23</td>
<td>1% C₂H₂</td>
<td>1000</td>
<td>75 / 25</td>
<td>7 / 7</td>
<td>2.0 / 2.0</td>
<td>Degradation at beginning</td>
</tr>
</tbody>
</table>

FIGURE 4. (a) The Overpotentials Versus Reversible Hydrogen Electrode Measured During NH₃ Contamination and Recovery of a 25 cm² MEA; (b) Contamination of 25 cm² MEA With 50 ppm NH₃ and Recovery Process. (The cell was operated at 400 mA/cm² at 60°C with relative humidity at 50% NH₃ flow was introduced at 20 hours and shut down at 36 hours, followed by pure H₂.)


V.C.4 Effect of System and Air Contaminants on PEMFC Performance and Durability

Objectives

Our overall objective is to decrease the cost associated with system components without compromising function, fuel cell performance, or durability. Our specific project objectives are:

- Identify and quantify system derived contaminants.
- Develop ex situ and in situ test methods to study system components.
- Identify severity of system contaminants and impact of operating conditions.
- Identify poisoning mechanisms and investigate mitigation strategies.
- Develop models/predictive capability.
- Develop material/component catalogues based on system contaminant potential to guide system developers on future material selection.
- Disseminate knowledge gained to community.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost

Technical Targets

This project focuses on determining the effect of system components on fuel cell performance and durability. Insights gained from these studies will be applied toward the development of a catalogue of system component materials that help meet the following DOE 2010 targets:

- Cost: $30/kW for transportation, $750/kW for stationary
- Lifetime: 5,000 hours for transportation, 40,000 hours for stationary

Accomplishments

- Established a standard set of experimental protocols for analysis, including leaching, cyclic voltammetry, and analytical characterization protocol(s).
- Performed leachant experiments on 10 polymeric material sets.
- Evaluated and applied multiple techniques for analyzing leachants (e.g., gas chromatograph mass spectroscopy [GCMS], Fourier transform infrared-attenuated total reflectance [FTIR-ATR], inductively coupled plasma [ICP], pH, conductivity, total organic content [TOC], contact angle).
- Identified leachants via GCMS for the ten polymeric materials studied.
- Performed electrochemical tests on leachants to determine effect on electrocatalysts and recovery after exposure.

Introduction

Cost and durability issues of proton exchange membrane fuel cell (PEMFC) systems have been challenging in the fuel cell industry. The cost of the balance of plant (BOP) ($51/kW in 2010 [1]) system has risen in importance with decreasing fuel cell stack
lowering the cost of PEMFC system components requires the understanding of the materials used in the system components and the contaminants that derive from them, which have been shown to affect the performance and durability of fuel cell systems. Unfortunately, there are many possible contamination sources from system components [3-5]. Currently deployed high-cost, limited-production systems are not limited to low-cost materials for system components. In order to make fuel cell systems commercially competitive, the cost of the BOP components needs to be reduced without sacrificing performance and durability. Fuel cell durability requirements limit the performance loss due to contaminants to at most a few mV over required lifetimes (thousands of hours), which means close to zero impact for system contaminants.

As catalysts loadings decrease and membranes are made thinner, both are current trends in automotive fuel cell research and development, fuel cells become even more susceptible to contaminant effects. In consumer automotive markets, low-cost materials are typically required but lower cost typically implies higher contamination potential. The results of this project will provide the information necessary to help the fuel cell industry make informed decisions regarding cost of specific materials versus the potential contaminant impact on fuel cell performance and durability.

**Approach**

Our goal is to provide an increased understanding of fuel cell system contaminants and help provide guidance in the implementation, and where necessary the development, of system materials that will help enable fuel cell commercialization. While much attention has been paid to air and fuel contaminants, system contaminants have received very limited attention publicly and very little has been publicly reported [6-9]. Our approach is to perform parametric studies of the effects of system contaminants on fuel cell performance and durability to identify poisoning mechanisms, recommend mitigation strategies, develop predictive modeling, and disseminate material catalogues that benefit the fuel cell industry in making cost-benefit analyses of system components. We will identify and quantify potential contaminants derived from stack/component fabrication materials and quickly screen the impact of the leachants on fuel cell catalyst and membrane via ex situ tests. Model compounds capable of replicating the deleterious impact of system-based contaminants are also studied. Developing standard test protocols to evaluate materials is important as this approach will allow for broader studies to be performed. Furthermore, information obtained from ex situ methods will be validated with in situ testing.

Our system materials selection is based on properties such as exposed surface area, total mass/volume, fluid contact, function, cost, and performance implications. Current material prioritization to study is based on perceived impact of potential system contaminants (based on GM internal knowledge): structural materials, coolants, elastomers for seals and (sub)gaskets, assembly aids (adhesives, lubricants), hoses, membrane degradation products, bipolar/end plates, ions from catalyst alloys. Our project has a strong polymer focus, as much of the system is polymer-based. Furthermore, our approach is to study commercially available, commodity materials. These materials are generally developed for other applications, where common additives/processing aids may not be a concern, but may present problems for fuel cells.

**Results**

We investigated 10 commercially available polymers (see Table 1) for their potential impact as system contaminants in fuel cell systems. These 10 polymeric materials underwent leaching protocols for two months to derive potential contaminants from the parent materials into solution. The leaching protocols were provided to the group by GM prior to the kick-off of the project. We tested three different leaching conditions (deionized water, 0.1 M H₂SO₄, and 0.1 M H₂SO₄ + 3% H₂O₂ at 80°C) and found that soaking in deionized water was the best leaching condition as it reflected the most realistic fuel cell condition. Acid solutions were eliminated as test conditions as they were found to be excessively aggressive compared to a fuel cell environment.

We evaluated various techniques for analyzing leachants. These include GCMS, FTIR-ATR, ICP pH, conductivity, TOC, contact angle, and electrochemistry. The results of the GCMS and electrochemistry are summarized below.

The leachant solutions derived from soaking the ten polymeric materials were analyzed via FTIR-ATR for functional groups and by GCMS to determine the identity of the leachants in solution for each polymer. TOC was measured in the final solutions at the end of the trials to determine quantitatively the total amount of leachant from the solid that made it into solution. Table 1 summarizes the starting materials, the TOC values in parts per million (ppm), and the predominant leachants identified for each sample. Due to the number of materials tested, discussion will be limited to styrene-butadiene-rubber (SBR). SBR was chosen because it was a good example to illustrate the type and number of contaminants that leached from the material as well as the effect of contaminants on catalysis.

SBR is synthetic polymer, derived from styrene and butadiene and an alkyl mercaptan chain transfer agent,
and is widely used in car tires. Identified contaminants, aniline and other thiol-based aromatics, seem reasonable given the chemical structure of the polymer and possible additives. TOC values for SBR rubber show final amounts of carbon at levels of 314.7±0.3 ppm. Aniline was the major leachant identified, and was present at levels nearly an order of magnitude higher than other identified constituents. Calculated areas show that it comprised 80% of the total leachant.

Cyclic voltammetry (CV) is extremely useful to quickly screen changes in electrochemical response of Pt catalysts in the presence of leachants. Two types of experiments were used: a quick screen, and a recovery screen (protocols provided by GM). Figure 1 shows a baseline polycrystalline Pt CV in leachant-free electrolyte solution compared to the response of this electrode with increasing amounts of SBR rubber leachant added to the solution. The CV shows that SBR rubber leachant decreases the active surface area, and is oxidized at high potential. The presence of the leachant reduces the extent of Pt oxidation as witnessed by the decreased charge associated with oxide reduction. After removing the electrode from the leachant containing solution and testing again in leachant-free electrolyte, it was observed that the leachants impact on electrochemical response was not permanent (Figure 2).

**Conclusions and Future Directions**

- Leaching experiments should be performed in deionized water for most BOP materials. Acid solutions are not representative of the state-of-the-art fuel cell system and are too aggressive for many materials.
- Ten polymeric sealant materials were characterized with GCMS, FTIR-ATR, pH, conductivity, and TOC. Most of the materials analyzed leached out a number of organic compounds common in the

<table>
<thead>
<tr>
<th>Material</th>
<th>TOC (ppm)</th>
<th>Predominant Leachants Identified via GCMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized Water Control</td>
<td>N/A</td>
<td>Hexamethyldisiloxane-column bleed</td>
</tr>
<tr>
<td>Acrylic Buna-N Blended Rubber</td>
<td>304.7±0.3</td>
<td>N,N Dibutyl formamide</td>
</tr>
<tr>
<td>Aramid/Buna-N Gasket, Green</td>
<td>238.4±0.3</td>
<td>Aniline</td>
</tr>
<tr>
<td>Abrasion-Resistant SBR Rubber, Red</td>
<td>314.7±0.3</td>
<td>Aniline</td>
</tr>
<tr>
<td>Weather-Resistant EPDM Rubber, Black</td>
<td>N/A</td>
<td>2-Methoxythiobenzamide</td>
</tr>
<tr>
<td>FDA-Compliant Silicone Rubber, Black</td>
<td>86.9±0.8</td>
<td>Dimethylsilanediol</td>
</tr>
<tr>
<td>Corrosion-Resistant Viton® Fluoroelastomer</td>
<td>722.6±0.9</td>
<td>Triphenylphosphine oxide</td>
</tr>
<tr>
<td>Amber Polyurethane Sheet</td>
<td>653.0±1.4</td>
<td>1,2-Ethandiol</td>
</tr>
<tr>
<td>M-Strength Neoprene Rubber, Black</td>
<td>1,347±0.0</td>
<td>4,4-Methylenebis-benzoxanemine</td>
</tr>
<tr>
<td>Silicone Gasket</td>
<td>294.6±0.3</td>
<td>dimethylsilanediol</td>
</tr>
<tr>
<td>Teflon®-coated fiberglass, Furon®</td>
<td>6.92±0.9</td>
<td>x</td>
</tr>
</tbody>
</table>

EPDM = ethylene propylene diene monomer

**TABLE 1.** Identified Leachants and TOC Values for Ten Commercially Available Polymers Tested and Deionized Water Control

**FIGURE 1.** Effect of SBR rubber leachant amount on Pt catalysis in 0.1 M HClO₄ solution. Cell volume was 150 ml. Scanning rate was 20 mV/s.

**FIGURE 2.** Comparing the baseline Pt CV in 0.1 M HClO₄, Ar purged, 20 mV/s with the CV obtained after a contaminated Pt electrode was rinsed with water and immersed in fresh electrolyte solution. The Pt electrode was contaminated with SBR rubber leachant.
synthesis and processing of the materials, as was expected.

- Based on CV results, extracted molecules from SBR rubber are a potential source of performance loss in fuel cells when operated at low potentials. At high potentials when the exposure to the contaminant was removed, changes in the electrochemical response were found to be recoverable.
- We have selected to focus our studies on polymeric structural materials because they have the highest perceived impact of potential system contaminants.
- We will continue establishing standard ex situ and in situ testing protocols to evaluate system contaminant materials.
- We will benchmark equipment and testing methods among all project partners.
- We will establish correlations between analytical screening of extract solutions, CV results, and fuel cell performance loss.

**FY 2010 Publications/Presentations**


**References**

V.D.1 New Polyelectrolyte Materials for High Temperature Fuel Cells

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  Jeff Reimer (Lawrence Berkeley National Laboratory)
• James Boncella (Los Alamos National Laboratory)

Project Start Date:  March 1, 2007
Project End Date:  February 28, 2011

Objectives

- Develop durable water-free membrane materials with properties that meet the 2015 DOE targets as set out in the Multi-Year Research and Development Plan:
  - Conductivity: 0.1S/cm at operating temperatures ($\leq$120\degree C) and inlet water vapor partial pressures $<1.5$ kPa.
  - Durability with cycling $>5,000$ hours at $>80$\degree C.
  - Oxygen and hydrogen cross-over currents $\leq$2mA/cm\textsuperscript{2}.
  - Durable membrane electrode assemblies (MEAs) with rated power at 1,000 mW/cm\textsuperscript{2} 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

Technical Targets

- Development of membranes that contain tethered heterocyclic bases (imidazole, triazole), which do not require added water to achieve adequate conductivity and can achieve performance with only the presence of the water produced by the fuel cell reaction: 0.1 S/cm (120\degree C), 0.07 S/cm (20\degree C) and 0.01 S/cm (-20\degree C) at relative humidity (RH) values between 25 and 50\%.
- Achieved 0.005 S/cm at 120\degree C under bone dry conditions and 0.01 S/cm at 25\% RH.
- Conductivities at ambient temperatures ($10^{-2}$ S/cm >80\degree C) are too low to be practical without a high degree of morphological control to provide connectivity through the membrane.
- Demonstrated that morphological control to achieve high connectivity through the membrane is possible through use of phase separating polymers (block and random copolymers) but is hard to maintain.
- Plasticization of the polymers by water can lead to significantly improved conductivities but at a potential cost of loss of connectivity.
- The presence of imidazole and other heterocyclic bases in the polymers leads to increased conductivity at low water content (RH 25-50\%) and to significantly lower water uptake in some cases.
- Three-dimensional (3-D) modeling shows that loss of connectivity can be compensated for by multiple pathways through the membrane.

The provision of membranes and MEAs that need no humidification provides significant system simplifications and large cost advantages over conventional materials

Accomplishments

- It has been determined that solid state membranes with imidazole as proton solvating solvent cannot achieve 0.1 S/cm without added mobile solvents such as water unless a high degree of connectivity through the membrane can be achieved.
• It has been shown that the presence of imidazoles tethered to the polymer backbones improved the conductivities of sulfonated polyetherpolysulfones and poly fluoro sulfonic acid (PFSA) polymers at low water content (25% RH). It has been further shown that presence of bases affects the water uptake and can be used to control swelling as well as to improve conductivity.
• Synthesis of polymers with tethered imidazoles has been achieved with several different polymer backbones – polystyrene, polyether polysulfone, and polyfluorinated ethylene with different side chain lengths.
• Studies of proton conducting ionic liquids in polymer matrices show that they support Grothuss transport and morphological control in block copolymers can maintain high conductivities at lower temperatures.
• Composite electrode and MEA fabrication methods have been developed for hydrocarbon polyelectrolytes in anticipation of the availability of imidazole-containing material for testing.

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 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 (FY) 2008-2009 annual reports, 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 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 crossover. 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(a) shows a schematic of the type of polymer structure that appears to be desirable to achieve fast proton transport through the membrane. Results obtained in FY 2009 on ionic liquid models and on synthesized polymers with tethered imidazoles indicate that the nanoscale morphology shown is necessary to promote the Grothuss 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. Figure 1(b) shows how the pore structure could be arranged on the microscopic scale in order to provide connectivity across the membrane. The molecular-level mechanism of
proton transport 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. In previous years of this project the low activation energy for proton transport associated with the Grotthuss mechanism has been inferred from the temperature dependence of the conductivity. Pulsed field gradient spin-echo nuclear magnetic resonance measurements on ionic liquid samples prepared from imidazole and bis(trifluoromethylsulfonyl)imide have indicated faster diffusion of the positively charged protons in the liquid than diffusion of the other solvent molecules. These results confirm the reports of Watanabe et al. [6] and support the proton hopping mechanism of proton transport. Experiments are now underway to examine the effect of a block co-polymer matrix on the mechanism to observe whether ordering may result in more efficient operation of the proton hopping mechanism.

The phase separation is best promoted by use of block copolymers with appropriate backbones. Figure 1(c) shows two examples of the polymer structures that have been prepared for this purpose (polystyrene and polyether polysulfone) and which are under continuing study. Also shown are two fluorinated polymers which can be used to immobilize heterocyclic bases. The imidazole group (e.g. Z in Figure 1(c)) 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 attachment of the imidazole through positions other than the nitrogen is not trivial and generally requires the use of protecting groups on the nitrogen which can be cleanly removed once the polymer is prepared. However, some success has been obtained with syntheses that avoid the use of protecting groups. The use of triazoles has also been explored to avoid some of the synthetic difficulties involved with the imidazoles although in general triazoles have shown slightly lower conductivity that imidazole.

Figure 2(a) shows the results of conductivity measurements made on polymers that contain the imidazole tethered in the 2-position as shown by the structure of the polymer denoted IMBVCl. The polymers are blended with Nafion® where the
numbers 4-1 represent the ratio of the imidazole molecules to the acid groups in the blend. The unblended, neat polymer exhibits very low conductivity as expected since the self-dissociation of the imidazole does not provide a sufficient concentration of charge carriers. Provision of acid groups from the Nafion® results in higher conductivity under dry conditions. Measurements performed under 25% and 50% RH show increasing conductivity as the water content is increased although they are still too low to be practical. The shape of the conductivity curve as a function of temperature is very characteristic of ion transport control by segmental motion of the polymer indicating that no proton hopping occurs in this case. Dynamic mechanical analysis (DMA) of the polymer blends indicate that considerable plasticization of the polymers occurs which results in inefficient phase separation. This hypothesis remains to be confirmed with small angle X-ray scattering measurements.

Figure 2(b) shows the effect of humidity on the through-plane conductivity of 5M PFSA doped with imidazole. The undoped material measured at 25% RH shows a low dependence upon temperature that is characteristic of proton hopping. While the low ratio of imidazole to acid (1:1) blend has a poor conductivity even in the presence of water, the more highly doped blends (1:4 and 1:8) show better conductivity at these low RH values indicating that combinations of water with imidazole may well lead to higher conductivities. Interestingly, the bend in the curves at low temperatures for the doped polymers indicates that phase separation is not as complete with the doped polymers, which is consistent with the previously reported DMA of the doped polymers that shows increased plasticization of the PFSA by the imidazole. Figure 2(c) shows conductivities of polymer blends of imidazole and benzimidazole-containing polymers with sulfonated polyetherpolysulfone (BPSH-35). Again, the presence of
the heterocyclic bases clearly improves the conductivity at low water content. However, Figure 2(d) shows that the presence of the bases lead to lower uptake of water so that at a given RH value the actual conductivity of the blend is lower than that of the acid polymer alone. These results illustrate that the heterocyclic bases such as imidazole can provide increased conductivity at low water contents and they also potentially can be used to control water uptake and swelling of a polymer material. These results are intriguing and indicate how greater understanding of the action of the bases for both conduction and water uptake could lead to greater control of the behavior of membrane materials that includes more than just conductivity.

The plasticization effects of the solvent molecules such as water and imidazole upon the polymer morphology are of considerable importance. Figure 3 demonstrates the changes that result in morphology upon uptake of water that can seriously impact the conductivity. A block copolymer consisting of styrene and hydrogenated isoprene blocks was prepared with a variety of block lengths. The styrene units were sulfonated to different degrees. This resulted in various different morphologies which could be altered by variation of the block lengths and sulfonation degree. The morphologies were determined by tunneling electron, scanning electron, and atomic force microscopy and scattering measurements such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) an example of which is shown in Figure 3. During the course of SANS measurements at 90% RH it was noted that the morphology would change from one temperature to another. Conductivity measurements were also affected by the uptake of water and time at elevated temperature. The conductivity plot shown in Figure 3 shows that the initial high conductivity decreases irreversibly with time. These observations...
are rationalized by the schemes shown at the bottom of Figure 3. The left hand scheme represents the change in morphology from lamellar to cylindrical upon uptake of water while the right hand scheme represents the loss of connectivity across the membrane that results from the change in morphology and leads to the loss of conductivity. When experiments such as this are carried out with imidazole present in the polymer changes in the morphology were observed in SAXS experiments depending upon the amount of imidazole present. The presence of the imidazole did not suppress the water uptake and the conductivity was lower but stable over time. These results are consistent with plasticization of the polymer by the imidazole which results in lower conductivities but prevents the motion of the polymers that leads to loss of conductivity.

To understand the conductivity results and also the impact of morphology, acid and base site concentrations, etc. on conduction, a network model was developed in FY 2009 to ascertain the importance of bottlenecks on performance and provide guidance to the membrane synthesis efforts. The concept of the bottlenecks is shown in Figure 4 in the cartoon of the classical Gierke model of Nafion® where the fast proton transport pores are interspersed with bottlenecks where transport is controlled by segmental motion of the polymer. In the initial results shown in the top graph of Figure 4, relatively simple calculations in a one-dimensional mode showed that in a membrane with only a few linkages where the vehicle or segmental motion mechanism dominates, the overall conduction suffers greatly due to the much slower diffusion. Extension of the model to two-dimensional and 3-D cases where alternative connection pathways become available, shows that the effects of the segmental motion bottlenecks need not be so severe as can be seen in the lower two plots in Figure 4. Hence there is reason to believe that some degree of plasticization of the polymer morphology can be tolerated without ruining the connectivity through the membrane.

![Figure 4](image_url)

**FIGURE 4.** Models of the effect of segmental motion bottlenecks on overall conductivity. (a) Gierke model of Nafion® showing slow segmental motion segments and fast proton transport segments; (b) effect of bottlenecks on overall conductivity for one, two, and three dimensions.
Conclusions and Future Directions

Conclusions

- Conductivity of polyelectrolyte systems that contain no mobile solvents appears to be too low unless a high degree of connectivity is achieved through the membrane.
- Connectivity though the membrane is very difficult to achieve and to maintain.
- Conductivities of imidazole-containing systems are improved considerably by the presence of some water in the system. However, water uptake by many polymer systems is suppressed by the presence of the imidazole.
- Modeling shows that increasing the segmental motion transport by plasticization of the polymer by water or other solvents increases the overall conductivity but also increases the loss of connectivity. Polymer dynamics are of critical importance.
- 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.
- 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 underway at LANL.
- 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.
- Gas permeability and crossover measurements will be initiated.
- Modeling of the system and cell issues (conductivity, low catalyst activity at low RH) will continue to guide experimentation.

FY 2010 Publications/Presentations


References


V.D.2 Membranes and MEAs for Dry, Hot Operating Conditions

Objectives

- To develop a new proton exchange membrane (PEM) with higher proton conductivity and improved durability under hotter and drier conditions, in order to meet DOE Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan 2010 commercialization targets for automotive fuel cells.
- Test new membrane in fuel cell membrane electrode assemblies (MEAs).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.3) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

TABLE 1. Progress towards Meeting Membrane Technical Targets

<table>
<thead>
<tr>
<th>Membrane Property</th>
<th>Units</th>
<th>3M 2010 Status</th>
<th>2010 target</th>
<th>2015 target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area Specific Resistance at 120°C (H₂O pp 40-80 kPa)</td>
<td>Ohm cm²</td>
<td>0.038 (50 kPa)</td>
<td>0.02 (80 kPa)</td>
<td>≤0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>625 EW PFIA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area Specific Resistance at 80°C (H₂O pp 25-45 kPa)</td>
<td>Ohm cm²</td>
<td>0.017 (25 kPa)</td>
<td>0.006 (44 kPa)</td>
<td>≤0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>625 EW PFIA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area Specific Resistance at 30°C (H₂O pp 4 kPa)</td>
<td>Ohm cm²</td>
<td>0.03 (3.8 kPa)</td>
<td>≤0.03</td>
<td>≤0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>625 EW PFIA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area Specific Resistance at -20°C</td>
<td>Ohm cm²</td>
<td>0.14</td>
<td>≤0.2</td>
<td>≤0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700 EW PFSA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ cross-over</td>
<td>mA/cm²</td>
<td>&lt;0.5</td>
<td>≤5</td>
<td>≤2</td>
</tr>
<tr>
<td>H₂ cross-over</td>
<td>mA/cm²</td>
<td>&lt;2</td>
<td>≤5</td>
<td>≤2</td>
</tr>
<tr>
<td>Durability</td>
<td>Cycles</td>
<td>10,000</td>
<td>≥20,000</td>
<td>≥20,000</td>
</tr>
<tr>
<td>Mechanical (%RH Cycle)</td>
<td></td>
<td>625 EW PFIA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical (OCV)</td>
<td>Hours</td>
<td>450</td>
<td>625 EW PFIA</td>
<td>≥500</td>
</tr>
</tbody>
</table>

Accomplishments

- Conductivity, fuel cell and diffusion measurements on a broad range of EWs and varied side-chains have provided insight into structure/conductivity relationship.
- We have synthesized new two and three acid-per-sidechain ionomers. These show:
  - Enhanced conductivity vs. starting PFSA.
  - Lower swelling in boiling water compared to PFSAs with the same EW.
  - High hydrolytic stability (no hydrolysis >1 week in hot H₂SO₄ or in 250°C H₂O).
  - One of these, the PFIA ionomer allows us to make membranes which have conductivity in excess of 100 mS/cm below 40% RH at 120°C.
- Hetero poly acids (HPAs) have provided enhanced conductivity and chemical resistance. Inorganic
oxide/HPA composites have shown partial stability to boiling water.

- We have shown that 825 EW 3M ionomer with new additives and optimized fabrication process provides:
  - >20,000 cycles in %RH cycle test.
  - >800 hours in OCV test.
  - >18,000 hour MEA lifetimes in accelerated tests.
- Polymer and model compound stability studies are providing insight into degradation pathways and relative stability.
- Dissipative particle dynamics simulations show morphologies consistent with clipped random wave analysis of small angle X-ray scattering (SAXS) data and conductivity measurements.
- Electron spin resonance (ESR) measurements indicate that the rate constant for the reaction of hydroxyl radicals with the 3M membranes is significantly slower compared to that for Nafion®.

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 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 membranes. 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

In the past we have shown that lower EW ionomers, based on our 3M perfluorinated sulfonic acid (PFSA, Figure 1), provide higher proton conductivity under drier conditions. PFSA membranes with EW under about 700 can meet DOE conductivity targets [2]. Unfortunately, the mechanical integrity of these membranes is poor. The 3M ionomer swells excessively at EWs below about 750 and becomes soluble in boiling water at EWs below about 650-700. At an EW of 700 the tetrafluoroethylene (TFE) segments in the polymer backbone are short, and the crystallinity index, measured by wide angle X-ray scattering (WAXS) is nearly zero, this is shown in Figure 2. Even lower EW, non-soluble membranes (about 700 EW) swell excessively. Figure 3 shows that membranes prepared from ionomers with EWs above about 750 show a gradual increase in hydration in boiling water with decreasing EW, increasing from about 14 moles of water per sulfonic acid group ($\lambda = 14$) for an EW of 1100, to about 35 waters of hydration per sulfonic acid group ($\lambda = 33$) for an EW of 750. Below this EW water absorption increases dramatically. The 700 EW ionomer has a $\lambda$ value of >100. As shown in Figure 2, membranes from ionomers with EWs below...
700 partially dissolve in boiling water so this test cannot be performed [3]. This excessive swelling or membrane solubility is known to lower MEA durability during fuel cell operation [4].

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 side-chain. Towards this end, we have used the bis sulfonyl imide acid as a protogenic group and linking moiety to prepare several multi-acid side-chain ionomers, some of which are shown in Figure 1. The bis sulfonyl imide acid is highly acidic, in some cases more acidic than a structurally similar sulfonic acid [5]. Fuel cell membranes from polymers containing this functional group have been prepared in the past through the polymerization of imide functional monomers with TFE [6]. We have prepared new, very low EW ionomers from sulfonyl fluoride ionomer precursors with sufficient backbone crystalinity to prevent excessive swelling. Swelling data for examples of low-EW ionomer prepared by this method are shown in Figure 3. Membrane samples prepared from both the ionomer labeled Ortho Bis Acid and PFIA absorb about 40 waters per acid group, much lower than the 700 EW PFSA. We have prepared samples of the 625 EW PFIA with in plane linear swelling as low as 20%, similar to what we see for 825 EW membranes which have provided up to 18,000 hours in accelerated durability tests in 50 cm² MEAs [2]. We are optimizing the membrane construction and fabrication process for this ionomer.

Figure 4a shows conductivity of two PFSAs (825 and 700 EW), the same 625 EW PFIA whose water absorption is shown in Figure 3, and a 450 EW sample of the “Bis/Tris acid”. The Bis/Tris acid has very high conductivity at higher relative humidity compared to either PFSAs, but the conductivity drops off at lower %RH and is lower than both PFSAs below about 40% RH. This lower conductivity at lower %RH is similar to what is observed for sulfonated arene ionomers which show significant drop off in conductivity at lower

![FIGURE 1. Structure of Selected Ionomers Based on the 3M Ionomer Backbone](image1)

![FIGURE 2. Water solubility and crystalinity index for a range of different EW 3M PFSAs. Water solubility was measured after 3 hours in boiling water. The inset shows the WAXS spectra from which the crystallinity index was calculated.](image2)

![FIGURE 3. Water absorption in boiling water as a function of EW. Absorption is given as lambda (λ), or the number of water molecules per acid group.](image3)
%RH and may be due to the lower pKa of the aromatic sulfonic acid groups compared to the perfluoroalkyl sulfonic acid groups of the PFSA [7]. The 625 EW PFIA has conductivity at high %RH between the 700 and 825 EW PFSA, but shows higher conductivity than either at low EW. The higher conductivity at lower EW may be due to the higher acidity of the perfluoro bis sulfonyle imide (one of the most acidic acids known). Figure 4b compares the performance in a fuel cell of this 625 EW PFIA to our 825 EW PFSA. At the higher temperature and lowest humidity (120°C, 23 % RH) the fuel cell performance is over 100 mV higher and the through plane resistance is more than 0.100 Ohm-cm² lower than the 825 EW PFSA.

MEAs prepared from this ionomer have also lasted 450 hours in the DOE prescribed chemical durability (OCV) test and about 10,000 cycles in the DOE prescribed mechanical durability (RH Cycle) test (Table 1) [8]. Based on this and other testing, we have down-selected the PFIA as the ionomer to use in the remainder of this project and focus on further improvements in the chemical and mechanical durability of membranes made from this ionomer to allow them to meet these durability requirements.

During the course of this year we have also performed work to optimize the electrode. The early work looked at different ionomer equivalent weights, ionomer to carbon ratios, catalyst types, gas diffusion layer types, and process variables. Test methods were developed that screened electrodes over a variety of test conditions to optimize performance over the whole range of automotive operating conditions – cool/wet to hot/dry and high current. Results of that work led to gains in performance and a 38% reduction of catalyst loadings compared to the initial baseline. Gains were also realized in catalyst cycling stability and in the reduction of the overall MEA fluoride release rate. New processing methods and catalyst morphologies are showing promise of further gains in both performance and catalyst stability. As we demonstrated early during this contract, an important variable in electrode performance under dry conditions is the thickness of the PEM and its ability to maximize the water management [9]. Gains have also been achieved in chemical stability through use of additives in the electrode formulation that we have observed diffusing into the PEM. We have evaluated stabilized HPAs that have reduced fluoride release rate at no cost to conductivity at levels added so far. These HPAs show partial stability to boiling water.

Conclusions and Future Directions

The focus of this project has been to develop new polymers and new stabilizing or conductivity enhancing membrane components to provide a membrane which can meet all DOE 2010 and 2015 targets including both conductivity and durability. We have also focused on gaining a better understanding of structure property relationships relevant to conductivity and durability to aid in this development. We have met all of the DOE membrane targets with at least one of the materials tested, and our new PFIA ionomer met the 30°C and 80°C conductivity targets, has nearly met the 120°C conductivity target (>100 mS/cm above 40% RH), has come very close to meeting all conductivity targets and has come very close to meeting all durability targets as well. We are confident that we will meet our goal in the final year of this project. Future activities include:

- Continue preparation and optimization of the conductivity and durability of the PFIA ionomer with membrane additives.
- Continue to probe factors in transport using nuclear magnetic resonance 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.

**FIGURE 4.** a) The conductivity at 80°C for selected ionomer membranes. Conductivity was measured using a 4-point, in-plane conductivity cell inside a constant humidity oven. b) The voltage of two 50 cm² MEAs with an 825 EW PFSA and a 625 EW PFIA membrane at 0.8 A/cm² running on hydrogen/air at ambient pressure. The cell inlet humidification is held constant with an 80°C dew point and the cell temperature is raised from 80°C to 120°C. This causes the relative humidity to drop from 100% to about 24%.
• Develop a better understanding of role of crystallinity on swelling in new polymers using X-ray scattering, mechanical properties testing and modeling.
• Use atomistic and mesoscopic simulations to study the hydrated morphology of 3M PFSA and multi-acid side-chain membranes.
• Provide completely water stable membranes comprising HPAs. Evaluate additional stabilizers.
• Describe degradation pathways and rates for current group of model compounds and correlate with membrane stability.

Special Recognition & Awards/Patents Issued

1. US Patent application 20090269644, Hamrock; Steven J.; Schaberg; Mark S.; Sharma; Neeraj; Abulu; John E.; Proton Conducting Materials, Published October 29, 2009.

FY 2010 Publications/Presentations


References


V.D.3 Dimensionally Stable Membranes (DSMs)

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).
- Demonstrate, by the 3rd quarter 2007, membrane conductivity of 0.07 S/cm, at 80% relative humidity, at room temperature (RH), 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, 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 (3.4.4) of the Fuel Cell 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 Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan. 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>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>2010 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Water Vapor</td>
<td>kPa</td>
<td>1.5</td>
</tr>
<tr>
<td>Oxygen Crossover</td>
<td>mA/cm²</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogen Crossover</td>
<td>mA/cm²</td>
<td>2</td>
</tr>
<tr>
<td>Membrane Conductivity</td>
<td>S/cm</td>
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</tr>
<tr>
<td>Operating Temperature 20°C</td>
<td>°C</td>
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</tr>
<tr>
<td>Operating Temperature 20°C</td>
<td>°C</td>
<td>≤120°C</td>
</tr>
<tr>
<td>Area Resistance</td>
<td>Ohm*cm²</td>
<td>0.02</td>
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<tr>
<td>Cost</td>
<td>$/m²</td>
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<tr>
<td>Durability with Cycling below 80°C</td>
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<td>Unassisted Start from Low Temperature</td>
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<tr>
<td>Thermal Cyclability in Presence of Condensed Water</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Accomplishments

- Successfully demonstrated that 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 2DSM support material, resulting in passing the...
go/no-go project 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 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 polyether sulfone (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 PFSA materials 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 using commercially available PFSA materials as well as generating new PFSA polymers, 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 membrane 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 relative humidity 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 the dimensional stability and improved mechanical properties of the 2DSM. We successfully incorporated both 1,100 EW and 830 EW PFSA ionomers into commercially available PES and UPE and tested the membranes under electrolysis conditions. Figure 3 compares the electrolysis performance of a 3-mil 3DSM prepared with 830EW ionomer and UPE support to that of an 1,100 EW electrolysis membrane electrode assembly with comparable thickness. Electrolysis
conditions were used as the poor membrane-electrode interface in fuel cell membranes contributes to the overall resistance and thereby decreases fuel cell performance. 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. The thinnest PES porous support commercially available is 4 mils thick. We are currently working with Millipore on thinner supports, and they have supplied us with 1- and 2-mil-thick UPE. We have successfully incorporated low EW PFSA ionomers into these 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 mil with only a 20% conductivity penalty compared to neat 1,100 EW PFSA.

The mechanical durability of the 3DSMs was tested through RH-cycling performance of the resultant thinner 3DSMs prepared with the materials from Millipore and the low EW ionomers at 80°C. Cast Nafion®, NR211, failed around 4,500 cycles, before the 1-mil 3DSM, as seen in Figure 4. The 3DSM Condition B, which failed early, was sintered to 200°C, well above the supports melting temperature. The sample (3DSM Condition A) which was sintered to 140°C, just below the support melting temperature lasted longer than NR211, the cast Nafion® reference. The 2-mil 3DSM which was also sintered to 200°C did not fail in the first 5,000 cycles. The samples were taken off test at 5,000 cycles because the test stand was needed for another project.

To further increase conductivity PFSA 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 years we demonstrated that this material has a conductivity that is approximately twice that of the

TABLE 2. Through-Plane Conductivities of Differently Prepared Samples

<table>
<thead>
<tr>
<th>Material/ Pore Size</th>
<th>Ionomer Starting Thickness (mils)</th>
<th>Final Thickness (mils)</th>
<th>Through-Plane Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion® 111</td>
<td>1,100 EW</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>0.45 μm UPE</td>
<td>1,100 EW</td>
<td>2</td>
<td>0.023</td>
</tr>
<tr>
<td>0.7 μm UPE</td>
<td>1,100 EW</td>
<td>0.4</td>
<td>0.040</td>
</tr>
<tr>
<td>0.7 μm UPE</td>
<td>850 EW</td>
<td>1</td>
<td>0.045</td>
</tr>
<tr>
<td>0.7 μm UPE</td>
<td>700 EW</td>
<td>0.6</td>
<td>0.018</td>
</tr>
</tbody>
</table>
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 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 (PVEPVE)-based polymer was cast and characterized for conductivity at GES. 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 PFSAs 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 PFSAs 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 5,000-10,000 cycles, including a 1-mil 830 EW membrane. We are currently focusing on preparing even thinner (~15 μm) 3DSMs with lower EW (700 EW) ionomer for fuel cell testing. Millipore and the Solar Energy Research Center in Florida are assisting in this effort.

Special Recognitions & Awards/Patents Issued
1. 2009 DOE Hydrogen Program Review R&D Award.

FY 2010 Publications/Presentations
V.D.4 Lead Research and Development Activity for DOE’s High Temperature, Low Relative Humidity Membrane Program

Objectives

- Fabricate membrane electrode assemblies (MEAs) from Team membranes.
- Test Team MEAs for fuel cell performance.
- Standardize methodologies for in-plane and through-plane membrane conductivity measurements.
- Provide High Temperature Membrane Working Group (HTMWG) members with standardized tests and methodologies.
- Organize HTMWG bi-annual meetings: http://www1.eere.energy.gov/hydrogenandfuelcells/htmwg.html

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(C) Electrode Performance

Technical Targets

FSEC plays a supporting role to the six teams who are tasked with developing an improved high-temperature, low relative humidity (RH) membrane for proton exchange membrane (PEM) fuel cells. FSEC has developed standardized experimental methodologies to:
- measure conductivity (in-plane and through-plane);
- characterize mechanical, mass transport and surface properties of the membranes as working MEAs;
- and predict durability of the membranes and their MEAs.

This project manufactures, tests and evaluates MEAs for performance and stability. Test results will be evaluated against DOEs 2010 membrane targets:

- Oxygen Cross-Over 2 mA/cm²
- Hydrogen Cross-Over 2 mA/cm²
- Membrane Conductivity at 120°C 0.10 Siemens/cm

Accomplishments

- Verified ability to prepare an MEA using the DOE-recommended Pt/Co on carbon catalyst from Tanaka.
- Developed procedure for making and spraying ink based upon the use of 3M ionomer, as recommended by DOE.
- Prepared and tested MEAs fabricated from membranes provided by Giner, Fuel Cell Energy and Case Western.
- Established pinhole test method.
- Obtained and tested mechanical test apparatus.

Introduction

Generally, two regimes of PEM fuel cell 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 MEAs that could
operate at temperatures of up to 120°C, low RH and near atmospheric pressure.

The objective of this phase of the program is to fabricate and test MEAs from fuel cell membrane materials that meet the goals outlined by the DOE in the multi-year plan. Specific 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).

**Approach**

The High Temperature, Low Relative Humidity Membrane program encompasses six teams, each of which is skilled in producing novel membranes expected to meet the goals of the program. Some of these teams are not necessarily skilled in the ability to produce an MEA, or to test the MEAs in a fuel cell. FSEC's objective is to provide the expertise to test the membranes under fuel cell conditions. FSEC is working closely with the membrane manufacturers to develop appropriate methods for manufacture of the MEA and to test the MEAs according to a procedure that has been developed at FSEC. This approach involves a detailed logic flow chart that itemizes each step of the manufacture, fuel cell testing and post test analysis of the MEA. Each membrane manufacturer approves the steps of the logic flow chart in advance of the process. Furthermore, FSEC iterates with the teams to optimize the results.

**Results**

During this year, a total of 19 membranes were received from four of the teams. These varied from an extremely brittle membrane that required recasting to some high quality materials. Each was tested for material characteristics to determine suitability for fabrication into MEAs, see material characterization box of logic flow chart, Figure 1. Eight of the membranes were fabricated into MEAs and tested, and the procedures developed for the testing. For each MEA tested, a detailed report was prepared and sent to the supplier, along with photos of each step, data collected

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**FIGURE 1. Logic Flow Chart**
and, when possible, a coupon that was prepared identically to the MEA.

All membranes received to date were preliminary or baseline materials. The goal of using these materials for the development of MEAs was to resolve any issues resulting from the use of these novel materials. This will allow easier handling of the final membranes, which are not yet available. Three of the six teams have indicated that they are prepared to send next generation or final membranes for testing.

A previous method [1] for determining pinhole locations in MEAs from tested fuel cells was found not to be reproducible and was potentially damaging to the MEAs. This method was based upon the location of bubbles that appeared in a liquid injected to the cathode flow field of a transparent plate with controlled gas pressure applied to the anode. An alternative method has been developed based upon applying 4% hydrogen to the anode side of a fuel cell, with controlled flow and with the cathode side of the MEA exposed to the atmosphere. This results in the development of “hot-spots” at pinhole locations due to the direct reaction of hydrogen with oxygen. An infrared camera was used to determine the locations of these hot-spots. This method has been found to be reproducible and since the MEA is not exposed to substances it would not be exposed to during fuel cell testing, damage to the MEA is minimized. An example of an image of the pinholes taken using an infrared camera is shown in Figure 2. In this image hot spots are noted with approximate temperatures based on the emissivity of carbon.

An in-house built stress-strain setup was acquired and a procedure was formalized for stress-strain testing of team member membranes. Reproducibility and repeatability will be established as a part of completing the protocol. Team member membrane samples will be tested once the protocol is finalized, to ensure all samples were tested to the same procedure.

Conclusions and Future Directions

• Reached agreement with all six Teams on logic flow chart for MEA development.
• Developed and tested MEAs from eight Team member membranes.
• Established collaboration with 3M to obtain advanced ionomer for use in MEAs.
• Fabrication and testing of additional MEAs will be done as membranes are received.
• Formalize the procedure for pinhole testing, and characterize the observed pinholes with scanning electron microscopy.

FY 2010 Publications/Presentations

1. Rodgers, Marianne P.; Agarwal, Rohit; Pearman, Benjamin P.; Li, Bo; Slattery, Darlene K.; Bonville, Leonard J.; Kunz, H. Russell; Fenton, James M. Accelerated durability testing of perfluorosulfonic acid MEAs for PEMFCs using different relative humidities. ECS Transactions (2009), 25(1, Proton Exchange Membrane Fuel Cells 9), 1861-1871.


References

V.D.5 Poly(p-Phenylene Sulfonic Acids): PEMs with Frozen-In Free Volume

Objectives

The project objectives are to optimize routes to rigid rod poly (phenylene sulfonic acids), polymers that retain high conductivity at low humidity, develop methods to make water insoluble polymers and characterize the materials as proton exchange membranes (PEMs). The requirements are:

- Analyze the Ullman polymerization reaction in order to increase polymer molecular weights and decrease reaction time.
- Increase the polymer sulfonic acid density and water absorption: use phenylene disulfonic acid monomer to make homo- and co-polymers.
- Develop reliable methods for grafting non-polar groups on the backbone to make water insoluble, dimensionally stable PEMs.
- Synthesize comonomers that can be copolymerized to produce water insoluble copolymers either directly or in a subsequent step.
- Characterize polymers, copolymers and grafts to understand the relationship between molecular structure, supramolecular 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 (3.4.5) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost

Technical Targets

This project involves the synthesis and characterization of homo- and co-polymer rigid-rod aromatic sulfonic acids.

- Our ionomers have passed the 2005 goals for membrane conductivity and probably reach the 2015 goals.
- Earlier tests of MeOH permeability (<0.04 mA/cm² for a 20 μ thick film at 100°C with a 2/1 MeOH/H₂O gas input) imply that the very polar membrane environment should reduce oxygen and hydrogen cross-over to values much lower than the target values.
- The starting materials are relatively cheap; there are only two steps from commercial starting materials, fuming sulfuric acid and dibromo-biphenyl or dibromo-benzene, to the homopolymer sulfonic acids. Copolymers will raise the cost.
- Some of our early graft copolymers showed 27% expansion (z direction only) from 22 to 100% relative humidity (RH) while retaining high conductivity at 50% RH and 80°C.

Since the polymers have not yet been tested in a fuel cell configuration, we cannot be certain that they meet the requirements but the indications are that they will do so.

Remaining Barriers:

- The homo- and graft polymers tested so far have very low elongation; the best was 8% at 40% RH. They are brittle when very dry. However, these were low molecular weight polymers, molecular weight at 10,000.
- Homopolymer molecular weights are limited because they crystallize from solution and stop growing. The maximum molecular weight for poly(p-biphenylene disulfonic acid) is ~10,000. It is higher for poly (p-phenylene disulfonic acid),
PPDSA, up to 100,000, but the homo and graft polymers become very soft above 50% RH.

- We have not yet developed a reliable, scalable method for making water insoluble copolymers by direct grafting of a large non-polar moiety. Grafting is difficult to control since it is a heterogeneous reaction. Normal copolymerization approaches have failed. Other approaches are being studied.
- Long chain alkyl benzenes grafted on PPDSA-generated water insoluble materials that could form good films but swelled rapidly and disintegrated in water to a suspension of particles. We think that grafting is inhomogeneous, which is why they shear easily above 50% RH and are not water stable.

Accomplishments

- The two base monomers were found to copolymerize well. The copolymer precipitated from solution but at higher molecular weight.
- The grafting procedure has been improved; oxygen is now completely excluded. Recent grafts are light in color and cast films are easily handled. They hold water very well and have high conductivity at low humidity; the best conductivity found was 0.1 S/cm at 30% RH and 80°C. The copolymer and its grafts hold more water than the homopolymers and their grafts at a given RH, but they have comparable conductivities.
- We have finally developed a polar comonomer that copolymerizes well with the base monomers. It contains a weakly acidic CH2 group. Once copolymerized, these hydrogens can be replaced by non-polar chains to generate water insoluble copolymers. This has been demonstrated but films have not yet been cast.
- We have made nano-pore containing two-dimensional (2-D) polymers (ion exchange capacity [IEC] = 5.5 mEq/gm) that have no non-polar groups but are water insoluble; they aggregate during preparation. We are still learning how to handle them to cast good films. We expect that the volume will be independent of humidity.

Introduction

There are many problems associated with the normal aromatic sulfonic acid PEMs. The better conducting materials swell very much in water. Even with these materials, conductivity drops rapidly as humidity is lowered [1]. Block polymers swell less at high humidity, but conductivity is still poor at low RH [2]. They can be used only at high humidity which limits the fuel cell operating temperature to <90°C. The materials described below were designed to hold water...
very strongly at low humidity. They could be used effectively at higher temperatures, up to at least 120°C, with little or no added water in the fuel stream since the water generated in the reaction should be sufficient to maintain high conductivity. High temperature operation has the additional advantages that kinetics are faster, lower purity hydrogen can be used and heat can be removed easily.

**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 PPDSA, 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 molecules still have voids which hold water (frozen in free volume): further water loss generates compression which distorts bond angles and requires high energy. The last few waters are removed with difficulty and are reabsorbed rapidly. 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]. This structural design generates non-collapsible nanopores lined with a high density of sulfonic acid groups which hold water very strongly.

Attached non-polar groups interact by hydrophobic bonding which restricts swelling as humidity rises. Because the molecules are rigid rods, non-polar groups on a chain can interact only intermolecularly, with similar groups on neighboring chains. Thus, a relatively low mole fraction of non-polar groups should make such polymers water insoluble and dimensionally stable with little loss of conductivity. This was demonstrated earlier for poly(p-biphenylene disulfonic acid), PBPDSA, grafts but has not yet been achieved for PPDSA grafts [3].

**Results**

**Copolymerization:** Over the past year we have copolymerized several mole ratios of the two base monomers. They reacted well but we have not yet determined how random the copolymerization is. During the reaction the copolymer takes longer to precipitate and the solution (2 to 3% copolymer) becomes viscous, showing that high molecular weight copolymer is soluble. The copolymers hold water very strongly. The best PPDSA reduced viscosities (0.5% solution) were in the range of 0.7–0.9 dL/gm. A copolymer (80/20 ratio, P80B20) had a reduced viscosity of 1.1 dL/gm. An earlier copolymer (P55B45) had a reduced viscosity of 1.5 dL/gm.

We have made a new comonomer, 2,7-dibromofluorene 3,5-disulfonic acid, F. It copolymerized well with the two base monomers to give water soluble copolymers. The fluorene group has two active hydrogens which can be replaced easily with alkyl groups, see Scheme 1. We have demonstrated this

**SCHEME 1.** Approach to Synthesis of New Random Copolymer, P10F1, and Preparation of Water Insoluble Materials for PEMs
with one of its copolymers, P10F1, adding two \(\text{C}_{22}\text{H}_{45}\) groups to each residue. (Calculated IEC = 6.7 mEq/gm.) Unfortunately, we have not been able to find a solvent for the reacted copolymer; it does not swell in water even with such a high IEC. Work is continuing in this area.

**Grafting:** PPDSA homopolymer and the P80B20 copolymer were grafted with n-octyl benzene (nOB) and/or n-dodecyl benzene (nDDB). Various mole ratios of alkyl benzene to sulfonic acid were used during grafting. At 100/40 and 100/100 (SO\(_3\text{H}/\text{alkyl benzene}), grafting went smoothly; grafts containing between 7 and 23 mole\% alkyl benzene were obtained. The grafting procedure was improved during the year; oxygen was systematically excluded. Films cast early in the year were black and very brittle. It was difficult to get strips large enough to make conductivity measurements. After oxygen was excluded, cast films were pale yellow and could be easily handled. The new procedure was used for most of the nOB grafts. Figure 1 shows before and after cast films.

Grafted polymers with more than 10 mole\% graft were water insoluble. However, all the films swelled rapidly in water and eventually disintegrated to a cloudy suspension. The films became very soft above 50% RH. We think this is because the grafting of non-polar groups was inhomogeneous, with regions of high graft density and long stretches of ungrafted polymer. The homopolymer loses modulus rapidly as humidity rises and becomes a gel above 75% RH.

**Water Absorption:** Homo and graft polymer water absorption was measured in several ways: weight gain, \(^1\text{H}\) nuclear magnetic resonance analysis and titration. Figure 2 shows the average \(\lambda\)s as a function of RH for the homopolymer, copolymer, and their grafts with n-octyl benzene. The copolymer holds more water at a given RH than the PPDSA homopolymer. The grafted copolymers hold more water than the starting material, possibly because the hydrocarbon groups force the chains apart. This is best seen at 0% RH (drying at 10 mm and 90°C for one day); the P80B20 grafts have \(\lambda\)s of two versus one for the starting copolymer. Lambda decreased slightly for the PPDSA graft polymers compared to the starting polymer.

Water absorption was compared to that of Nafion117\(^®\). The copolymer and its grafts have \(\lambda\)s about 1.5 to 2 higher over the whole RH range. New preparations of PPDSA have lower \(\lambda\)s than those reported earlier [5], possibly due to higher molecular weight and better crystallinity, but are still higher than Nafion117\(^®\). Grafting lowered \(\lambda\) but did not seem to affect conductivity.

**Conductivity:** Conductivity versus RH data for the nOB grafts on PPDSA and the P80B20 copolymer are shown in Figure 3. Conductivity of the PPDSA/nDDB grafts, not shown, was about the same at a given mole fraction of graft. Samples were sent to the Florida Solar Energy Center. The P80B20 GnOB 7.3% conductivity at 80°C was measured there and also at Case; the
values agreed within experimental error. This gives us confidence in our measurement procedures. The data show that conductivity at lower RH remains high for these PEMs if there is less than 10% grafting. It parallels the PPDSA homopolymer at 80°C [5] but is slightly lower, dropping to 100 mS/cm at 50% RH. At 16 to 18% grafting, conductivity drops further by a factor of two, but is still very high.

When the new PEM conductivities are compared to that of Nafion212®, it is obvious that the better retention of water generates much higher conductivity at low RH. The 20 to 50% RH conductivity of the best materials is an order of magnitude higher than that of Nafion212®. The conductivity drop at 120°C is unexpected and is possibly due to starting the testing at 50% RH. The sample would be so soft at that RH and temperature that the electrode pressure could thin it at the electrode edges, raising its resistance. Several attempts were made at the Florida Solar Energy Center to make a membrane electrode assembly (MEA) using a film of P80B20 GnOB 16%. Under their preparation conditions, the polymer was so soft that it was pressed into the gas diffusion layer; no testable MEA could be made. We expect this problem to vanish when we have dimensionally stable PEMs.

2-D Polymers: These were discussed fully in a special report sent in as a quarterly report, dated April 6, 2010. Unfortunately, Casey Check had to stop research in order to write up his his doctorate thesis. We expect to start research again in September.

We have succeeded in finding procedures and reagents that enabled us to make very large planar molecules in the form of a hexagonal lattice of p-biphenylene disulfonic acids interconnected through benzene rings at the 1, 3, 5 positions (Suzuki reaction using starvation polymerization conditions). The hexagons are calculated to be about 2.2 nm from side to side with a central hole about 1.5 nm in diameter. Wide angle X-ray diffraction scans do not show any sharp reflections; this implies that there may be some pentagonal or heptagonal holes in the structure.

Because the molecules were very large, they coalesced towards the end of the polymerization into water insoluble aggregates. Since the IEC is ~5.5 mEq/gm and there are no large non-polar groups, this was unexpected. If crosslinking had occurred, the whole solution would have gelled early in the reaction rather than becoming cloudy towards the end. The aggregates could be dispersed by sonication into smaller particles. Films of the sonicated materials were cast from water; they were stable to water after drying and could be handled easily. However, they were brittle in water. Preliminary characterization of initial aggregates by scanning electron microscopy and atomic force microscopy (AFM) showed that the molecules had coalesced into large stacks, showing that they were planar. Figure 4 shows an AFM scan of one of the better polymerizations, after sonication to break up secondary association. Such stacks should contain nano-pores parallel to the stack direction. Water was held very tightly; lambda for the best preparations was ~6 at 50% RH. For such systems, conduction would be one dimensional, along the pore axis. These must be perpendicular to the film surface to get high through conductivity. We have not found casting conditions that would do this properly; the work is suspended for the time being.

**Conclusions and Future Directions**

- Since grafting of long chain alkyl benzenes on PPDSA did not give water-stable materials, probably due to heterogeneous grafting, we are shifting to the production and study of cross-linked films. Biphenyl groups can be grafted homogeneously on the sulfonic acids; they are too small to promote inhomogeneous grafting. Because the biphenyl reactivity is reduced after one end is grafted, it is possible to get water-soluble polymer with as much as 15% grafting. Materials with 5 to 15% graft will be cast and the films will be crosslinked by heating under vacuum at 175°C or higher. (Preliminary studies show that these conditions can be used.) We are determining the reaction conditions needed to get complete crosslinking at a degree of substitution that gives dimensionally stable films, hopefully with high conductivity.
The new copolymers made using dibromo fluorene disulfonic acid did not have as high viscosity as the homopolymers. We are studying reaction conditions and have made copolymers with higher viscosity. Molecular weight is very important in improving mechanical stability at high humidity. We will make a series of copolymers with various mole ratios of fluorene comonomer (5 to 20 mole%) and graft on alkyl chains, C₈ to C₂₂, to determine which combination gives the best final properties. If these cannot give satisfactory mechanical properties, fluoroalkyl groups can be grafted on the backbone.

Work will continue on the 2-D polymers. The first task is to find counterions or additives that will keep the material soluble throughout the polymerization to enable us to cast good films. The additive and/or counterion should also be easily removable or replaceable by protons. We have some ideas that will be tested soon. The second task is to make sure that the final structure is completely regular, a purely hexagonal lattice. We will be working on that problem also. Cast films should have the molecules parallel to the film surface and very well stacked. Molecular overlap should be high between the primary stacks to give materials with reasonable strength, though low elongation. Such films should have good conductivity, high modulus and constant dimensions, independent of RH.

Special Recognitions & Awards/Patents Issued

1. A patent application on Liquid crystal poly(phenylene disulfonic acids) by Morton Litt and Junwon Kang was submitted to the U. S. Patent Office early in 2008. It is still pending.
2. An invention record for the 2-D polymers is being processed.

FY 2010 Publications/Presentations

2. Talk at University of Genoa, Genoa, Italy 7/8/10.
3. Talk at IUPAC meeting, Glasgow, Scotland 7/13/10.

References

2. J. McGrath et al, DOE Program review, 6/08 Washington, D.C.
V.D.6 NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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Eric Fossum, Wright State University, Dayton, OH

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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’s technical targets for membranes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell 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 for 2010.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2010 DOE Targets</th>
<th>2010 Project Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Water Vapor Pressure</td>
<td>kPa</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>Oxygen Cross-Over</td>
<td>mA/cm²</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogen Cross-Over</td>
<td>mA/cm²</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Membrane Conductivity at Inlet Water Vapor Partial Pressure</td>
<td>S/cm</td>
<td>0.10</td>
<td>0.107¹</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>-20°C</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>-20°C</td>
<td>S/cm</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Operating Temperature (T)</td>
<td>°C</td>
<td>&lt;120</td>
<td>120</td>
</tr>
<tr>
<td>Area Specific Resistance</td>
<td>Ohm-cm²</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>Durability with Cycling</td>
<td>At operating T &gt; 80°C</td>
<td>~2,000</td>
<td></td>
</tr>
</tbody>
</table>

¹Proton conductivity at 120°C and 50% relative humidity (RH) – data from Bekktech LLC

Accomplishments

• A new nanofiber membrane fabrication method was developed, where a separate impregnation step for the inert (uncharged) polymer was eliminated and where Norland Optical Adhesive 63 was replaced with a commercially-available polyphenylsulfone.
• Fabricated nanofiber composite membranes via a dual-fiber electrospinning, where perfluorosulfonic acid (PFSA) proton conducting nanofibers and uncharged polyphenylsulfone (PPSU) nanofibers are simultaneously electrospun.
• Developed two methods for processing the dual fiber mat into a fuel cell membrane: (i) “melting” PFSA ionomer around a PPSU nanofiber mat (where the nanofiber mat acts as a reinforcement)
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 fast 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. Unfortunately, the conductivity of PFSA membranes drops dramatically at T >100°C under low humidity conditions [1] 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 has been 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 exchange capacity sulfonic acid polymer to ensure high water swelling of the nanofibers/nanocapillaries and structural stability. The inert (hydrophobic) polymer matrix controls water swelling of the nanofibers/nanocapillaries and provides overall mechanical strength to the membrane. First-generation membranes [2] were made using sulfonated poly(arylene ether sulfone) with sPOSS to further boost conductivity. Norland Optical Adhesive 63 was employed as the inert embedding polymer. Second-generation membranes were fabricated with nanofibers containing 850 EW PFSA (from 3M Corporation) with/without sPOSS [3]. Films with sPOSS met the DOE’s Year 3, 3rd quarter Go/No-Go conductivity target of 100 mS/cm at 120°C and 50% RH.

Approach

Membranes were prepared by a newly developed dual nanofiber electrospinning technique using either 1,100 EW Nafion® or 825 EW PFSA from 3M Corporation as the proton conducting material and Radel® R-5500NT PPSU from Solvay Advanced Polymers LLC as the inert/uncharged polymer. PFSA materials were electrospun using a high molecular weight (MW) polymeric carrier, 500,000 MW poly(ethylene oxide) (PEO) for Nafion® or 400,000 MW PEO for 3M 825 PFSA (where the PEO concentration was 1-2 wt% of the total polymer content). PFSA/PEO and PPSU nanofibers were electrospun simultaneously using two separate spinnerets. Suitable post-treatment converted the dual-fiber mats into fully dense and defect-free membranes, while maintaining the nanofiber morphology of one polymer component. Membranes were made where: (i) PFSA nanofibers were surrounded by an inert (uncharged) PPSU matrix and (ii) inert (uncharged) PPSU nanofibers were surrounded by PFSA ionomer. After processing, membranes were boiled in acid and then water to remove the PEO carrier polymer. Both membrane structures were fabricated, but characterization work was only performed on the morphology where PFSA was surrounding a PPSU nanofiber mat. Membranes were evaluated in terms of: (i) in-plane proton conductivity (in room temperature water), (ii) in-plane volumetric and gravimetric swelling in boiling water, (iii) mechanical properties of dry films (from stress-strain curves), and (iv) H2/air fuel cell tests (after converting the membrane into a membrane-electrode-assemblies).

Results

Preparing Dual Fiber Electrospun Mats with PFSA and PPSU – High quality dual fiber mats (Nafion®/PEO and PPSU nanofibers), of uniform thickness and fiber volume fraction were prepared, where approximately 70% of the fibers in the mat were composed of Nafion®/PEO. PFSA fibers were electrospun using a rotating drum collector, where the total polymer concentration in the electrospinning solution was 20 wt% (with a 99/1 PFSA/PEO wt ratio), the solution flow rate was 0.60 ml/hr, the electrospinning solvent was a 1-propanol/water mixture (2/1 vol ratio), the applied voltage was 4 kV, and the spinneret-to-collector distance was 5.5 cm. For PPSU electrospinning, a 25 wt% polymer solution was used with a N-methylpyrrolidone/
acetone solvent (4/1 vol ratio), with 7.5 kV potential, 8.5 cm spinneret-to-collector distance and a solution flow rate of 0.12 ml/hr. The mat was then compacted and annealed to produce a functional fuel cell membrane (a scanning electron microscope [SEM] image of the membrane is shown in Figure 1).

Membrane Evaluation - Physical property data for a nanofiber composite membrane (PPSU nanofiber mat surrounded by Nafion® PFSA polymer) are contrasted with data for Nafion® 212 in Table 2 for a 60 μm thick membrane containing 70 vol% PFSA nanofibers. Proton conductivity scaled linearly with PFSA content, but water swelling did not. Of particular note is the very low in-plane (areal) swelling (six-times lower than that of commercial Nafion®). As expected, the mechanical properties of the nanofiber composite membrane improved, as compared to Nafion® 212; the proportional limit stress of a dry nanofiber membrane at 80°C was 50% higher than that of Nafion®.

The low in-plane swelling of the nanofiber composite membrane improved membrane electrode assembly (MEA) in a fuel cell humidity cycling durability test. A 30 μm thick nanofiber composite membrane was fabricated into a H₂/air fuel cell MEA, using the decal method of electrode attachment (0.4 mg/cm² Pt loading for the anode and cathode with 30% Nafion® binder content). Voltage-current fuel cell performance curves (5 cm² MEA) at 80°C with fully humidified feed gases are shown in Figure 2. The performance of the nanofiber membrane MEA is very good and essentially identical to that of Nafion® 212. To evaluate durability, a 25 cm² MEA was subjected to an open circuit voltage (OCV) humidity cycling experiment (80°C with repeated cycling of 2 minutes 100% RH H₂ and air and then 2 minutes 0% RH H₂ and air). The OCV was monitored with time during humidity cycling and the hydrogen crossover was periodically measured in situ at 100% RH using a standard limiting current technique [4]. Durability results are shown in Figure 3. With a failure criteria defined as a drop in the OCV below 0.8 volts, it was found that Nafion® 212 failed after 546 hours whereas the nanofiber composite MEA failed after 842 hours (a 54% increase in lifetime vs. Nafion® 212). There was a dramatic increase in hydrogen crossover current density when the OCV dropped below 0.8 V, from 2 mA/cm² to 13 mA/cm².

Conclusions and Future Work

Conclusions

- Norland Optical Adhesive was replaced by polyphenylsulfone as the inert/uncharged component in nanofiber composite membranes.

![FIGURE 1. Freeze-fractured SEM cross-section of a Nafion®/PPSU nanofiber composite membrane (with Nafion® surrounding PPSU nanofibers; 70 vol% Nafion®).](image)

![FIGURE 2. H₂/air fuel cell performance of a nanofiber composite membrane MEA and a Nafion® 212 MEA. The nanofiber composite was 30 μm thick (dry). Fuel cell conditions: 80°C, fully humidified gases, 100 mL/min H₂ flow rate, 500 mL/min air flow rate.](image)

![TABLE 2. Conductivity, Swelling, and Mechanical Properties of a Nafion®-Based Nanofiber Composite Membrane and Nafion® 212](table)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Conductivity [mS/cm]</th>
<th>In-Plane Swelling (%)</th>
<th>Volumetric Swelling (%)</th>
<th>Mass Swelling (%)</th>
<th>Proportional Limit Stress [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanofiber Composite 4</td>
<td>66</td>
<td>6%</td>
<td>42%</td>
<td>31%</td>
<td>10.3</td>
</tr>
<tr>
<td>Nafion® 212</td>
<td>95</td>
<td>37%</td>
<td>75%</td>
<td>37%</td>
<td>6.8</td>
</tr>
</tbody>
</table>

1 In water at 23°C; 2 - In water at 100°C; 3 - Dry membrane at 80°C; 4 - 70 vol% Nafion® PFSA, 30 vol% polyphenylsulfone
A new method for nanofiber composite membrane fabrication was developed (dual polymer fiber electrospinning followed by mat processing) with the elimination of a separate polymer impregnation step. Using the dual fiber approach, two types of nanofiber composite membranes were made: (1) a PPSU nanofiber mat embedded in PFSA polymer and (2) a PFSA nanofiber mat embedded in (surrounded by) a PPSU matrix. The proton conductivity of the processed dual fiber mats (where the PFSA polymer is either DuPont’s Nafion® or an 825 EW polymer from 3M Corporation) scaled linearly with the membrane  ionomer content.

All dual fiber membranes exhibited very low in-plane (areal) swelling and reduced volumetric and gravimetric swelling. MEAs fabricated from a nanofiber composite membrane (Nafion® polymer with a reinforcing mat of PPSU nanofibers) performed well in a H₂/air fuel cell at 80°C and 100% RH. The fuel cell polarization curve (power output) of a 30 µm thick composite membrane was identical to that of commercial Nafion® 212.

The durability of MEAs made with a nanofiber composite membrane was significantly improved, as compared to Nafion® 212 (a 70% increase in MEA lifetime, as determine from OCV humidity cycling tests).

Future Work
- Prepare and test nanofiber composite membranes with PFSA + sulfonated polyphenylene + polyphenylsulfone (using the dual fiber electrospinning approach).
- Examine different inert/uncharged polymers
- Prepare and test MEAs with nanofiber network composite membranes.
- Investigate and test electrospun nanofiber fuel cell electrodes (focus on the cathode).

Patents

FY 2010 Publications/Presentations
References


V.D.7 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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Contract Number: DE-FG36-06GO16032

Subcontractor:
Matthew H. Frey, and Hui Ren
3M Corporate Research Materials Laboratory
St. Paul, MN

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 heteropolyacid (HPA) functionalized with organic monomers (poly-polyoxometalates, 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 Fuel Cell 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>
<thead>
<tr>
<th>Target Date met</th>
<th>80°C/100% RH April 2008</th>
<th>30°C/60% RH August 2008</th>
<th>120°C/≤50% RH January 2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+ conductivity</td>
<td>300 mS cm⁻¹</td>
<td>126 ms cm⁻¹</td>
<td>&gt;100 ms cm⁻¹</td>
</tr>
</tbody>
</table>

RH – relative humidity

Accomplishments

- Fabricated new HPA-based polymers based on three distinct polymer chemistries which are all designed to allow the fabrication of films that will be highly proton conducting, durable, cost-effective and have the required mechanical properties of the PEM fuel cell membrane.
- Showed that the HPA linkages in these systems are robust and will survive 10 hrs of boiling water.
- Demonstrated that the new polymers systems are able to show as high proton conductivities as the generation I model system films studied previously.

Introduction

Currently, fuel cells based on perfluorosulfonic acid (PFSA) PEMs are limited to operating conditions of ≤80°C and very high inlet relative humidities, 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 relative humidity 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 H₂ economy and enable a smooth transition from fossil fuels to H₂ produced solely from renewable resources. Materials suitable for use in automotive PEM fuel cells are
being developed that have high proton conductivities, >0.1 S cm⁻¹ at 50% RH and operating temperatures of -30 to 120°C, low area specific resistance, <0.02 Ωcm⁻², and suitable for incorporation in a fuel cell membranes 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 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°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 initially chose to use acrylates as the co-monomers in this project as their commercial availability and large variation made them a virtual polymer system in a kit, leaving the synthetic effort to be devoted to making the HPA monomers. This polymer system allowed 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 obtained easily 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 previously been synthesized as gels [3], we are able to fully disclose our research using this model system. However, the system has certain inherent disadvantages that could include that the acrylate ester linkage is unstable to hydrolysis and that polymers contain readily oxidizable methylene groups.

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 new polymer chemistries so that we can address the additional criteria, such as cost, durability, and mechanical integrity that are needed for a practical proton conducting polymer. We have also used nuclear magnetic resonance (NMR) to measure both 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 correlating proton conductivity with morphology as observed by atomic force microscopy (AFM) and small angle X-ray scattering (SAXS) to enable us to understand structure proton conductivity relationships.

**Results**

We maximized the loading of HPA, the protogenic group in the acrylate model system. In Figure 1 we show data for an 85 wt% HPA substituted polymer. The proton conductivities at 95% RH are very impressive, 0.48 S cm⁻¹ at 90°C. The Ea for this is 10 kJmol⁻¹ similar to the 11 KJmol⁻¹ reported for PFSA polymers [4]. At an RH of ≤80% the Eₐ more than doubles to 23 kJmol⁻¹. At 50% RH the material achieves a proton conductivity of >0.1 S cm⁻¹ at 80°C. These results are extremely encouraging, but unfortunately the material is somewhat brittle and seems to undergo morphological changes with RH and time from film forming. In Figure 2 we show some details of the morphology of these generation I films. The AFM image shows that the protogenic HPA part of the polymer forms a channelized network with channel diameter around 50-100 nm. These same channels that facilitate proton conduction are also speculated by us to be the micro-structural cause of the films inherent brittleness. We also show in this figure the stacked SAXS patterns for the material hydrated from a RH of 30% to 95%. A strong ionomer peak is
observed at 5Å⁻¹ which shifts to the left with hydration. Using a unified Guinier and Porod fitting of the data gives a number of useful parameters, some of which are plotted at the bottom of the figure. The level 1 parameters are for the HPA moieties which maintain a diameter of 10 Å and spherical symmetry (p =4). The level 2 fit corresponds to the clustering of the HPA moieties, it can be seen that these clusters generally swell from 120 to 160 Å and become more symmetrical with more moisture (p increase from 3 to 4).

While the proton conductivities of these generation I acrylate films are impressive, they have a number of design flaws: 1) hydrolyzable ester linkages, and 2) a potentially oxidatively unstable methylene based backbone. To overcome these deficiencies and so that we can optimize the mechanical properties of the film we investigated two new generation II systems, designed to have no ester linkages. In system A the HPA was functionalized so that it could be co-polymerized into a perfluoro polymer. In system B a very simple polymerization scheme has been investigated. In a generation III approach, no ester linkages or methylene groups, being investigated at 3M, a perfluorinated polymer is functionalized such that the HPA can be directly attached to the preformed polymer. Great difficulty was found in forming insoluble films from systems A and B, however we have recently found success blending these co-polymers with similar non-ionomeric polymers and have formed robust thin films.

The generation III films are the most advanced. Robust thin films have been obtained. These materials have been boiled in water for 10 h to investigate the robustness of the linkages to the HPA. Thermogravimetric analysis data for this test is shown in Figure 3. This figure shows that before leaching that polymer contained 34 wt% inorganic material and that after the leaching study the organic material was reduced to 21 wt%. Considering the severity of the test and that this system is still not optimized this result is remarkable and bodes well for future development of the system. In Figure 4 we show the proton conductivity data for the generation 3 film compared with the 3M 825 equivalent weight PFSA ionomer at 95°C. The conductivity is lower than the 3M ionomer, but consider that there is only 34 wt% of HPA in this material. The material does achieve 0.1 Scm⁻¹ at 80% RH and 95°C. It should be obvious that the impressive conductivities obtained for

**FIGURE 2.** Morphological data for a co-85 wt% H₄[SiW₁₁O₄₀(Si(CH=CH₂))₂]–co-butyl acrylate-co-hexanediol diacrylate polymer, upper left AFM under ambient conditions, upper right, SAXS patterns, bottom, selected unified fit parameters from SAXS patterns.
We will continue to optimize generation II and III films for proton conductivity, oxidative stability and mechanical integrity. We will use SAXS, pulsed field gradient spin echo NMR and proton conductivity measurements to understand structure activity relationship sin these films.

**FY 2010 Publications/Presentations**


5. “Understanding the high proton conductivity observed in the polypoms in terms of morphology.”

**Conclusions and Future Directions**

- Very high proton conductivities were obtained for generation I films with high loadings of HPA at 50% RH.
- Two new co-polymer systems were developed which have now been fabricated into films.
- A generation III film was developed in which significant amount of HPA were immobilized with respect to boiling water and adequate proton conductivity was observed.


References


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 2015 targets).
- Improve mechanical properties to significantly increase the durability and reduce the gas cross-over.
- Reduce the membrane area specific resistance (ASR) to increase cell performance and lower the capital and operating costs.

Technical Barriers

This project addresses the following technical barriers from the Multi-Year Research, Development and Demonstration Plan [1] of the DOE Fuel Cell Technologies Program:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project is developing a composite membrane (mC²) to meet the following DOE 2015 technical targets for membranes:

- Membrane Conductivity: At ≤120°C: 0.1 S/cm; at room temperature: 0.07 S/cm; at -20°C: 0.01 S/cm
- Membrane ASR: 0.02 Ωcm²

Accomplishments

- Conductivity: Met DOE conductivity targets (both in-plane and through-plane).
- ASR: Met DOE membrane ASR target.
- Cross-Over: Almost met DOE hydrogen cross-over target.
- Polymer Development: Prepared three batches of improved low equivalent weight (EW) co-polymer, with increased molecular weight for higher mechanical strength.
- Additive Development:
  - Identified an improved protonic conductivity enhancer with 80% higher density of mobile protons.
  - Synthesized the improved protonic conductivity enhancer in 25 g batch size.
  - Fabricated and characterized nine additive batches (water retaining and proton conducting).
- Cost Reduction: Reduced the cost of the protonic conductivity enhancer by >80% by reducing cost of starting materials by 93%, reducing the number of processing steps from 12 to 7 and increasing the batch size by 25x.
- Composite Membrane Fabrication:
  - Developed new solvent system for better compatibility with the improved protonic conductivity enhancer.
  - Incorporated additives into mC² at the nano-scale, without significant agglomeration.
  - Synthesized over 13 batches of mC².
- Membrane Characterization:
  - Measured in-plane conductivity of over 18 membrane samples.
  - Measured through-plane conductivity of two membrane samples.
- Membrane Electrode Assembly (MEA) Fabrication:
Developed process compatible with mC² components in collaboration with the University of Central Florida (UCF).

Fabricated >8 MEAs of up to 25 cm² active area (UCF).

• MEA Testing: Two MEAs comprehensively tested by UCF in 11-day cell tests (DOE protocol).

Introduction

This project is focused on the development of composite proton exchange membranes (PEMs) that can operate at low relative humidity (RH) and over a wide temperature range (-20 to 120°C). Their main application is in transportation fuel cells. In addition, FCE is considering use of these membranes for co-production of hydrogen from high-temperature fuel cells. The higher operating temperature imparts improved tolerance to impurities, such as carbon monoxide, thereby increasing the co-production efficiency and simplifying the system.

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 2015 goals for transportation fuel cells.

Approach

The approach to address each of the DOE target parameters is summarized in Table 1. The emphasis in the past year has been to develop and integrate additives with a greater density of highly mobile protons.

Results

This year’s efforts were focused on improving the performance and lowering the cost of the multi-component composite membrane, named mC². The efforts were centered on improving the following mC² components:

• Co-polymer
• Water retention additive
• Protonic conductivity enhancer

<table>
<thead>
<tr>
<th>Target Parameter</th>
<th>DOE Target (2015)</th>
<th>Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity at:</td>
<td>0.1 S/cm</td>
<td>Multi-component composite structure, lower EW, additives with highly mobile protons</td>
</tr>
<tr>
<td>≤120°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Room Temperature</td>
<td>0.07 S/cm</td>
<td>Higher number of functional groups</td>
</tr>
<tr>
<td>-20°C</td>
<td>0.01 S/cm</td>
<td>Stabilized nano-additives</td>
</tr>
<tr>
<td>Inlet water vapor</td>
<td>&lt;1.5 kPa</td>
<td>Immobilized cluster structure</td>
</tr>
<tr>
<td>partial pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen and</td>
<td>2 mA/cm²</td>
<td>Stronger membrane structure; functionalized additives</td>
</tr>
<tr>
<td>oxygen cross-over</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 1 atm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area specific</td>
<td>0.02 Ωcm²</td>
<td>Improved bonding capability for MEA</td>
</tr>
<tr>
<td>resistance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost</td>
<td>$20/m²</td>
<td>Simplified polymer processing</td>
</tr>
<tr>
<td>Durability with</td>
<td>5,000 hours</td>
<td>Thermo-mechanically compliant bonds, higher glass transition temp.</td>
</tr>
<tr>
<td>cycling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unassisted start</td>
<td>-40°C</td>
<td>Stabilized cluster structure design</td>
</tr>
<tr>
<td>from low temp.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The co-polymer provides the basic building block for the membrane. It is an advanced perfluoro sulfonic acid polymer (PFSA) with a short side chain. It has a higher density of functional groups (lower EW) compared to long side chain polymers, such as Nafion®. The lower EW leads to significantly higher proton conductivity. It comes without a reduction in mechanical strength, due to a higher crystallinity of the short side chain PFSA. During this year, the molecular weight was increased. This leads to greater polymer chain entanglement and therefore better mechanical properties. The higher molecular weight has the added benefit of improving the film forming properties of the polymer dispersion.

The membrane 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 [2]. This path is designed to efficiently transport protons at high temperature as well as subfreezing conditions. Zeolite nanoparticles have been developed to retain water in the membrane. They have a high water uptake capacity without dimensional change, since the water is contained within the three-dimensional tunnel structure. To enhance the proton conductivity of the membrane, a novel superacid was developed. It has highly mobile protons to increase the transfer rate of protons through the membrane. During the past year, its further development was focused on increasing proton density and lowering the cost.
**mC² Conductivity:** The composite membrane concept has been validated by demonstrating conductivity exceeding the DOE conductivity target at 120°C (Figure 1). This data was obtained with mono-valent protonic conductivity enhancer. An improved, di-valent conductivity enhancer was identified, which contains two highly mobile protons per molecule. Compared to the mono-valent conductivity enhancer, the molecule size is only about 10% larger. Therefore, the proton density is increased by 80%. The conductivity of a composite membrane incorporating the water retaining additive as well as the improved conductivity enhancer is expected to exceed that shown in Figure 1. The benefits of the improved conductivity enhancer are summarized in Table 2.

**mC² Fabrication:** Due to the altered chemistry of the improved conductivity enhancer, the mC² fabrication process used successfully for the mono-valent conductivity enhancer resulted in undesirable additive interaction and a poor quality membrane. This made changes to the solvent system and processing conditions necessary. The requirements of the solvent system include: (i) ability to fully disperse the co-polymer as well as the nano-additives, (ii) prevent agglomeration of the nano-additives, (iii) favorable film forming properties, (iv) evaporate from the membrane film in a reasonably short period of time (minutes to hours) without affecting additive dispersion and, (v) do not affect the mobility of the protons in the additives or the co-polymer. Since the processing steps have to be compatible with all membrane components, the changes in conductivity enhancer and solvent system have also required changes in the processing conditions.

In order to facilitate mC² fabrication, the following improvements were made:

- Increased molecular weight of co-polymer to enhance chain entanglement and additive immobilization.
- Synthesized dispersion with 3x higher polymer content, to lower the solvent content and increase viscosity for improved film formation.
- Eliminated hot acid treatment step from mC² processing to avoid stability issues of the nano-additives.

While the membrane quality and conductivity have significantly improved after these changes, a stability problem has been identified. Further optimization of the solvent system and processing conditions are necessary to realize the full potential of the improved conductivity enhancer and obtain the expected conductivity results exceeding those shown in Figure 1. A systematic optimization study is underway. It includes microstructural analysis of the components and mC², in order to detect interactions at the nano-scale level and guide the materials and processing changes.

**Membrane Characterization:** Membrane samples were supplied to UCF for characterization. Through-plane conductivity and resistance measurements for these membrane samples were obtained by UCF from its team member Scribner Associates, Inc. Figure 2 shows the through-plane conductivity at 120°C as a function of RH. The solid squares represent the conductivity before correction for non-membrane ohmic resistance. The estimated corrected conductivity for sample #2 at 30% RH is 122 mS/cm, shown by the red empty circle. The extrapolated corrected conductivity up to 50% RH is shown by the dashed line. It significantly exceeds the DOE target. The correction is based on Scribner’s previous data obtained with Nafion® membranes.

Through-plane membrane ASR measurements at 120°C are shown in Figure 3. The uncorrected resistance values are shown by the solid squares. The corrected ASR for sample #2 is shown by the
empty circles at 20 and 30% RH. When this data is extrapolated to 50% RH, it suggests that the membrane itself meets the DOE target. The ASR correction is based on Scribner’s previous data obtained with Nafion® membranes. A study to determine the resistance contributions other than the membrane itself in the case of FCE’s membrane is planned. It will allow estimating the (corrected) membrane conductivity and ASR with greater accuracy.

**MEA Fabrication and Testing:** UCF has been tasked by DOE to fabricate MEAs using membrane samples supplied by FCE, to independently validate their performance. The MEA fabrication process developed by UCF was adapted for the mC², to avoid ion exchange with metal ions that could potentially have an adverse effect on additive stability. The modified process also significantly reduces the number of processing steps and processing time (lower cost). Using this process, MEAs were successfully fabricated by UCF, as shown in the inset in Figure 4. This MEA was fabricated using a 25 µm thick baseline membrane and matching co-polymer in the electrodes. The MEA was subjected to an 11-day cell test protocol developed by UCF in collaboration with DOE. The performance at 120°C, 35% RH and 7 psig on H₂/air was over 600 mV, and about 750 mV at 95°C and 83% RH. The hydrogen cross-over was determined by linear sweep voltammetry, as shown in Figure 4. It meets the DOE 2015 target of 2 mA/cm² at 95°C and closely approaches it at 120°C. It can be seen that the hydrogen cross-over did not increase (day 6 vs. day 4) after testing at 120°C (day 5). The area specific cell resistance was 0.045 Ωcm² at 95°C, 83% RH and 0.105 Ωcm² at 120°C, 35% RH. It includes contributions from membrane, electrodes, gas diffusion layers and interfacial resistances between all cell components. The increase in cell resistance with increasing temperature and decreasing RH suggests that incorporating the additives developed in this program for the membrane into the electrodes has the potential to lower the overall cell resistance and increase the cell performance, especially at high temperature and low RH.

**Conclusions and Future Direction**

A multi-component composite membrane design for high temperature and low RH operation has been implemented to fabricate membranes with enhanced performance at the DOE target conditions (Table 1). Accomplishments include:

- Validated mC² concept by demonstrating conductivity in excess of the DOE targets via in-plane (Figure 1) and through-plane measurements (Figure 2).
- Identified and synthesized a protonic conductivity enhancer with 80% greater proton density and lower cost (Table 2).
- Measured membrane ASR that is estimated to meet the DOE 2015 target (Figure 3).
- Determined that the hydrogen cross-over of a 25 µm membrane almost meets the DOE 2015 target (Figure 4).

In the final year of the current project we will continue the composite membrane development, with an emphasis on the following activities:

- Continue to develop advanced polymer dispersions with low equivalent weight (higher number of functional groups) and high molecular weight.
- Optimize and further simplify integration of the advanced additives.
- Continue to compare membrane conductivity and area specific resistance to the DOE 2015 targets (UCF).
Perform fuel cell testing at 95°C and 120°C.
Perform MEA characterization and durability testing per DOE protocol (UCF).

**FY 2010 Publications/Presentations**


**References**

V.D.9 Improved, Low-Cost, Durable Fuel Cell Membranes

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 hr with cycling

Accomplishments

- Demonstrated and reproduced order-of-magnitude increase in conductivity for M70 lab-produced materials versus M43.
- Completed scale-up of novel monomer to multi-kilo scale for M70 polyelectrolyte (PE) synthesis.
- Identified (and eliminated) cause of PE leaching in initial batches of M70 membranes.
- Identified (and eliminated) cause of defects present in initial batches of M70 membranes.
- Completed successful M70 pilot blend production and membrane casting campaign.
- Demonstrated and optimized blending parameters to incorporate biPhenyl-based disulfonated polysulfone (BPSH)-type PEs into Kynar® poly(vinylidene fluoride) (PVDF) blend membranes.

Introduction

Proton exchange membrane (PEM) fuel cells rely on perfluorosulfonic acid containing perfluoropolymers (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 automotive applications. To overcome these limitations, new membrane chemistries are needed, preferably based on readily available materials that will help keep the cost of commercial production of membranes low. The improvement of the proton conductivity of these materials under low RH conditions will allow for a wider range of operation of fuel cell stacks and reduce the complexity of the balance of plant, leading to lower overall cost and faster adoption of hydrogen fuel cells into automotive applications.
**Approach**

Arkema’s approach comprises the preparation of blends of PVDF and highly sulfonated PEs, in which, the two polymers are very intimately mixed. The originality of this approach is to have a methodology to independently vary material properties that govern ion conductivity from other requirements. Kynar® PVDF provides an exceptional combination of properties that make it ideally suited as the non-sulfonated component in the polymer blend membranes. 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 H₂SO₄). As evidence of the exceptional electrochemical stability and mechanical toughness of Kynar® PVDF, it is widely used as binder material in lithium ion batteries. Also, these novel materials exhibit a design flexibility inherent to their production process and can offer a much lower cost than PFSA-type membranes (at equal production volume) because synthetic requirements and their preparation process is simpler.

**Results**

The new PE family (M70), is based on novel monomers, each bearing more than one sulfonate group as depicted in Figure 1. This material (PE alone) has an extremely low equivalent weight of ~150 g/molH⁺. When incorporated into a blend with a non-sulfonated polymer (Kynar® PVDF), we have found that an optimum equivalent weight of between 400 and 600 g/molH⁺ is best to produce membranes displaying adequate mechanical properties as well as high proton conductivity. The new materials are hydrolytically stable at 80°C under hydrated, acidic conditions and we have optimized the blending process with Kynar® PVDF and the membrane activation (protonation). The process conditions have been found to significantly influence membrane appearance, morphology, and conductivity.

While the proton conductivity versus RH of M70 is below that of a PFSA-based membrane, particularly at low RH (Figure 2) we understand that ex situ conductivity measurements are only general trend indicators of in situ fuel cell performance. As such, we are moving forward with MEA fabrication and in situ testing of this material. In addition, we expect further improvement as work continues on the synthesis of this new PE, the blending process and membrane processing/activation.

The PE and the PVDF blend membrane produced using it are hydrolytically stable at 80°C, showing no chemical degradation in ex situ durability tests, but the blend membrane showed signs of sulfur loss due to leaching of the PE during aqueous processing/washing. The leaching was traced back to the synthesis of the PE. Specifically, one of the monomers used was not homogeneously distributed in the copolymer. A kinetic study of the polymerization revealed that this monomer is consumed at approximately twice the rate of that of the other species, and this problem was addressed by optimizing the monomer feed method during polymerization.

It was found that the M70 PE was not an exact ‘drop-in’ for the process previously used to produce M43 membranes. Therefore the blend formulation parameters were systematically explored to generate membranes with intimately-mixed PE and PVDF components (Figure 3). The new M70 membrane shows very impressive conductivity at 90% RH (>200 mS/cm), but has roughly half of the conductivity of NR-211 at 50% RH. MEA results of lab-produced membranes show that M70 has comparable beginning-of-life performance to PFSA membranes at high and moderate RH conditions at 80°C (Figure 4).
Based on these promising results, a pilot-scale campaign of M70 was run to perform more detailed studies of its properties, including beginning of life performance, open circuit voltage durability, and RH cycling. Early in the fourth quarter of 2009 we produced kg-scale quantities of M70 PE, which unfortunately produced severe defects in the lab-cast membrane made to qualify the material. After a careful analysis of the materials tested, we traced the problem back to two parameters associated with the polymerization. These parameters were adjusted to make a second kg-scale batch that has not produced any substantial amount of defects. A pilot production run of this material was conducted in May 2010 and is currently under evaluation.

As an alternative to the PE materials generated in-house, polyether-sulfone copolyelectrolytes (bisphenolsulfone [BPS]-type) have remained interesting due to their extreme thermal stability. BPS materials containing higher sulfonic acid contents (BPS-100) with and without crosslinkable endgroup functionality have been investigated in PVDF-blend membranes for conductivity under varying RH conditions. As these materials have vastly different chemical structures from those used in M43 and M70, reoptimization of blending parameters has been necessary. It was found that intimately-mixed blends of PVDF and BPS-100 without crosslinkable endgroups could be produced under the proper conditions. However, these materials showed a significant amount of PE leaching during processing and operation due to the lack of crosslinking in the BPS-100 materials. To address the polyelectrolyte leaching, Prof. McGrath’s group at Virginia Tech has provided BPS-100 materials bearing amine or alkyne end-group functionality to crosslink the BPS. We have investigated the blending of these materials as well as the concurrent crosslinking during membrane production on the laboratory-scale. We have seen success in reducing the amount of leaching observed using these materials but the conductivities of the membranes are not as high as M70 (Figure 2).

**Conclusions and Future Directions**

- Evaluated and addressed blending and defect problems in M70 materials.
- Completed successful pilot casting campaign of M70 membrane.
- Confirmed order-of-magnitude increase in conductivity of M70 versus M43.
- Confirmed improved in situ MEA performance under low RH conditions of M70 vs. M43.
- Evaluated and successfully blended BPS-100 materials.
  - Continuing testing of pilot-produced M70 membranes.
  - Continuing process development toward commercialization of M70 membranes.

**Special Recognitions & Awards/Patents Issued**

FY 2010 Publications/Presentations


V.D.10 Protic Salt Polymer Membranes: High-Temperature Water-Free Proton-Conducting Membranes

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Contract Number: DE-FG36-06G016029

Subcontractors:
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- Wiley Youngs, 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) and up to 50% relative humidity (RH).
- Effectively no co-transport of molecular species with proton.
- Reduction of fuel cell overvoltage.
- Durable, good mechanical strength and stability.

Technical Barriers

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

(A) Durability
(C) Performance

Technical Targets

The DOE goal is to make a stable electrolyte membrane that has a proton conductivity greater than 0.1 Siemens centimeter-1 at 120°C when supplied gases with low 25 to 50% RH and greater than 0.01 at -20°C.

Accomplishments

The DOE targets and summary of the major works and accomplishments in 2009 and 2010 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

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
</table>
| **DOE Targets** | Make a membrane with conductivity of 0.1 S/cm at 0 to 50% RH over the full range of temperature (-40 to 120°C).  
Determine and report best membrane conductivity by February 2009.  
| **Current Year Summary** | Liquid and polymeric high temperature proton-conducting protic salt membranes were made and tested for conductivity and stability in fuel cell conditions, namely:  
(i) Seven new stable fluorinated protic ionic liquids (pILs).  
(ii) Protic ionic membranes (pIMs) with non-leachable salt moieties.  
Selected new inorganic indium tin phosphate (ITP) membranes were sent to Scribner and Bekktech for validation of conductivity at various temperatures and relative humidities. |
| **Accomplishments February 2009** | A neat ITP membrane [1] was made that has conductivity of 0.16 S/cm from 25°C to greater than 120°C and 0% RH.  
Crossover in pure ITP membrane was eliminated by blending 70 wt% ITP with 30 wt% of a proton-conducting organic polymer, polyvinyl pyridinium phosphate (PVPP) [2], but at a cost of reduced conductivity. |
| **Accomplishments 2010** | Improved synthesis and processing of ITP and organic polymer blended membranes. Mixing of reagents during heating was found to be critical for reproducibly making ITP.  
Membrane samples were sent to Scribner and Bekktech for conductivity testing |
Scribner and Associates checked the conductivity of an indium tin phosphate (In$_{0.1}$Sn$_{0.9}$P$_2$O$_7$ or ITP) sample that was 1.23 mm thick x 12 mm diameter. This sample was tested using electrochemical impedance spectroscopy (EIS) in a H$_2$ atmosphere at 30, 80, and 120°C from 20 to 95% RH and the result are shown in Figure 1. The conductivity was evaluated from the impedance data using an equivalent circuit model and the ITP data taken at 80°C, 70% RH with this model gives a membrane resistance of 0.754 ohm, which corresponds to a conductivity of ~1.40 mS/cm. The conductivity was found by Scribner to decrease when the temperature was raised to 120°C, which was unexpected, because for tests done at Arizona, the conductivity increased smoothly with increasing temperature from room temperature up to 250°C.

**Introduction**

A membrane that has high proton conductance at temperatures up to 120°C without the need for water would allow for a more efficient and compact PEM fuel cell. Presently PEM fuel cell electrolyte membranes need water as an ionizing solvent which results in three consequences: 1) operation below 80°C and complex humidifiers to maintain solvent water, 2) large radiators to reject waste heat, and 3) lower performance of platinum catalysts. 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 three consequences of using water present barriers to the use of fuel cells as power sources. This project aims to make a membrane with anhydrous proton-containing salts to conduct proton from -40 to 120°C and to study the fundamental mechanism of proton conduction in these salt membranes. Our team discovered that neat pIL electrolytes and crystalline solid versions have high proton conductivities from ambient temperatures to over 200°C. A pIL 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: i) the rotational freedom of the nearly symmetrical constituent ions and, from ii) having an optimal difference in pKa of the constituent acid and base.

**Approach**

The approach has two parts: 1) synthesis of pILs and solid membranes and 2) characterization of the membranes for conductivity, stability, and elucidation of the proton conduction mechanism.

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. Polymer backbones, acids and bases have been varied to optimize PEM proton conduction, stability, and other properties. Liquid and solid membrane salt-electrolytes are characterized for proton conductivity by EIS and for stability by thermal gravimetric analysis (TGA) and by monitoring fuel cell performance in time. The mechanism of the transport of protons, anions, and molecules in pILs and protic ionic membranes (pIMs) is being investigated by: 1) pulse field gradient nuclear magnetic resonance (NMR) to measure the diffusivity of ions in liquid and solid states, 2) multipulse solid-state NMR to measure the molecular motions and interactions of species in solid membranes, and 3) electrochemical NMR to measure distribution of species during proton conduction in solid membranes.

**Results**

The preparation and processing of the ceramic (ITP) membranes [1] were further developed so that these high-performance advanced materials can be made reproducibly. These ITP ceramic materials and blends with organic polymers, like PVPP [2] and polyphosphazenes (PPhz) have shown proton conductivities in excess of 0.1 S/cm.

**Preparation and Performance of ITP**

A mass of indium oxide (0.5027 g), tin oxide (4.8933 g) and aqueous phosphoric acid reagents (85%, 12.1685 g) were mixed in a ceramic crucible while stirring at 500°C for approximately 1 hour and then calcined in the crucible (uncovered) at 650°C for 2.5 hours. The calcined material was ground in a mortar and pestle and then cold pressed at 6,000 lbs for 1 minute to form a pellet membrane. The pellet was heated at 200°C for 1 hour. Each side of the membrane
pellet surfaces was coated with a 20 nm thick Pt layer by direct current sputtering. The ITP membrane was then characterized for proton conductivity as shown in Figure 2.

Recently a new inorganic/organic composite was made using 90 wt% ITP with 10 wt% of organic binder PVPP. The conductivity is shown in Figure 3.

This 90% ITP and 10% PVPP blend showed over an order of magnitude greater conductivity than 70% ITP and 30% PVPP shown last year.

**pILs**

In addition to the work on ITP, a number of fluorinated and heterocycle rich pILs were synthesized including: 2-fluoro-pyridinium triflate (2-FPTf), 2,6-difluoro pyridinium triflate (2,6–dFPTf), 2-fluoro-pyridinium trifluoromethyl sulfonimidate (2-FPTfSi), 2-fluoro-pyridinium trifluoromethyl sulfonimidide (2-FPTfSi), 1,2,5 triazole fluoroborate (1,2,5-tABF4), 1,2,4 triazole fluoroborate (1,2,4-tABF4), and guanadinium thiocyanate (GdSCN). These neat liquid salts had conductivity comparable to liquid aqueous electrolytes and were characterized in Walden plots (conductivity versus fluidity at different temperatures). Two of these, 2-fluoro-pyridinium triflate and guanadinium thiocyanate, displayed super protonic conductivity, that is, their proton conductivity increased with temperature more rapidly than their fluidity (inverse of viscosity) and both 2-FPTf and GdSCN showed proton conductivity >0.1 S/cm at 120°C and 0% RH. These two salts are recommended as the pendant groups in polymers for making a PEM with high conductivity with no need for hydration.

Non-platinum metals can be used for catalyzing oxygen electroreduction in these anhydrous proton conducting salts. In particular palladium and tungsten appeared good candidates as they had comparable oxygen reduction overpotentials as Pt as indicated by preliminary voltammetry experiments.

**Conclusions and Future Directions**

**Conclusions**

- Fiscal Year (FY) 2009: Protic liquid and solid salt electrolytes give “dry” proton-conducting membranes with conductivities found at Arizona to be ≥ 0.1 S/cm at 120°C and 0% RH but not confirmed at Bekktech or Scribner to date.
- FY 2010: Non-aqueous electrolytes could enable use of non-Pt catalysts.
- FY 2009–FY 2010: Inorganic/organic polymer blends of dry proton conductors give non-porous proton-conducting membrane for simplified fuel cell operation in more compact system (no humidifier and smaller radiator).
Future Directions

- Make and test proton conductivity and fuel cell behavior for membranes based on:
  - ITP
  - blends of ITP and organic polymers
- Send to Bekktech for confirmation of conductivity found at Arizona State University.
- Correlate NMR and conductivity measurements.
- Study voltammetry of Pt on a solid salt (ITP) membrane electrolyte to find electrochemical active area of Pt in a salt membrane electrode assembly (MEA) and compare to the Pt area in a well-engineered MEA. Normalize performance in terms of electrode area for fair comparison of these two systems.
- Interpret voltammetry of Pt on ITP for Pt-oxide. If Pt-oxide free, consider inspection by X-ray irradiation to confirm if Pt stays metallic at high potential (1.2 V) or not. This X-ray work would be done with Dr. Deborah Myers at the Advanced Photon Source at Argonne National Laboratory.
- Optimize membranes from inorganic (ITP) and organic polymer blends:
  - Synthesis of ceramic/organic membranes of ITP and organic polymers (such as polyphosphazene triazoles with various immobilized salts).
  - Process ITP/polymer blend membranes for higher conductivity, flexibility, and toughness.
  - Test the ITP membrane conductivity as a function of humidification of gases and test samples after exposure to water (to probe for conductivity/performance changes if any free ions are removed).

Special Recognitions & Awards/Patents Issued


FY 2010 Publications/Presentations


References

V.E.1 Advanced Cathode Catalysts and Supports for PEM Fuel Cells

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Contract Number:  DE-FG36-07GO17007

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• Jet Propulsion Laboratory (JPL), Pasadena, CA (Charles Hays, S.R. Narayanan)

Project Start Date:  April 1, 2007
Projected End Date:  March 31, 2011

Objectives

The objectives of this project are development of a durable, low cost (both Pt 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 PGM 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°C for 2,000 hours, ≤80°C for 5,000 hours, with cycling for transportation applications,
• 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (FCT 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 (NSTF) roll-good fabricated electrocatalysts and MEAs. Table 1 compares the NSTF current 2nd quarter, calendar year (CY) 2010 status with DOE electrocatalyst targets for 2010/2015 from Table 3.4.12 of the FCT MYRDDP. Additional rows were added to summarize recent accelerated durability test results. Unless noted otherwise, all metrics were obtained with the 2009 NSTF “best of class” catalyst-coated membrane (CCM) containing 0.10 mg-Pt/cm² on the cathode and 0.05 mg-Pt/cm² on the anode using a PtCoMn alloy catalyst. 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 mgPt/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

Water Management for Cool/Wet Operation (Task 5.2)

• Demonstrated new paradigm for water management of thin layer electrodes based on sub-atmospheric anode pressure and high liquid water permeability anode GDLs that: a) enables steady-state current density up to 2.0 A/cm² at 30 to 35°C with NSTF MEAs in 50 cm² single cells, and b) 5 second 0 -1 A/cm² load transients at 50°C and 140% relative humidity (RH).
• Demonstrated hybrid MEA with gradient cathode catalyst construction that enables steady-state 1 A/cm² at 30°C, successful load transient 0 -1 A/cm² step at 40°C, 140% RH, and which does not reduce performance at 80°C over the standard NSTF CCM.
<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>Targets 2010 / 2015</th>
<th>Status: Values for roll-good CCM w/ 0.15mg_Pt/cm² per MEA or as stated</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM Total Content</td>
<td>g_Pt/kW Rated in stack</td>
<td>0.3 / 0.2</td>
<td>&lt; 0.18g_Pt/kW for cell V &lt; 0.67 V in 50 cm² 2 cell at 150 kPa inlet, and 0.19 g_Pt/kW in OEM 400 cm² 2 stack</td>
</tr>
<tr>
<td>PGM Total Loading</td>
<td>mg PGM / cm² total</td>
<td>0.3 / 0.2</td>
<td>0.15, A+C with current PtCoMn alloy</td>
</tr>
<tr>
<td>Durability under Load Cycling (membrane lifetime test)</td>
<td>Hours, T ≤ 80°C Hours, T &gt; 80°C</td>
<td>5000 / 2000</td>
<td>&gt; 6500 hrs. 3M PEM (20μm, 850 EW w/ stabilizers), 50cm², 80/64/64 °C 2000 hrs (OEM short stack, 0.1/0.15)</td>
</tr>
<tr>
<td>Mass Activity (150kPa H₂/O₂, 80°C, 100% RH, 1050 sec)</td>
<td>A/mg-Pt @ 900 mV, 150kPa O₂</td>
<td>0.44 / 0.44</td>
<td>0.24 A/mg in 50 cm² w/ PtCoMn 0.40 A/mg in 50 cm² with new Pt₃Ni₇</td>
</tr>
<tr>
<td>Specific Activity (150 kPa H₂/O₂ at 80°C, 100% RH)</td>
<td>μA/cm²-Pt @ 900 mV</td>
<td>720 / 720</td>
<td>2,100 for PtCoMn, 0.1mg_Pt/cm² 2,500 for new Pt₃Ni₇, 0.1mg_Pt/cm²</td>
</tr>
<tr>
<td>Accel. Loss: 30,000 cycles, 0.7 – 0.9V step, 30 s hold at 80/80°C</td>
<td>- mV at 0.8 A/cm²</td>
<td>&lt; 30mV &lt; 40%</td>
<td>~ 0 mV / -10mV, Cat=0.15/0.1 mg/cm² ~ 0% / -22%, Cat=0.15/0.1 mg_Pt/cm²</td>
</tr>
<tr>
<td>Accel. Loss: 200 hr hold @ 1.2 V at 95°C, H₂/N₂, 150kPa, 80% RH</td>
<td>- mV at 1.5 A/cm²</td>
<td>&lt; 30mV &lt; 40%</td>
<td>+ 25mV gain at 1.5 A/cm² ~ - 17% loss (Cat. = 0.15 mg_Pt/cm²)</td>
</tr>
<tr>
<td>OCV hold without PEM failure under 250/200 kPa H₂/air, 90°C, 30%RH</td>
<td>Hours</td>
<td>500 / 20</td>
<td>610/1200 for Cath. = 0.1/0.15mg_Pt/cm² H₂ Crossover &lt; 20 mA/cm², F⁻ ion release rate &lt; 0.5 µg/cm²/day</td>
</tr>
<tr>
<td>Accel. Loss: 4,000 cycles 0.8 -1.2V, 20mV/sec, 95/95/95°C, 200kPa H₂/N₂</td>
<td>Specific Activity</td>
<td>?? ??</td>
<td>-14 ± 15% loss in mA/cm²_Pt -23 ± 6% loss of cm²_Pt/cm²_plonew</td>
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Catalyst Activity and Understanding (Task 1)

- Increased PtCoMn mass activity 30% to 0.24 A/mg and demonstrated Pt₃Ni₇ alloy with mass activity of 0.40 A/mg and absolute activity at 900 mV of 40 mA/cm² with 0.1 mg/cm².
- Developed a post-fabrication treatment process that is roll-good compatible and increases oxygen reduction reaction (ORR) mass activity up to 50% for as-made PtCoMn and Pt₃Ni₇ alloys.
- Made catalyst deposition process improvement that gives NSTF pure Pt performance equal to PtCoMn with much greater Pt face centered cubic (hkl) grain sizes.

Catalyst and MEA Durability (Task 2)

- Demonstrated MEA load cycling lifetime of >6,500 hours with 0.05/0.10 mg/cm² loaded 20 µm membrane having no reinforcement.
- Demonstrated that with chemical stabilizers in the membrane, the 500 hour DOE target for open circuit voltage (OCV) hold under H₂/air is exceeded by a factor of 2X for anode/cathode loadings of 0.05/0.15 mg_Pt/cm² respectively.

Large Area Short Stack Test Durability Testing (Task 3)

- Initiated large area short stack testing with Nuvera Inc. to evaluate for the first time, the combination of the 3M NSTF electrode technology with the Nuvera open flow field bi-polar plate technology. Three short stacks were built and initiated beginning of life testing.

Membrane-Electrode Integration and CCM scale-up (Task 5.1)

- Produced 37,000 linear ft combined of NSTF substrate, coated catalyst supports, and CCM for process development, qualification and customer use.

Break-In Conditioning (Task 6)

- Developed more user friendly MEA conditioning protocols that can provide 90% of full performance in 2 to 5 hours depending on the material set.

Introduction

State-of-the-art proton exchange membrane (PEM) fuel cell electrocatalyst technology utilized in today’s prototype fuel cell vehicles reveals 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 to achieve the above objectives builds on a 13-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, demonstrates much lower losses due to Pt dissolution and membrane chemical attack [3-6], and has significant high-volume all-dry roll-good manufacturing advantages [7].

The scope of work in the three-year initial 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-rotating disk electrode catalyst evaluation technique with JPL. Research during this third year has focused on: a) water management improvements for cool/wet operation through optimization of materials, electrode structure and operating conditions; b) continued investigation of multiple strategies for increasing NSTF support surface area, catalyst activity and durability with total loadings of ≤0.25 mg-Pt/cm² per MEA; c) continued fundamental studies of the NSTF catalyst activity for ORR in general and methods to achieve the entitlement activity for NSTF catalysts; d) more severe accelerated testing to benchmark the NSTF-MEA durability; e) development of faster, easier MEA break-in conditioning protocols; and f) work with system integrators to validate NSTF functional properties and issues in short stacks.

**Results**

The technical accomplishments for the third year fall into five areas of research and development corresponding to Project Tasks 1, 2, 3, 5 and 6. We briefly summarize the main results from each of these areas.

**Task 1**

Work under Task 1 had three primary areas of focus this year. The first and largest effort investigated a specific PtNi alloy in greater depth. At the end of 2008 and early 2009 we were investigating a broader compositional range for various PtM and PtMN alloys, when we noticed that for PtNi binaries, there appeared to be a significant and sharply defined increase in ORR activity around 70 at% Ni as best determined using thin film gravimetric methods. This year we fabricated many more samples over a broad range of composition with sufficient resolution to try to better reveal the peak width and composition. Although most accurate, the gravimetric measurement of the Pt/Ni content has only ±5% precision so higher precision X-ray fluorescence (XRF) and electron microprobe (EMP) were also used. Both show that there is indeed a finite peak width, although it is very narrow, with the mass activities approaching 0.4 A/mg. The results for mass activity vs at% Ni by EMP is shown in Figure 1(a). The peak position by EMP occurs at 60 at% Ni. By XRF the peak appears to be at about 75% Ni [8]. Since the more accurate gravimetric peak is at 69% Ni, we are calling this a PtₓNi₇ alloy composition. Once we saw this strong compositional effect with PtNi, we then investigated PtCo over a similar range of compositions, and although it also shows a sharp peak, it is not as dramatic as that for PtNi.

Figure 1(b) compares the mass activity as a function of Pt loading of the PtₓNi₇ with our more standard PtCoMn composition. Specific activity and absolute activity for ORR of the PtₓNi₇ and PtCoMn are shown in reference [8]. Increases in both specific activity and surface area of the PtₓNi₇ contribute to its higher mass activity. There is also a process affect in the catalyst deposition that has a significant effect on the PtₓNi₇ activity as indicated by the process A or process B labeled data points. The PtₓNi₇ alloy by process A was made on full-scale roll-good manufacturing equipment, while process B was lab-based and limited to 50 cm² areas.

The second focus area under Task 1 was development of a surface energetic treatment for treating the catalyst to effectively anneal it. It is roll-good compatible so it can eventually be done as the catalyst is made. Many process parameter values were studied and slide 10 of reference [8] shows examples of how mass activity and surface area of the PtₓNi₇ alloy made by process A and our standard PtCoMn are affected by these process parameter values. Compared to the untreated values, the activity of both catalyst types are increased by about 50% for the most effective treatment parameter values. The red stars data in Figure 1(b) are the activities from the process A-made PtₓNi₇ after the surface energetic treatment with the most effective treatment parameter. The surface energetic treatment has further increased the PtₓNi₇ activity made by process A to be similar to that of the PtₓNi₇ made by process B. The mass activity values are now even closer to the targets. Figure 1(c) is a summary plot of absolute activity versus mass activity, updated from last year’s report, for a variety of alloys we have made and
characterized in the past year. Compared to last year, we have now many more candidates closer to this DOE electrocatalyst target.

The Pt$_{1-x}$Ni$_x$ alloy is a unique model system, but not a practical catalyst yet. The as-made composition is not stable and quickly de-alloys in situ in the working fuel cell, giving the resultant state of high activity. Although the higher mass activity translates into higher $\mathrm{H}_2/\mathrm{air}$ polarization curve kinetics [8], due to the excess Ni diffusing into the PEM that in turn affects cathode to anode water transport, there are severe performance limitation above 1 $\mathrm{A/cm^2}$ from mass transport overpotential increases [8].

The final focus area under Task 1 was to revisit pure Pt with NSTF catalyst deposition process improvements in our manufacturing facility. Most notably the Pt(111) grain sizes of the Pt made by the improved process are substantially higher (8.5 nm at 0.1 mg/cm$^2$) than those made by the standard process conditions, or those of our standard PtCoMn (5 nm at 0.1 mg/cm$^2$) [8]. The polarization curves are very similar to those from our PtCoMn with nearly the same loading. There appears to be about a 10 mV improvement in the polarization curve of the pure Pt by the new process conditions versus the standard. The impact on durability of the larger grain size of the pure Pt made by the improved process is still being determined. We will be extending these process improvements to the Pt alloys in the future.

Task 2

Our work under the second area (Task 2) continued this year to focus on three types of accelerated durability tests using the 2009 ‘best of class’ NSTF MEA having 0.15 mgPt/cm$^2$ of total loading but with a thinner membrane and MEA modifications of the latter. These three tests are load cycling, high voltage cycling and OCV hold. Figure 2(a) is an update of the load cycling tests under 80°C that we have shown results from in previous years. Cell voltages at various current densities are measured versus time under an 80°C cell temperature, 64°C dew point, constant flow of gases to keep the membrane hydrated, and current densities are measured versus time under an 80°C cell temperature, 64°C dew point, constant flow of gases to keep the membrane hydrated, and OCVs (measured daily) are used to determine end of life in this test (<0.8 V). At the end of last year we had obtained ~5,000 hr lifetimes with the 2009 best of class NSTF CCM with the 0.05/0.10 mg/cm$^2$ Pt loadings on a 3M 850 equivalent weight PEM that did not contain any chemical stabilizer or mechanical reinforcement (blue crosshatched bars in Figure 2(a)). The set of black crosshatched bar graphs on the right side of Figure 2(a) are new results this year, and show that MEAs with our 2009 best of class CCM, with 0.05/0.1 loadings and a 20 micron 3M PEM with a chemical stabilizer, but still no reinforcement, have survived 6,500 hours without failure and are still going strong.
Cumulative results from the second type of durability test, OCV hold at 90°C under H₂/air at 22.1/14.7 psig, 30%/30% RH, 22.1/14.7 psig. GDLs were constant, only the membranes and catalyst loadings were varied.

Under this test we have found that chemical additives to the membrane are very important to enable exceeding the OCV hold targets (500 hours). Second, the Pt₃Ni alloy at the same 0.1 mg/cm² Pt loading on the cathode is slightly better than the standard PtCoMn (698±184 vs. 610±40 hrs.). Finally, higher loading helps to improve lifetime (1,145±195 hrs. for 0.1/0.15 mg/cm² vs. 610±40 hours for 0.05/0.10 mg/cm²) as does a thicker membrane. A number of combinations can exceed the new 500-hour targets for this test.

The third type of durability testing under Task 2 was testing of catalyst stability under high voltage cycling to simulate start-up and shut-down. The cathode under N₂ is cycled (relative to the anode under H₂) 4,000 times between 0.6 and 1.2 V at 20 mV/sec at 95°C and 100% inlet RH. Slide 15 of reference [8] summarizes results with both the low loading standard PtCoMn and the Pt₃Ni, under more severe conditions than we have reported previously. For this test we cycle from 0.6 to 1.2 V at 95°C and saturated inlets. Nine samples were tested with varying catalyst and membrane lots, and test cells. A key result was that the amount of surface area loss after 4,000 cycles depended on how the catalyst and CCM were made. The roll-good manufactured CCMs fared better than hand-laminated CCMs, loosing 23% versus 36% surface area respectively. Fuel cell polarization curves before and after cycling for the manufactured versus hand-made MEAs show the performance loss mirrors the surface area loss, with the manufactured MEA loosing less performance. A second key result is that the relative performance loss of the Pt₃Ni alloy, also at 0.1 mg/cm² loading of Pt, is less than the standard Pt₆₈(CoMn)₃₂. It doesn’t start with as high of performance above 1 A/cm², but after the 4,000 cycles, the Pt₃Ni, performance is similar or slightly better than the PtCoMn [8].

Task 3

Initiated about the first of this calendar year, Task 3.2 is focused on preliminary large area cell tests for performance and durability prior to starting the final stack testing under Task 5.3. An opportunity to combine the uniqueness of the 3M NSTF electrode technology with the Nuvera open flow field plate technology approach motivated going directly into full size area short stack testing of both the 2008 (0.1/0.15 mg/cm² loaded NSTF) and the 2009 (0.05/0.1 mg/cm² loaded) MEAs in 8 and 16 cell stacks at both 3M and Nuvera with the Nuvera Andromeda stack design. After just six months we are still investigating the best operating conditions to use (e.g. lower pressure and drier) and learning to marry the materials and the hardware. However fit and function went very smoothly, there does not seem to be contamination issues to any significant degree based on 3,000 hours of assembled shelf time and occasional operation. We have verified that there is a large opportunity to improve the performance by reducing the in-cell impedance that is roughly 50% larger than we expect based on single cell 50 cm² cells. Slides 16 and 41 in reference [8] compare the single cell 50 cm² test results with the first 16 cell stack tested at 3M and very preliminary 8 cell short stack performance at Nuvera. The average stack performances are roughly 75 mV below the single cell out to 2 A/cm², while the best cell performance of the 16 cell stack reduces this to about 50 mV.
Task 5

Task 5 embodies all work done under catalyst/membrane integration and scale up (Task 5.1) and GDL integration and water management (Task 5.2). Task 5.2 and the area of water management was our primary focus area for the year and the one with the most significant results. The NSTF electrodes are submicron in thickness and this leads to cathode flooding under cool/wet conditions if conventional water management approaches are used. This year we made significant changes in both material factors and operating conditions to demonstrate two independent paths to solve this cathode flooding issue.

Water Management – Path 1

For the first path, based on use of sub-atmospheric anode pressure, we changed the paradigm for conventional MEA water management by removing cathode product water (liquid and vapor) out the anode instead of the cathode. This is possible with the hydrophilic ultra-thin NSTF catalyst electrode layers because they are in intimate contact with the membrane, and have high permeability for liquid water. Key material parameters to enable this include removing the hydrophobic microporous layer (MPL) from the anode GDL, use of a thinner membrane, use of anode GDL backing layers with adequate liquid water permeability and thickness, use of higher cathode pressure than anode pressure, and most effective, use of subatmospheric anode pressure. Low temperature operation is critical for rapid stack start-up from temperatures below 60°C. Figure 3(a) shows steady-state current density at 0.4 volts versus absolute anode pressure at 30°C for various combinations of anode GDL, all with no MPL except the baseline GDL (open squares). The anode absolute pressure is seen to be a very effective boundary condition for reducing cathode flooding. The Freudenberg GDL backing layers are much more effective than the baseline Mitsubishi Rayon Co. (MRC)-type GDL backing layer we had been using, improving the effectiveness of the sub-atmospheric anode pressure significantly. Over the past two-three years we had made simple liquid water permeability measurements for a whole series of difference GDL backing materials, (see slide 18 of reference [8]) and it was on this basis that we started testing the Freudenberg GDL on the anode versus the MRC baseline GDL backing layer since it had a much higher liquid water permeability (6x). The improvement in fuel cell performance is consistent with that property, but since then we have determined that that measured property is not the only factor determining the fuel cell response at 30°C.

Figure 3(b) shows galvanodynamic scan (GDS) polarization curves as a function of 50 cm² cell temperature under 50/150 kPa anode/cathode absolute pressures of H₂/air. The MEA uses the 2009 best-of-class CCM and the as-received Freudenberg GDL backing layer on the anode (no MPL or Teflon® treatment). With the proper anode GDL and reduced anode pressure, it is possible to run the cell stably at 2 A/cm² even at 30°C. The high temperature curve at 80°C and 68°C dew points in Figure 3(b) also shows there is no impact of the anode GDL on standard higher anode pressure/temperature operation. Operating at equal anode/cathode pressures (150 kPa) or higher, the same MEA will flood out at a limiting current of <0.4 A/cm² at 30°C. But if the cathode pressure exceeds sufficiently the anode pressure, then the cell can hit 2 A/cm² even with the anode at atmospheric pressure (Reference [8], slide 19).

Load transient performance under cooler wet conditions is very important for stack operation. We find this is also significantly helped by this new water management strategy. Figure 4(a) shows 0.02 to
1 A/cm² load steps under 60°C and 140% RH, using the same MEA as discussed with Figure 3(b). The impact of the reduced anode pressure greatly improves load transient performance at 140% RH, and for values below 25 kPa, there is no delay in response with the 50 cm² cells. “Steady-state” (>15 seconds after the load step) performance is also improved with reduced anode pressure (+60 mV as anode pressure decreases from 100 kPa to 25 kPa.). Finally we note that reduced anode pressure also assists load transients at 50°C, 140% RH similarly [8]. Since the heat capacity of these single cells is much higher than one would have in a stack, this is a very good indicator that load transient power up in a stack will be improved even further. In summary, this approach of managing cathode flooding under cool/wet conditions by pulling the product water through the CCM and out the anode is very effective for steady state and transient operation.

**Water Management – Path 2**

The second path pursued for resolving the cool-start water management issue involves using a gradient cathode catalyst such as described in reference [9], to more effectively remove water from the cathode in a more conventional manner. This involves a hybrid electrode, consisting of both an NSTF catalyst layer and a lower loading of a conventional Pt/C dispersed catalyst layer. Slides 43-45 of reference [8] show other data relative to this water management approach, and in particular, slides 44 and 45 show an alternative solution which was nearly as effective in which a small amount of additional dispersed Pt/C (< 0.05 mg/cm²) of catalyst layer is added to the cathode electrode outside the NSTF cathode. With the right choice of Pt/C catalyst, this also helps improve the steady state and transient response under cool, wet conditions without loss of high temperature performance. Figure 4(b) shows comparative load transient responses of four hybrid MEAs, each slightly different, with the same test conditions as used for 4(a) except that the anode and cathode pressures are equal at 150 kPa. These hybrid MEAs use NSTF CCMs with 0.05 mgPt/cm² anode loadings, 0.1 or 0.15 mgPt/cm² cathode loadings, the same PEM type, the as-received Freudenberg GDL discussed above, and 0.05 mg/cm² of a specific Pt/C applied to the cathode GDL. All easily make the 0.02 to 1 A/cm² load step. Such a hybrid MEA shows promise for further extending the high temperature limiting current density as well, with recent results attaining 2.4 A/cm² (at 0.55 V) with only 40 mV of mass transport overpotential below a 70 mV/decade Tafel slope, with 0.2 mg/cm² total per MEA. Further optimization is underway.

**Task 6**

The last area of work focused on improving break-in conditioning of the NSTF MEAs. This activity was incorporated last year as a new Task 6. Significant work prior to the current project had 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 focuses on both materials effects and the protocol effects in order to significantly reduce the time and simplify the procedures for conditioning a new MEA. Last year new test station protocol work was successful in reducing the conditioning time with our current test stations from over 24 hours to less than 6 hours. In the current year protocols were developed that both reduced the time...
for reaching full power and were more stack friendly to implement. (Our standard protocol we call thermal cycling, requires at least 24 hours and the use of liquid water to flood the cells during the cool down periods.) Since this task started last year, over 40 new protocols were investigated. Slide 20 in reference [8] shows a recent fast conditioning protocol that produces nearly the same performance break-in as the standard thermal cycling, but requires 4-5 hours and operates with completely dry input gases. The same slide also shows a graph demonstrating a material effect, that is the Pt3Ni7 alloy conditions faster than our standard PtCoMn with the standard thermal cycling protocol.

Conclusions and Future Directions

This project has met or exceeded the currently specified DOE electrocatalyst and MEA performance and durability targets for 2015 using the same MEA component set in 50 cm2 cell tests. Furthermore, the NSTF catalyst based MEAs used outside this project in original equipment manufacturer 400 cm2 (>20 cell) short stacks have generated specific power densities of <0.2 gPt/kW, successful 10°C cold and -20°C freeze-start [8], and lifetimes of 2,000 hours under various automotive system relevant cycling. Significant improvements in ORR activity with new alloys and processing methods were demonstrated and further improvements are anticipated. Probably the most significant advances this past year were understanding and improving major water management issues associated with the ultra-thin NSTF electrodes. Future work will be strongly focused on down-selecting and incorporating these advanced components into a robust, durable, high-performance, roll-good manufactured MEA containing no more than 0.2 mg/cm2 of PGM total for the final stack testing-deliverable. Specific future directions include:

Water Management Improvement

- Continue to combine the improvement factors now identified that significantly enhance cool operation and load transient start-up; determine best synergistic combinations towards the 2010 best of class MEA for final stack testing.

Cathode Catalyst Mass Activity Gain

- Down-select the final catalyst and configuration to be scaled up for the final stack testing.
- Optimize fabrication processes for the down-selected catalyst.

MEA Integration

- Down-select the final 2010 best-of-class MEA (catalysts for each electrode, processes, etc.) under Task 5, for final stack testing.

Stack testing

- Continue Task 3 short stack evaluations with 2009 best-of-class MEA, upgrading to 2010 best of class MEA.
- Identify original equipment manufacturer stack for final stack testing under Subtask 5.3.

Start-up conditioning and reversible stability

- Continue to develop simplified break-in conditioning protocols and catalyst/membrane components to reduce MEA break-in conditioning time to <3 hours for full performance.

FY 2010 Publications/Presentations

Debe – 3M Company

V.E Fuel Cells / Catalysts

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DOE Hydrogen Program

FY 2010 Annual Progress Report

References


V.E.2 Highly Dispersed Alloy Catalyst for Durability

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Contract Number: DE-FG36-07GO17019

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: October 31, 2010

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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) Durability
(B) Cost
(C) Performance

Technical Targets

<table>
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<tr>
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ECA = electrochemical area; TBD = to be determined; MEA = membrane electrode assembly, T = temperature
* Durability data measured after 30,000 cycles under UTC Power-defined accelerated test protocol.
† Based on current scaled-up 30% Pt₂IrCr MEA; anode/cathode loading – 0.1/0.3 mg/cm² (PGM).
† Five year average PGM price $51.55/g (Pt = $1234.33/troy oz; Ir = $369.06/troy oz); costs not projected to high volume production.

Accomplishments

• Down-selected a carbon (C4) that exceeds DOE’s corrosion targets and verified a 30% Pt/C4 and a more active PtIrCo/C4 alloy catalyst in a subscale fuel cell which showed that PtIrM/C4 are more active and durable compared to the Pt/C4. Scale up of a 30% Pt₂IrCr alloy on C4 is in progress.
• Completed the scale up of both down-selected dispersed catalysts PtIrCr and PtIrCo for MEA optimization. Currently testing performance and durability of first trial full size MEA of 30% Pt₂IrCr/C.
• Modeling results show that Ir in the dispersed PtIrM (M=Co or Cr) ternary alloy catalysts imparts stability to the surface Pt atoms. The benefit of Ir in PtIrM alloy catalysts was evaluated and compared to PtM alloys.
Sub-scale MEA catalyst layer optimization was completed to improve the ternary alloy MEA performance in H₂/air at high current densities with total PGM loading of 0.3 mg/cm².

Correlation between segregation energies, activity and stability of core-shell catalysts based on their composition and surface characterization during potential cycling explains differences in the surface activity during core metal dissolution and the durability of core-shell catalysts.

Activity and stability of Pt₅₆/Pd₃Co core-shell catalysts prepared using scalable chemistries were evaluated using both rotating disk electrode (RDE) and sub-scale fuel cell tests.

**Introduction**

It is well known that, in order for the proton exchange membrane fuel cell (PEMFC) 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 somewhat conventional but high performance highly dispersed Pt alloy catalyst on a carbon support. The second system utilizes a novel “Pt monolayer (ML) core-shell” approach capable of achieving very high Pt mass activities [1-3]. Under this latter concept, the main objectives are 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 to 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). The research focus and the role of all partners were reported previously [4]. BNL’s role on the project focuses on the development of Pt ML “core-shell” systems 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. 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 including scale up on conventional and advanced carbon supports, (ii) novel synthesis methodologies to scale up Pt ML core-shell catalysts and (iii) MEA optimization and fabrication. 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, carbon support corrosion studies, fuel cell testing on single-cell level and fabrication and test of a 20-cell short stack for verification.

**Molecular Modeling**

The main topic that was studied this year was calculation of activity and stability of PtIrM ternary alloys based on surface segregation, Bader charge, d-band center analysis of Pt and potential shifts in the dissolution potential for Pt in these alloys. It was previously reported that, in Pt₅₆ binary alloys, electronically the Pt atoms on skin surfaces differ little from those on the non-segregated alloy surface [4]. In contrast, incorporating Ir into the bimetallic alloy increases the tendency of Pt-skin formation and enhances the stability of the alloy systems. Since Ir has a smaller atomic volume and higher surface energy than Pt, a much stronger Pt segregation trend is expected in the ternary PtIrM alloy system. The calculated segregation energies (in vacuum) of -2.90 eV for Pt₅₆IrCr, -2.10 eV for Pt₅₆IrCo, and -1.60 eV for Pt₅₆IrCo₇ suggests that the presence of Ir reduces the lattice mismatch between Pt-Co and favors the formation of a Pt monolayer skin surface. However, the trend to form Pt-skin in PtIrCr alloys is lower compared with the corresponding PtIrCo alloy surfaces. Bader charge analysis (shown in Table 2) on the Pt-skin surfaces, indicates that Pt surface atoms have an excess of electrons in their valence shell and a deficit of electron charge on the subsurface atoms (Ir, Co and Cr), which suggests a higher oxygen reduction reaction (ORR).

**Table 2.** Average valence charge for surface and subsurface atoms of PtₓIrₗₘ systems.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Charge surface Pt atoms</th>
<th>Charge subsurface Co/Cr atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure Pt(111)</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>PtIrCr (Pt-skin)</td>
<td>-0.25</td>
<td>1.22</td>
</tr>
<tr>
<td>Pt₂IrCr₅ (Pt-skin)</td>
<td>-0.25</td>
<td>1.11</td>
</tr>
<tr>
<td>Pt₄IrCr₂ (Pt-skin)</td>
<td>-0.40</td>
<td>0.77</td>
</tr>
<tr>
<td>Pt₅IrCr (Pt-skin)</td>
<td>-0.14</td>
<td>0.57</td>
</tr>
<tr>
<td>Pt₅IrCo (Pt-skin)</td>
<td>-0.25</td>
<td>0.43</td>
</tr>
<tr>
<td>Pt₇IrCo (Pt-skin)</td>
<td>-0.24</td>
<td>0.37</td>
</tr>
</tbody>
</table>
activity for these alloy catalysts compared to a pure Pt (111).

Ir also induces a larger average d-band center shift for the Pt-skin surfaces on PtIrM compared to PtM. For comparison, the average d-band center shift for Pt-skin on PtIrCo and PtIrCr is -2.23 eV and -2.18 eV respectively. This negative shift is due to the presence of Ir in the subsurface and thereby modifying the electronic structure of the surface Pt atoms. A d-band center shift to more negative values indicates that the Pt-skin surface is less reactive and hence, certain repulsion towards oxygenated species is expected due to the negative charges located on the surface atoms. The calculated d-band centers relative to the Fermi level also show a shift towards lower energies in the alloys as a function of the amount of Ir in the alloy as shown in Figure 1 for PtIrCo alloys.

The electrochemical stability of Pt atoms shown in Table 3 indicates that the Pt atoms are more stable on the alloy surfaces than on pure Pt (111) surfaces as shown by the positive shift in potentials on surfaces covered with 1/8 ML of O. The maximum values found for an intermediate amount of Ir suggests that further lowering the amounts of Ir in the alloy compositions may result in less stable surfaces due to the large lattice mismatch between Pt and transition metal atoms [5].

In the core-shell catalyst concept, the activity and stability trends of Pt ML on various Pd-containing metal cores such as PdCo, PdCr and PdTi were investigated. Adsorption energies of OH, O and H2O suggest that both Pt/PdCo and Pt/PdCr are more active than a pure Pt although the Pt/PdCo shows the weakest adsorption energies. The electrochemical stability investigation of Pd, Co and Cr in these core-shell catalysts shows that Pd, Co and Cr are more stable in the alloy cores than in their pure state and their stability towards leaching follows the order Pd > Co > Cr. Based on these activity and stability results, PtML/Pd3Co is estimated to be a more favorable core-shell system for ORR compared to Pt/Pd3Cr.

### Dispersed Pt Alloy Catalyst

Many factors such as structure, particles dispersion, particle size, type of carbon support used etc., influence the electro-catalytic activity of Pt and Pt alloy nanoparticles. Previously, within this project a 30 wt% Pt2IrCo and a 30% Pt4IrCo3 exhibited an activity almost two times higher than pure Pt based on RDE and MEA testing. The Ir containing ternary alloy catalysts also showed more durability in both their ECA and mass activity (MA) under potential cycling which show much lower loss (~30% ECA and MA) compared to the standard Gore Pt/C which showed ~50% loss. Based on these results the PtIrM ternary alloys were down-selected for further development [4]. In the past year, a significant amount of effort was focused towards scale up of a large size batch (200 g) of the down-selected ternary alloys 30% Pt4IrCo3 and 30% Pt2IrCr, development and optimization of the cathode catalyst layer in an MEA of PtIrM (M= Co, Cr) alloy catalysts to improve the catalyst utilization in an MEA keeping low PGM loading and enabling good performance at high current densities. This involved MEA iterations to identify key parameters such as catalyst ink formulations and ionomer content, to achieve optimum cathode catalyst layer capable of achieving good fuel cell performance operating on not only H2/O2 but also on H2/Air at high current densities.

Figure 2a shows the fuel cell performance curves in H2/Air for an optimized and un-optimized 50% PtIrCr/C MEA in a sub-scale size (25 cm2) solid plate fuel cell operating at 80°C, 100% relative humidity (RH) and 50 kPa backpressure compared to a commercial Gore 5710 Pt/C MEA. It should be noted that the Pt
loading in the commercial MEA is about two times of that of the alloy MEAs used in this project. The internal resistance for the PtIrCr MEA is also higher than the Gore 5710 MEA resistances which arise from differences in the membrane thickness and the catalyst layer fabrication process. The initial MA obtained for the alloy catalyst in the optimized and un-optimized MEA were 0.14 and 0.156 A/mg PGM, respectively compared to a MA of 0.17 A/mg PGM observed for the commercial Pt/C MEA. This observed low activity is attributed to the low utilization of the catalyst in the MEA as seen by their low ECA of ~30 m²/g. However, a clear evidence of improvement for high current density performance in H₂/Air in a solid plate fuel cell is observed from these catalyst layer optimization steps. The 30% PtIrCr ternary alloy MEA optimized for solid-plate fuel cell performance was also verified in a full-size UTC Water Transport Plate (WTP) fuel cell operating at 65°C, 100% RH and 0 kPa backpressure. Figure 2b shows the internal resistance (iR) corrected fuel cell polarization curves obtained in H₂/O₂ for the 30% PtIrCr in the WTP fuel cell. Our results shows clear evidence that lower catalyst loading of 0.2 mgPt/cm² in MEAs can achieve high initial performances, although lower than a commercial Pt/C which has 0.4 mg Pt/cm² in the cathode, in both solid plate and a WTP fuel cell. Our preliminary investigation into MEA fabrication process suggests that different ink formulations can significantly increase both mass transport properties and kinetic performance of alloy catalysts. Further optimization steps are currently being pursued to improve the MEA fabrication process and utilization of the catalyst in the MEA.

Core-Shell Pt Catalysts

The primary focus of core-shell development was (a) to synthesize Pt ML catalysts on Pd₃Co and Ir cores using scalable chemistries without compromising the intrinsic activity of the catalyst as demonstrated by BNL and (b) to incorporate these advanced catalyst concepts in an MEA. Previously, a large batch (30 g) of Pd₃Co and Ir cores and 5g batch Pt ML core-shell catalyst were synthesized successfully by JMFC via a chemical method.

Figure 3 shows the MA based on PGM loading for a scaled-up Pt₃ML/Pd₃Co core-shell catalyst prepared via chemical methods and a pure Pt/C catalyst obtained from RDE and MEA testing. Although the mass activity obtained on the pure Pt/C in an MEA is slightly lower than that obtained from RDE measurements, the Pt₃ML/Pd₃Co core-shell catalyst shows a significant lower activity in an MEA (0.044 A/mg PGM) than from RDE measurements (0.254 A/mg PGM). This is mainly attributed to (a) instability of Pt₃ML/Pd₃Co at 80°C under MEA test conditions and (b) to the incomplete or non-uniform coverage of Pt on the core Pd₃Co particles. Detailed studies of the Pt₃ML/Pd₃Co core-shell catalysts in 1M H₂SO₄ solution at 80°C using electrochemical and physical characterization using inductively coupled plasma shows substantial loss of Co and Pd on exposure to the acid which indicates incomplete coverage of Pt. Efforts are on currently to improve the Pt monolayer coverage by optimizing the catalyst preparation methods.

Durable Carbon Support

The main focus of this task was to explore alternate durable carbons capable of withstanding high voltage spikes relevant for automotive applications. In the past year, several carbon supports from a number of vendors available both commercially and under developmental proprietary agreements were investigated. Based on the ex situ testing of each of these carbon supports at a constant potential hold of 1.4 V in 0.5 M H₂SO₄ at 80°C for 5 hours and further testing in a fuel cell under the DOE 2008 carbon corrosion protocol, an alternate carbon C₄ was down-selected for incorporation of PtIrM ternary alloys into MEAs and demonstration in
a fuel cell. Figure 4a shows the iR-free performance curves at BOL for a 30% Pt/C4 compared to a standard 0.4 mgPt/cm² Gore 5710 Pt/C MEA obtained from 25 cm² WTP fuel cell testing at 80°C, 100% RH under H₂/O₂ at zero backpressure. Although the beginning of life performance for the 0.2 mgPt/cm² Pt/C4 low surface area carbon shows lower performance than that of a standard Gore Pt/C, its performance after the 1.2 V potential hold tests show considerable differences as shown in Figure 4b. The 30% Pt/C4 showed 59 mV loss after the fuel cell corrosion test of a total of 17 potential holds of 24 h each at 1.2 V at 80°C, 100% RH under H₂/O₂ at zero backpressure. All other carbons tested under this test protocol showed significant losses in performance after only 3-5 potential holds. Further, our preliminary sub-scale MEA testing of a 30% Pt₈IrCo₂/C4 under the 2008 DOE carbon corrosion protocol in a WTP cell at 80°C shows higher initial performance corresponding to 2x in MA compared to the Pt/C4. Figure 5 shows the performance curves for the 30% Pt₈IrCo₂/C4 and a 30% Pt/C4 in H₂/O₂ before and after 400 hours of potential hold at 1.2 V which shows that the PtIrCo/C4 is more stable than the Pt/C4 as it shows only ~12 mV loss at 1.5 A/cm² in O₂ after 1.2 V potential holds with negligible iR losses. Efforts to scale up and understand the stability of a 30% Pt₂IrCr alloy on C4 and mechanism for high current density performance loss is currently ongoing.

Conclusions and Future Directions

MAs of ~0.15 A/mg_{PGM} in sub-scale MEA testing have been reproduced and verified for a scaled-up 30% Pt₂IrCr and has been down-selected as the dispersed alloy catalyst system for full-scale fuel cell demonstration. The Pt₂IrCr alloy was chosen, over the PtIrCo alloy, based on the higher durability of Cr over Co in the alloy catalysts under the MEA fabrication process. Key barriers to overcome for the incorporation of the 30% Pt₈IrCr in an MEA are the low catalyst utilization in an MEA and the cathode catalyst layer optimization for high current density performance in a WTP fuel cell and are currently the main focus under this project. A key challenge for the core-shell catalysts is their poor durability in an MEA under operating fuel cell conditions and is an ongoing investigation in the project. All modeling activities under this project are complete and have clearly shown the benefit of Ir and the stability it imparts to the surface Pt atoms in the ternary PtIrM alloys. Also, our computational calculations played a significant role in identifying core materials and shell thickness and in understanding the activity and stability benefits of core-shell catalysts. A carbon support C4 with significant resistance to corrosion (<30 mV loss at 1.5 A/cm², 80°C in H₂/O₂) has been down-selected for further scale up of a 30% Pt₂IrCr alloy catalyst, MEA optimization and durability evaluation in a sub-scale fuel cell.
Future Directions

Our future objective is to demonstrate the durability of a highly active PtIrCr alloy catalyst in an MEA with a durable carbon support capable of withstanding high voltage spikes relevant for automotive applications. Some of the tasks undertaken to achieve these goals are listed below.

- Optimization of dispersed alloy catalyst systems in MEAs is in progress aiming to approach high mass activity and more importantly high current density performance in an operating fuel cell. This is being resolved by investigating:
  - MEA fabrication process to understand the gap between MEA and RDE data.
  - Electrode structure optimization for water-transport-plate cells.

- The fundamental benefit of PtlrM ternary alloys on C4 for activity and durability compared to Pt/C4 is being further investigated based on their particle size, particles dispersion and electronic properties.

- 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 by the development of various scalable methods specifically geared towards achieving uniform Pt coating.

FY 2010 Publications/Presentations


2. Ma, Y. and Balbuena, P.B. Surface adsorption and stabilization effect of Iridium in Pt-based alloy catalysts for PEM fuel cell cathodes, Transactions – 216th meeting of the Electrochemical Society, Vienna, Austria; (2009), 25, 1, 1037.


References


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: September, 2011

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 (CMO) for improved activity and durability over standard Pt/C.

• Demonstrate durability and performance advantages of alternative cathode supports such as carbon nanotubes (CNTs) ordered graphitic mesoporous carbon (OGMC) and grapheme.

• Demonstrate durability and performance of non-carbon CMO supports such as indium tin oxide (ITO).

Technical Barriers

This project addresses the following technical barriers from Fuel Cells section (3.4) of the Fuel Cell 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 DOE life time criteria.

Membrane electrode assembly (MEA) tests are in progress for lead supports, and have shown 2X improvement in stability over baseline vulcan carbon/ XC72 supports (Table 1). Alternative supports such as CNTs have shown no degradation after 100 hours, thus providing a synergistic opportunity for metal oxide modification of CNTs. Rotating disc electrode (RDE) tests have also shown significant improvement in durability over baseline.

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts for Transportation Applications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>2010 Stack Target</th>
<th>PNNL 2010 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerated test loss, 200 h @ 1.2 V at 80°C</td>
<td>mV at rated power</td>
<td>&lt;30</td>
<td>&gt;2X improvement over baseline for MEA</td>
</tr>
<tr>
<td>% ESA loss</td>
<td></td>
<td>&lt;40</td>
<td>&gt;2X improvement for RDE and MEA tests</td>
</tr>
<tr>
<td>Durability with Cycling at 80°C</td>
<td>hours</td>
<td>5,000</td>
<td>TBD</td>
</tr>
</tbody>
</table>

ESA – electrochemically active surface area; TBD – to be determined

Accomplishments

• Optimum ITO content in graphene found to maximize activity and durability:
  – Activity and durability are 1.5X and 1.7X of baseline.
  – Pt distributed uniformly at ITO/graphene interface as predicted by density functional theory (DFT) model.

• Demonstrated Pt/CNT stability of >2X over Pt/XC72.
• Demonstrated 2X durability of Pt/OGMC over Pt/XC72.
• Demonstrated 3X durability of Pt/ITO non-carbon support over baseline.
• Obtained consistency between RDE and MEA test results.
• Validated DFT prediction for higher Pt/WC activity and higher Pt/VC stability.

**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 ESA 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 DOE technical targets for durability and performance, we have developed new classes of alternative and durable cathode supports, based on modifying the carbon surface conductive metal oxides [4] such as ITO, TiO₂ and SnO₂. Alternate supports such as CNT, graphene sheets were also investigated to take advantage of their superior properties [5,6]. In addition, conductive metal oxides were also used as an alternative to carbon-based supports. 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 metal oxide substrates enhances the stability of Pt particles.
- More uniform dispersion of Pt, allowing better performance at equivalent loading.
- Higher activity and durability of CNT, OGMC and graphene over XC72 provides potential for an order of magnitude improvement with metal oxide modification.
- DFT modeling indicates stable Pt/ITO/graphene interface.
- Carbon-free metal oxides (ITO) successfully identified as candidates for catalyst support.

**Approach**

New classes of carbon supports modified by CMOs have been developed to improve durability and performance of the cathode catalysts. In order to prevent alloy formation, electrocatalysts were synthesized by the ethylene glycol method [7]. Durability of various carbon supports such as XC72, carbon multi-walled nanotubes (CMWNT, also referred to as CNT in this report), ordered graphitized mesoporous carbon and graphene were compared. DFT modeling was performed to identify potential supports with better oxygen reduction reaction (ORR) activity and stability than Pt-XC72. DFT predictions were validated by experiments.

Carbon supports were modified with WC and various conductive metal oxides such as TiO₂, SnO₂, and 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 (NHE). An investigation of the effect of CMO modification of various supports such as CNT, graphene and OGMC 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, and measurement of ESA, ORR activity at 0.9 V and polarization curves performed every 20 hours.

**Results**

DFT predictions for high activity of Pt/WC was validated with experiments, while DFT prediction for high Pt/VC stability was also validated with Auger electron spectroscopy (AES). Optimum CMO composition for graphene supported catalyst was found, leading to 50-70% improvement in activity and durability over baseline. DFT modeling predicted a stable Pt/CMO/graphene interface, with Pt nanoparticles in contact with both CMO and graphene, with verification from transmission electron microscopy (TEM) images. Durability for OGMC and CNT-supported catalysts was found to be >2X of baseline. CMO supported catalysts, which were previously shown to be highly durable, have shown rapid improvement in ESA and activity using RDE tests. MEA formulation methods for non-carbon and conductive metal oxide modified supports are currently being optimized. MEA tests were conducted on alternative carbon supports such as CNTs, OGMC and graphene, with tests ongoing on CMO modified graphene and non-carbon supports.

DFT analysis had predicted the superior activity and stability of Pt on WC (0001) and superior stability of Pt on vanadium carbide (VC). In order to verify the activity enhancement of Pt/WC (0001) over Pt, the performance of Pt-WC synthesized by atomic layer deposition (ALD) was determined by cyclic voltammetry (CV), with results corresponding to 30 ALD cycles surpassing Pt foil performance significantly. In order to verify superior stability of Pt on VC in the presence of oxygen, Auger electron spectroscopy was carried out on Pt/V(110) and on Pt/VC before and after exposure.
to 3,000 L oxygen at 300 K. For the former, Pt signal decreased, accompanied by an increase in the V signal, while for Pt/VC, the Pt signal did not decrease upon exposure to oxygen. These results were also confirmed by high resolution electron energy loss spectroscopy (HREELS).

The lead cathode catalysts developed are shown in Figure 1, with Pt/VC as the baseline. CNT and OGMC were found to be very stable supports. TiO₂ modification of Vulcan carbon improved both ESA and stability. The dispersion of Pt on graphene was not uniform, with agglomeration of Pt particles present. Modification of graphene surface with ITO resulted in better distribution of Pt nanoparticles, resulting in improved activity and durability. The results for Pt/ITO was very encouraging, with excellent durability. Based on these results, Pt/OGMC, Pt/CNT, Pt/graphene, Pt/ITO/graphene and Pt/ITO were selected for MEA testing.

The consistency between RDE and MEA results are shown in Figure 2 from some commercial ETEK catalyst, Pt/VC baseline, and Pt/CNT. The trends for ESA and durability are the same for both types of measurements.

Metal oxides protect carbon substrate from oxidation. Figure 3 shows the polarization curves and CVs of carbon with/without metal oxide coating. The oxidation current densities (A/g carbon) were reduced for metal oxides coated graphene and carbon black, indicating that metal oxides protect carbon from oxidation. The CVs of metal oxide coated carbon are similar to that of pure carbon in the potential range of 0-1.4 V (proton exchange membrane fuel cell electrode

![FIGURE 1. ESA and Durability for Lead Cathode Catalysts - RDE Potential Step between 0.85 V (30 sec) to 1.4 V (150 sec) vs. NHE](image)

![FIGURE 2. Consistency between RDE and MEA Results](image)

![FIGURE 3. Polarization Curves and CVs of Carbon With/Without Metal Oxide Coating in Nitrogen-Saturated 0.5 M H₂SO₄](image)
potentials), which reveals that metal oxides (ITO, SnO$_2$, TiO$_2$) are stable.

ITO/graphene nanocomposites were synthesized in organic solvent by the hydrothermal method. Graphene, indium precursors and tin precursors were mixed in the organic solvent. Under the proper temperature and reaction time, ITO nanoparticles nucleate and grow on the surface of the graphene. Through this one-pot synthesis, uniform ITO nanoparticles were evenly dispersed on the graphene sheets. High activity was obtained for ITO/graphene substrates. Optimization of ITO content showed that at 75% ITO, the activity and durability were maximized as shown in Figures 4a and 4b. TEM images show the uniform dispersion of Pt using ITO mediated graphene (Figure 4d), while Pt agglomeration on graphene is seen without ITO (Figure 4c). Tests are ongoing to determine its effectiveness in an MEA.

Periodic DFT calculations were done to study the thermodynamic stability of Pt/ITO-graphene in both vacuum and oxygen atmosphere. The Pt/ITO/graphene system was found to be the most stable compared to Pt/ITO and ITO/graphene, with the highest interaction energy. The DFT model structure shows Pt at the interface of ITO/graphene (Figure 5a). Figure 5b shows the cross-section TEM for Pt/ITO/graphene, with Pt present at the interface of ITO/graphene, as predicted by the DFT calculations. A schematic showing Pt location in the Pt/ITO/graphene system is also shown (Figure 5c).

MEA tests were conducted on select catalysts, with degradation done by potential hold at 1.2 V at 80°C/7.4 psig/100% relative humidity, followed by measurement of ESA, activity and polarization curves. As seen in Figure 6, significantly higher durability was achieved for Pt/CNT and Pt/OGMC compared to baseline both in terms of ESA degradation and decrease in current at 0.6 V. During MEA formulation for graphene-based support, some vulcan carbon was added to the Pt/graphene catalyst (Pt/graphene + XC72) in order to increase the space between graphene sheets, and thus allow access of Nafion$^\text{a}$ to the inter-sheet space.

Conclusions and Future Directions

Significant progress has been made in improving supported cathode performance and durability:

- DFT modeling predictions for higher Pt/WC ORR activity was verified by ALD deposition of Pt on WC and measurement of activity.
- DFT modeling prediction for higher Pt/VC stability in the presence of oxygen was verified by AES and HREELS.
- Optimum ITO content was found to maximize activity and durability.

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- DFT modeling prediction for higher Pt/VC stability in the presence of oxygen was verified by AES and HREELS.
- Optimum ITO content was found to maximize activity and durability.

- ITO mediation enabled uniform Pt distribution in the Pt/ITO/graphene system. DFT prediction of stable Pt/ITO/graphene configuration with Pt at the edge of ITO/graphene was verified by TEM.
- Demonstrated > 2X stability of Pt/CNT over Pt/XC72.
- Demonstrated 2X durability of Pt/OGMC over Pt/XC72.
Demonstrated 3X durability of Pt/ITO over baseline.

Obtained consistency between RDE and MEA results.

Future work will involve improving the performance of non-carbon CMO supports by incorporating mesoporosity within the supports and improving MEA formulation for these novel supports. CMO modification of alternative carbon supports such as CNT and OGMC, which show 2X higher durability than baseline vulcan carbon, will also be conducted.

**FY 2010 Publications/Presentations**


References


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

• Overall objective:
  - Develop a non-platinum cathode electrocatalyst for polymer electrolyte membrane fuel cells (PEMFCs) 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 μA/cm² @ 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).

• Specific objectives for Fiscal Year (FY) 2010:
  - Prepare/characterize model systems (bulk electrodes) and nano-particles 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:
    - Varying Pd to base metal ratio, annealing temperature, and annealing atmosphere.
    - Characterizing oxygen reduction reaction (ORR) activity, surface composition, and electronic structure.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell 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 μA/cm² @ 0.9 V.
• Durability: 5,000 h @ 80°C, <40% electrochemical area loss.
• Cost: $5/kW, 0.3 mg platinum group metal (PGM)/cm².

Accomplishments

• Calculated the ORR energetics for Pd and Rh alloys and the effect of water solvent on these energetics.
• Calculated the effect of adsorbed oxygen on surface segregation energies of Pt and Pd alloys.
• Determined the effect of annealing temperature and atmosphere on the ORR activity of twenty-one bi-metallic and tri-metallic Pd bulk electrodes; highest ORR activity enhancement with alloying was 2.1x (Pd₃Mo).
• Synthesized and characterized the structure, oxidation state, particle size, and ORR activity of nano-particles in the Pd-W, Pd-Mo, Pd-Re, and Pd-Ni-Cu systems.
• Achieved a nano-particle ORR activity enhancement with alloying of 3.4x with an (ORR activity of 680 mA/mg Pd at 0.8 V and room temperature for a Pd₁₈Ni₁₈Cu₆₄ alloy).
• Determined valence band structure of highest activity bi-metallic Pd alloys (PdMo and PdCu).
Introduction

The platinum-based cathode electrocatalyst is a major contributor to the cost of PEMFC power systems [1,2]. The goal of this project is to develop active and stable non-platinum noble metal-base metal alloy ORR electrocatalysts to expand the availability of effective materials beyond Pt alloys and thereby reduce the cost of the cathode electrocatalyst.

Approach

Our approach to developing non-platinum noble metal PEMFC cathode electrocatalysts is to utilize noble metal-base metal alloys. The function of the base metal is to decrease the loading of the noble metal and to modify its valence band structure to make it more Pt-like in its bonding with ORR reactants, intermediates, and products. The choice of noble metal and base metal combinations are based on calculated valence band or “d-band center” shifts of the noble metal in noble metal-base metal alloys and on the tendency of the noble metal to segregate to the surface of the alloys [3-7].

Two project tasks guide the choice of alloy systems: (1) computational studies of preferred catalyst atomic structures, electronic structures, d-band centers, and preferred reaction pathways and activation energies and (2) model system (bulk electrode) fabrication and characterization. Favorable alloy systems are fabricated as high-surface-area-carbon-supported nano-particles using co-impregnation, colloidal, and strong-electrostatic adsorption techniques. The nano-particles are characterized by a variety of spectroscopic, microscopic, and electrochemical techniques to determine composition, phase structure, particle size, electronic structure, and ORR activity and stability.

Results

Computational Results

This year’s computational effort focused on the change in the energetics of the ORR on Pd and Rh with alloying, the effect of water solvent on these energetics, and the change in the alloys’ noble metal segregation energies in the presence of adsorbed O. The alloys studied, Pd,W, Pd,Mo, Pd,Re, Pd,Ta, Rh,Co, and Rh,Fe, were those with calculated d-band centers close to that of Pt and favorable energies for noble metal surface segregation, as detailed in last year’s report [8].

As shown in Figure 1, the ORR may proceed through various adsorbates and pathways. The binding energies of each of the potential ORR adsorbates and the activation energies of the reaction steps were determined using periodic quantum mechanic calculations on four-layer noble metal or noble metal-base metal alloy slabs. The trends determined from these calculations were:

- Alloying Pd decreases the binding energy of H, O, O₂, and H₂O₂ and increases the binding energy of OH, OOH, and H₂O.
- Alloying Rh increases the binding energy of OH.
- Alloying Pd decreases the barriers for H₂O formation and O hydration (two key steps in the ORR).
- Alloying Rh increases the barriers for H₂O formation and O hydration.

The presence of water solvent was found to alter the barriers for the ORR steps, thus modifying the preferred reaction pathway and overall reaction barrier. For Pd and Pd alloys the favored pathway in the gas phase is through OOH formation, OOH dissociation, O hydration, and HOH formation. In water solvent, the favored pathway is through the steps of O₂ dissociation, OH formation, and HOH formation. On Rh and Rh alloys the preferred steps in the gas phase are O₂ dissociation, O hydration, and HOH formation, whereas in the presence of water O₂ dissociation is followed by OH and HOH formation. The overall ORR barrier is reduced when alloying Rh with Co and increased when alloying with Fe. All Pd alloys showed lower overall barriers than Pd alone.

The computational studies of noble metal surface segregation energies for two Pt alloys (Pt,Co and Pt,Ni) and ten Pd alloys (Pd, Au, Pd,Cu, Pd, Ir, Pd, Mo, Pd, Os, Pd, Re, Pd, Rh, Pd, Ru, Pd, Ta, and Pd, W) showed that only Pd, Ir and Pd, Os segregate both in the absence and presence of adsorbed O. The alloys Pd,Mo, Pd, Re, Pd, Ta, and Pd, W were found to be extremely non-segregating in presence of adsorbed O, indicating that elimination of oxygen during the heat treatment/annealing step of alloy preparation is crucial and also a potential source of instability of the alloy materials during the ORR.

FIGURE 1. Potential Pathways for the Oxygen Reduction Reaction

- Alloying Pd decreases the binding energy of H, O, O₂, and H₂O₂ and increases the binding energy of OH, OOH, and H₂O.
- Alloying Rh increases the binding energy of OH.
- Alloying Pd decreases the barriers for H₂O formation and O hydration (two key steps in the ORR).
- Alloying Rh increases the barriers for H₂O formation and O hydration.
Experimental Results

This year’s experimental efforts focused on the synthesis and characterization of bulk alloys and nanoparticles of the Pd binary alloys Pd-Mo, Pd-W, Pd-Re, and Pd-Ta. These systems were identified last year as having favorable valence band energies, palladium surface segregation energies, and bonding characteristics with ORR reactants, intermediates, and products [7]. We also studied ternary systems based on the palladium-copper binary system to further enhance its activity and stability [8-10].

Model Systems

Ingots of 21 different compositions in six Pd alloy systems were fabricated by arc-melting. To promote surface segregation of Pd, the ingots were annealed at temperatures between 600 and 1,500°C in atmospheres of 3.5-3.7%H₂/He, 1% H₂/Ar, 100 ppm H₂/Ar, or Ar. The ingots’ ORR activity and the effect of annealing temperature and atmosphere on the activity were determined using cyclic voltammetry in a quiescent oxygen-saturated aqueous electrolyte. Using this method, the figure of merit for activity is the half-peak potential of the oxygen reduction current peak.

These studies showed that annealing Pd alloys promotes surface segregation of Pd, as evidenced by Pd-like voltammetry in deaerated electrolyte and positive shifts in the ORR half-peak potential (i.e., enhanced ORR activity). The degree of Pd segregation depended on the annealing environment and temperature, the oxophilicity of the base metal, and the Pd to base metal ratio. Of the 21 Pd alloy ingots tested, the Pd₇₂Mo₂₈ alloy showed the highest enhancement of ORR activity with an increment in ORR half-peak potential of 22 mV compared to Pd alone, but 28 mV lower than that of Pt. A 22 mV shift in half-peak potential translates to a 2.1x ORR activity enhancement assuming a Tafel slope of 68 mV/dec (Figure 2).

X-ray photoelectron characterization of the Pd₇₅Mo₂₅ alloy showed that Mo modifies the Pd valence band, extending the density of states (DOS) to higher binding energies as reflected in a d-band center shift of 0.38 eV (Figure 3). Compared to Pt, Pd₇₅Mo₂₅ lacks DOS near the Fermi energy and at >4 eV binding energy. These missing states may explain the lower ORR activity, however further studies are needed to determine the involvement of various states in the ORR.

Nano-Particles

High-surface-area carbon-supported nano-particles of Pd-W, Pd-Mo, Pd-Re, and Pd-Ni-Cu alloys were synthesized using colloidal and strong-electrostatic adsorption (Pd-W and Pd-Mo), co-impregnation (Pd-Re), and colloidal techniques (Pd-Ni-Cu). The atomic ratios of Pd to base metal of the various systems are listed in Table 1. X-ray diffraction confirmed the formation of alloys in all cases. In addition to the alloy, the Pd-Mo system also contained an additional molybdenum carbide.
phase was detected for the Pd-Mo system. Oxygen reduction reaction activity was determined using the rotating disk electrode (RDE) technique and aqueous acidic electrolyte. The highest ORR activities achieved for each system are summarized in Table 1. Of the systems studied, only Pd-Ni-Cu showed enhanced ORR mass activity. X-ray photoelectron spectroscopy analyses indicated that the inhibition of ORR activity for the binary alloy nano-particles may be due to the presence of base metal oxides on the nano-particle surfaces.

### TABLE 1. Summary of palladium alloy nano-particle catalysts synthesized this year and the highest mass (im) and area-specific (is) ORR activities achieved in each of the alloy systems. The atomic ratio of Pd to base metal and the post-deposition heat treatment resulting in the highest ORR activities are shown in parentheses.

<table>
<thead>
<tr>
<th>System</th>
<th>Pd:BM (at. ratio)</th>
<th>$i_{\text{m}}@0.8\text{ V}$ (mA/mg Pd)</th>
<th>$i_{\text{s}}@0.8\text{ V}$ ($\mu$A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-W</td>
<td>75:25, 50:50, 8:92, 15:85, 26:74, 42:58</td>
<td>93 (75.25@800°C)</td>
<td>830 (75.25@700°C)</td>
</tr>
<tr>
<td>Pd-Mo</td>
<td>90:10, 72:28, 55:45, 10:90, 14:76, 18:82, 26:74</td>
<td>138 (55.45@700°C)</td>
<td>600 (55.45@700°C)</td>
</tr>
<tr>
<td>Pd-Re</td>
<td>95:5, 75:25, 50:50, 33:67, 25:75</td>
<td>150 (3:1@300/450°C)</td>
<td>820 (1:1@300,450°C)</td>
</tr>
<tr>
<td>Pd-Ni-Cu</td>
<td>18:18:64</td>
<td>680 (550°C)</td>
<td>nd</td>
</tr>
<tr>
<td>Pd</td>
<td>100</td>
<td>200</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd = not determined

### Conclusions and Future Directions

Computational studies of the energetics of the ORR on Pd, Rh, and base metal alloys of Pd and Rh indicated that alloying Pd with Mo, W, Ta, or Re should increase ORR activity. Alloying Rh with Fe should decrease ORR activity and alloying with Co should increase activity. Experimental studies of the ORR activity of Pd alloy ingots showed that alloying with Re, Cu, W, and Mo at a 3:1 atomic ratio of Pd to base metal does enhance the ORR activity of Pd. The ORR activity increased in the order: Pd-Re<Pd-Cu<Pd-W<Pd-Mo, with Pd-Mo showing an area-specific activity enhancement of 2.1x versus Pd alone. Valence band characterization of Pd-Mo showed that Mo modifies the valence band of Pd, extending the density of states to higher binding energies. Though the overall d-band center of Pd is shifted toward that of Pt upon alloying with Mo, the valence band of Pd-Mo lacks states near the Fermi energy and at higher binding energies (>4 eV). Future efforts will focus on alloying Pd with other binary and ternary combination of base metals to mimic Pt's density of states to further enhance the ORR activity of Pd.

Future work:

- Perform RDE studies on bi- and tri-metallic model systems (bulk electrode ingots) that showed the highest ORR activities in quiescent electrolyte experiments.
- Determine the surface composition and valence band structure as a function of annealing temperature and atmosphere, using X-ray photoelectron spectroscopy, for these model systems.
- Continue synthesis of nano-particles of most promising compositions identified in model system and computational studies, with goal of achieving base metal oxide-free surfaces.
- Expand surface segregation calculations to include other noble metal:base metal ratios, ternaries, and effect of annealing atmosphere.
- Study segregation effect for binary and ternary systems in the presence of different adsorbed species on the surface.
- Study ternary systems, such as Pd-Cu-Mo, Pd-Cu-W, Pd-Cu-Re, Pd-Cu-Ta, Pd-Cu-Ni with varying Pd to base metal ratios to enhance the activity and stability of highest activity binary system identified to date.
- Continue determining alloy electronic structures using DOS spectra and perform detailed analysis of how the electronic structures affect ORR activity.

### FY 2010 Publications/Presentations

**Publications**


**Presentations**

1. D. Myers, “Non-Platinum Cathode Electrocatalysts and Platinum Electrocatalyst Degradation in Polymer Electrolyte Fuel Cells”, Indiana University-Purdue University at Indianapolis, IN, April 15, 2010. (Invited)


References


V.E.5 Advanced Cathode Catalysts

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Project Start Date: March 2007
Project End Date: 2011

Objectives

The main objective of this project is to:

• Develop oxygen reduction reaction (ORR) catalysts, alternative to pure Pt, capable of fulfilling cost, performance and durability requirements established by DOE for the polymer electrolyte fuel cell (PEFC) cathode; assure path to large-scale fabrication of successful compositions.

Individual objectives of this research are as follows:

• Design, synthesize and characterize new catalyst supports and electrode structures for new-generation ORR catalysts.

• 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 Fuel Cell 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 catalyst research in this project focuses on DOE’s 2010 technical targets specified in Table 3.4.12 (Electrocatalysts for Transportation Applications) of the Fuel Cell 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 shown in Table 1.

Accomplishments

• Significantly advanced knowledge of factors affecting ORR activity of the Pt monolayer-type catalysts (facet, shape, particle size, high coordination number).

• Specific and mass activity of ultra-low Pt-content core-shell catalysts significantly improved, up to 1,200 μA/cm² and 1.1 A/mgPGM (2.4 A/mgPt) at 0.90 V, respectively (rotating disk electrode [RDE] testing); DOE performance targets met and substantially exceeded.

• Excellent stability demonstrated with several platinum group metal (PGM) catalysts, including hollow-Pt nanoparticle catalyst (less than 17 mV performance loss at E½ after 20,000 scans) and Pt₅/Pd₂AuNi/C nanoparticles (ΔE½ limited to 6 mV after 10,000 potential cycles).
TABLE 1. Targets and Current Status

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2010 Stack Target (Anode + Cathode)</th>
<th>2010 Status (Cathode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM total loading (50 cm² fuel cell)</td>
<td>mg PGM/cm² electrode area</td>
<td>0.3</td>
<td>0.28¹</td>
</tr>
<tr>
<td>Mass activity</td>
<td>A/mg PGM @ 900 mV,</td>
<td>0.44</td>
<td>1.1², 2.4²</td>
</tr>
<tr>
<td>Non-Pt catalyst activity per volume of supported catalyst</td>
<td>A/cm³ @ 800 mV,</td>
<td>&gt;130</td>
<td>165²</td>
</tr>
<tr>
<td>Durability with cycling</td>
<td>5,000 hours at T ≤80°C</td>
<td>2,000 hours at T &gt;80°C</td>
<td>see results³</td>
</tr>
</tbody>
</table>

¹ Ptₓ/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/cm²; anode - 0.05 mg Pt/cm² Pt/C; MEA not optimized.
² Mass activity per mg PGM in Pt/Au/Pd/Co catalyst in RDE testing at 0.90 V.
³ Most catalysts tested using DOE electrocatalyst accelerated stress test protocol of cycling from 0.6 V to 1.0 V at 50 mV s⁻¹ for 30,000 cycles under N₂ gas flow.

- 2010 DOE activity target for non-PGM catalysts reached; open circuit voltage (OCV) of 1.04 V and volumetric ORR activity of 165 A/cm³ electrode (after mass-transport correction) achieved with cyanamide (CM)-Fe-C catalyst in fuel cell testing; rapid improvement in fuel cell performance of several other non-precious metal catalysts shown.
- High durability accomplished with polyaniline (PANI)-based catalysts to potential holding at OCV as well as to potential (RDE) and voltage (fuel cell) cycling, up to 30,000 cycles (DOE protocols followed).
- ORR activity of PANI-derived catalysts correlated to microporosity and Fe-N coordination; improved durability linked to graphene sheet formation (results of advanced spectroscopic and microscopic characterization).
- Synthesis of BNL’s Ptₓ/Pd/C core-shell catalyst scaled up to 20 g per batch.

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) non-precious metal catalysts obtained by high-temperature treatment of various precursors of carbon, nitrogen and transition metals. Understanding of the key factors impacting ORR activity and performance durability of catalysts in both classes is pursued through a major characterization effort including X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (TEM), among other techniques.

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 the 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) carbon- and non-carbon-based nanostructures for efficient mass transport, improved durability, and maximum catalyst utilization, and (ii) open-frame catalyst structures obtained using microemulsion/reverse emulsion techniques.

In addition to short-term testing and initial performance assessment, catalysts, supports, electrode structures, and membrane-electrode assemblies 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 — A variety of strategies were implemented in the past year to generate PGM-containing catalysts with high activity and stability. Three major ideas were applied:
(1) inducing proper degree of lattice contraction in the Pt surface layer to increase ORR activity, (2) removing low-coordination surface atoms that decrease activity and durability, and (3) partially substituting PGM with non-precious metals into the cores of the catalysts. A more flexible synthesis approach using Prussian blue analogs for the latter type of catalyst was also developed. Scale-up efforts on the more mature PtPd/C catalyst were also continued.

Several catalysts based on applying Pt monolayers to Pd cores were prepared. In general, depositing Pt onto Pd results in higher ORR activity because of the Pt lattice contraction (Figure 1a) and beneficial electronic interaction. The addition of an Ir layer onto the Pd core followed by annealing to bring Pd to the surface generates a contracted Pd layer. When the Pt monolayer is deposited, the additional lattice contraction due to the presence of subsurface Ir results in even higher ORR activity – \( \text{PtML-PdIr/C specific ORR activity: } 938 \, \mu\text{A/cm}^2 \) (3× that of Pt/C); mass activity: \( 2.17 \, \text{A/mgPt} \) (more than \( 20\times \) that of Pt/C) (Figures 1b and 1c). Pt\(_{80}\)Ir\(_{20}\)/Pd/C showed good fuel cell performance (0.55 A/mgPt), and the \( E_\circ \) of Pt\(_{ML}\)/Pd/C gained 27 mV (to 0.903 V) after a Br\(^{-}\) treatment that removed low coordination atoms.

The catalytic activity per gram of precious metal was further increased in this class of catalysts by mixing Ni into the Pd core, removing reactive Ni atoms with exposure to Au, and finally depositing a Pt monolayer (Figure 2). The obtained Pt/Au/PdxNi catalyst shows remarkable activity (by RDE testing) far exceeding the DOE target specified above – \( 1.10 \, \text{A/mgPGM} \) (2.41 A/mgPt). A synthesis involving Prussian blue analogs was developed allowing for surfactant-free synthesis of multi-metallic aggregates that include non-precious metals in the core (possibly convenient for further nanoparticle engineering). Using this approach, an active and durable Pt\(_{ML}\)/Pd\(_{x}\)Au\(_{y}\)Ni\(_{z}\) catalyst was prepared (\( E_\circ = 0.865 \, \text{V} \)). The catalyst loses only 6 mV in \( E_\circ \) after 10,000 potential cycles.

In an alternative approach, a Pt/Ni core shell catalyst was synthesized and the Ni was subsequently removed, resulting in a hollow Pt sphere with 1.2% Pt lattice contraction (Figures 3a and 3b). The hollow-sphere catalyst exhibits good durability, losing only 17 mV in \( E_\circ \) after 10,000 potential cycles and 10,000 potential pulse sequences (see figure caption for details) and maintaining a high activity of 0.62 A/mgPGM (Figure 3d).

**Scale-Up Synthesis of Catalysts with Ultra-Low Pt Content** — The synthesis of the Pt\(_{ML}\)/Pd\(_{x}\) catalyst was scaled up further to 20 g by Cabot Fuel Cells using a spray-pyrolysis approach. The catalyst delivered very good performance in fuel cell testing, matching mass-
activity of previous smaller batches (0.55 A/mg_{Pt} and 0.12 A/mg_{PGM} at 0.90 V).

Precious Metal-Free Catalysts — The focus of research in this catalyst category continued to be on materials obtained by heat-treating carbon supported precursors in the presence of transition metal salts (Fe and Co), with the scope now limited to CM-derived and PANI-derived catalysts. The ORR activity of both types of catalyst greatly increased over the Fiscal Year (FY) 2009 versions as shown in Table 2, with a nine-fold

TABLE 2. Progress in volumetric ORR activity as measured by RDE and fuel cell testing for CM-derived and PANI-derived catalysts according to project year.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Test Conditions</th>
<th>Measured Volumetric Activity per Electrode Volume at 0.8 V (A cm^{-3})</th>
<th>Improvement Factor (2008→2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDE at 25°C</td>
<td>900 rpm 0.5 M H_{2}SO_{4} mass-transport corrected</td>
<td>0.22 EDA-FeCo-C</td>
<td>5.4 EDA-FeCo-C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 PANI-FeCo(3:1)-C</td>
<td>36 (20) PANI-FeCo(3:1)-C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.4 PANI-Fe/EDA-Co-C</td>
<td>127 (60) CM-Fe-C</td>
</tr>
<tr>
<td>H_{2}-O_{2} fuel cell at 80°C</td>
<td>30 psig (11 psig) 100% RH</td>
<td>1.0 EDA-FeCo-C</td>
<td>36 (20) PANI-Fe/EDA-Co-C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.8 PANI-FeCo(3:1)-C</td>
<td>127 (60) CM-Fe-C</td>
</tr>
</tbody>
</table>

Average electrode density assumed as 0.4 g/cm^{3} (Neyerlin et al., J. Electrochem. Soc. 153, A1955, 2006; Lefèvre et al., Science 324, 71, 2009)
increase observed for CM-type catalysts and a five-fold increase observed for PANI-derived catalysts.

The activity of CM-derived catalyst was enhanced by (1) the use of a different carbon support, and (2) the addition of a second sulfur-containing precursor. With these changes, the activity of the catalyst was determined to be 165 A cm\(^{-3}\) (per electrode volume) at 0.80 V in fuel cell testing, using extrapolation to compensate for mass-transport losses (see Figure 4b). This value is comparable to the DOE 2010 performance target (see targets table above).

The PANI-derived catalysts were improved through the design of a two-step synthesis that was intended to maximize the benefits of using both Co and Fe precursors. Based on our previous results, Co has been shown to increase the presence of graphene-type structures (perhaps connected to durability) and pyridinic nitrogen content, whereas Fe has been shown to generate more active catalysts and perhaps to form more bonds with nitrogen. Introducing the metals in two separate steps indeed increases the catalytic activity as shown in Figure 5a with \(E_{\text{red}} = 0.82\) V, gaining 20 mV versus PANI-Fe-C and 40 mV versus PANI-FeCo(3:1)-C. The latter catalyst showed the best combination of activity
A comprehensive characterization effort has continued with a special focus on PANI-Fe-C catalysts prepared at different heat-treatment temperatures and having very different ORR activities. These samples have been thoroughly analyzed ex situ using spectroscopic and structural methods to gain insight into the nature of the active site. XAS, XPS, and pore-distribution results have been combined using the principal component analysis (PCA) method as shown in Figure 7 in an attempt to identify the strongest correlations between observations and catalyst activity. Fe-N-type coordination, as identified by XAS and XPS, remains strongly associated with oxygen reduction activity in ORR-active samples (900°C, 850°C, 800°C), and thus continues to be a primary candidate for the active site.

The most active, 900°C catalyst has the highest Brunauer-Emmett-Teller (BET) surface and microporous surface area (in agreement with Dodelet group results), a bimodal pore distribution, and high initial contents of Fe carbide, Fe in oxide-like coordination, and Fe in phthalocyanine-like coordination.

**Conclusions and Future Directions**

- Core-shell and core-less catalysts with greatly reduced Pt loading have been developed that 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 in FY 2010, the best of these catalysts can lose up to a factor of 3 activity (see Table 1) upon incorporation into stacks and still meet 2010 DOE stack performance targets, provided de-alloying and catalyst agglomeration can be avoided; FY 2010 RDE durability data

**FIGURE 6.** PANI-Fe-C catalysts prepared with different support materials: (a) 500-hour fuel cell life tests; (b) TEM images showing the presence of graphene-sheet “bubbles” in PANI-Fe-MWNT; “bubbles” (→) are co-located with the FeSx regions/particles (→); MWNTs are still present (→) after catalyst preparation.
Susceptibility of carbon-rich non-precious metal catalysts to flooding continues to be a major performance issue for non-precious catalysts, especially at high current densities; based on FY 2010 results, apparent durability is also impacted by water management in the electrodes; future research efforts must focus on designing electrode structures that allow for more efficient water management than traditional MEA designs.

Special Recognitions & Awards/Patents Issued

FY 2010 Publications


FY 2010 Presentations


11. 216th Meeting of The Electrochemical Society, Vienna, Austria, October 4–9, 2009. Title: “Carbon Nanotubes as Support for Heteroatomic Polymer-derived Non-precious Metal Oxygen Reduction Catalysts;” G. Wu, L. Xie, T. Zhang, Y. Yan, and P. Zelenay*.


V.E.6 Durable Catalysts for Fuel Cell Protection during Transient Conditions

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Subcontractors and Federally Funded Research
and Development Centers:
• Dalhousie University, Halifax, Nova Scotia, Canada
• Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date:  August 1, 2009
Projected End Date:  July 31, 2013

Objectives

• Develop catalysts that will enable proton exchange
membrane (PEM) fuel cell systems to weather the
damaging conditions in the fuel cell at voltages
beyond the thermodynamic stability of water during
the transient periods of start-up/shut-down and fuel
starvation.
• Demonstrate that these catalysts will not
substantially interfere with the performance of nor
add much to the cost of the existing catalysts.

Technical Barriers

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

(A) Durability
(G) Start-up and Shut-down Time and Energy/Transient
Operation

Technical Targets

While the number of start-up and shut-down cycles
for an automotive fuel cell has been estimated to be over
50,000, the number of these events when the cathode
electrochemical potential exceeds 1.23 V has not been
assessed.  In agreement with DOE, the technical targets
for the first year of the project have been defined as
follows:

• Develop cathode catalyst that can withstand currents
of 1 mA/cm² at potential of <1.45 V and 10 mA/cm²
at potential of <1.50 V with added oxygen evolution
reaction (OER) catalyst of no more than 2 µg/cm² of
platinum group metals (PGM).

Accomplishments

• Produced OER catalysts with 2 µg/cm² PGM that
achieved the first year milestone for OER activity of
1 mA/cm² at 1.45 V.
• Developed integrated OER/oxygen reduction
reaction (ORR) catalysts with only 2 µg/cm²
(Ru + Ir) showing no loss of ORR activity relative to
the baseline ORR catalyst.
• Canvassed the space around the components (Ru,
Ir, Ti) of the model OER durable catalyst in the real
PEM fuel cell environment.
• Established that Ru is the most active OER catalyst,
Ir is the most stable and that combinations of
Ru + Ir retain some of the properties of the two.
• Modified the anode catalyst to inhibit ORR while
preserving the same activity towards hydrogen
oxidation reaction (HOR).

Introduction

The project addresses a key issue of importance
for successful transition of PEM fuel cell technology
from development to pre-commercial phase (2010 -
2015).  This issue is the failure of the catalyst and the
other thermodynamically unstable membrane electrode assembly (MEA) components during start-up/shut-down and local fuel starvation at the anode, commonly referred to as transient conditions. During these periods the electrodes can reach potentials up to 1.5 V. One way to minimize the damage from such transient events is to minimize the potential seen by the electrodes. At lower positive potentials, increased stability of the catalysts themselves and reduced degradation of the other MEA components is expected. This project aims to develop catalysts that will reduce the potentials experienced during transient conditions. In order to achieve the above goal we are working on two major concepts:

- Cathode catalysts with high activity towards oxygen evolution from water
- Anode catalysts with low oxygen reduction reaction activity

**Approach**

This project will try to alleviate the damaging effects during transient conditions from within the fuel cells, via improvements to the existing catalyst materials. We will modify both the anode and the cathode catalysts to favor the oxidation of water over carbon corrosion by maintaining the cathode potential close to the thermodynamic potential for water oxidation. The absence of hydrogen and simultaneous presence of oxygen in separate regions of the anode is necessary to provoke and maintain cathode potential >1.23 V. Oxygen in these regions of the anode gets reduced. The protons for the reduction of oxygen are supplied from the cathode side via either carbon or water oxidation. The presence of a highly active OER catalyst on the cathode reduces the overpotential for a given current demand thus reducing the driving force for carbon and platinum dissolution. In addition, inhibition of the ORR on the anode side lowers the OER current through reduced proton demand which in turn decreases the OER current on the cathode resulting in reduced cathode potential.

Key requirements for both concepts are:

- **On the cathode**: implement the OER catalyst with negligible inhibition of the ORR on the existing cathode catalyst and with minimal addition of PGM, i.e. to deposit the OER catalyst as a separate, discontinuous phase - as nanoparticles.
- **On the anode**: implement the ORR inhibiting component with negligible inhibition of the HOR, either as a mixed or a separate phase.

**Results**

**Task 1. Efficient Oxygen Evolution Reaction Catalysts**

Most of the activity during the first year of the project was related to this task. The catalysts prepared were based around the model catalyst containing ruthenium, iridium, and titanium [1]. Since the oxides of ruthenium and iridium are known to have the best catalytic properties for OER in aqueous solutions, some of the catalyst syntheses were performed in the presence of oxygen [2,3].

In order to be able to properly examine the inherent activity of the OER catalyst, one needs a substrate with minimal interference from the underlying ORR catalyst. The unique features of 3M’s nanostructured thin film (NSTF) catalyst such as the lack of carbon that can corrode and the durability at high potential made it a logical choice as a support for the added OER catalyst. In addition, the NSTF fabrication process of physical vapor deposition via sputtering in vacuum allows for a wide range of materials in variety of compositions to be synthesized [4,5].

The OER catalysts synthesized and characterized can be grouped in four major categories, ranging from single elements up to a quaternary system.

1. **The Single Elements**

   To our knowledge, the most comprehensive study to date of the behavior of Ru, Ir and Ti in the real PEM fuel cell environment was completed during the first year of this project. In addition to testing samples with only 2 µg/cm² PGM, as required by the year one milestone, we have produced and tested samples with 10 µg/cm² PGM to enhance the impact of the presence of ruthenium and iridium on the cathode ORR catalysts. The OER activity was assessed by quasi-steady state measurements where polarization curves for oxygen evolution were recorded at 2 mV/s. Three consecutive potential sweeps were performed up to each of the voltages set for the year one milestones, 1.45 V and 1.5 V, as well as 1.55 V, 1.6 V and 1.65 V. The first sweep allowed us to assess the intrinsic activity. The second and the third sweep provided insights into the stability of the OER catalysts. The impact of the added OER catalyst on ORR activity was assessed through standard fuel cell performance testing before and after the OER test.

   In Figure 1 the OER polarization curves with 10 µg/cm² of either Ru (1A) or 10 µg/cm² of Ir (1B) over 0.15 mg/cm² Pt on NSTF are presented. The difference between the two OER catalysts is that Ru is initially more active than Ir, however, Ir preserves its activity even after excursions to very high potentials whereas Ru loses activity. It is worth noting that the OER activity of the platinum itself as well as Pt coated with 10 µg/cm²
Ti is extremely small, ~0.5 mA/cm² at 1.65 V. The likely cause for the loss of OER activity of the ruthenium catalyst during OER testing can be determined from the cyclic voltammograms before OER, and after exposure to 1.45 V and 1.65 V (Figure 1C). Initially, the cyclic voltammograms are dominated by the presence of ruthenium which is manifested in large capacitive current in the platinum double layer region and by the suppression of the characteristic peaks for hydrogen underpotential deposition (Hupd) and Pt oxide formation and reduction. After exposure to 1.45 V the features from the presence of ruthenium are substantially, but not completely diminished. The cyclic voltammograms only become platinum-like (as if ruthenium were completely removed) after reaching 1.65 V: well pronounced Hupd peaks, proper double layer and Pt-oxide formation/reduction. Thus, loss of Ru from the Pt ORR catalyst causes the loss of OER activity. In contrast, the cyclic voltammograms for Ir over Pt on NSTF are practically unchanged even after the exposure to 1.65 V.

The behavior of catalysts with only 2 µg/cm² additional PGM followed the same pattern as samples with 10 µg/cm² additional PGM. At the year one milestone potentials for both Ir and Ru catalysts are above the milestone OER activity of 1 mA/cm² at 1.45 V. However, only Ir catalysts exhibit activity above the milestone of 10 mA/cm² for 2 µg/cm² additional PGM at 1.5 V.

As indicated already, integration of the OER catalysts with the existing cathode catalyst, Pt in this study, was examined via 50-cm² MEAs (Figure 2). Within the reproducibility of the fuel cell testing, the integrated catalysts fall in two groups:

- No impact – no loss of ORR activity: Ir with 2 and 10 µg/cm² and Ru with 2 µg/cm².
- Negative impact – significant loss of ORR activity: high Ru content (10 µg/cm²) before OER testing and Ti.

Loss of Ru during OER testing allowed the 10 µg/cm² Ru cells to move from the negative impact group to the no impact group after OER testing. ORR activities measured at 0.9 V according to the DOE protocol follow the same pattern as the fuel cell polarization curves.

In order to get insights into the composition of the OER catalysts, X-ray photoemission spectroscopy (XPS) and electrochemical surface area measurements (via Hupd) were completed on all samples. For all samples assessed, the OER catalysts were deposited over 0.15...
mg/cm² Pt on NSTF. The atomic concentrations and ratios of Ti, Ir and Ru coatings vs. Pt reveal that Ti covers more of the Pt surface than the other elements. The fraction of the platinum surface covered by the deposited elements is higher than would be expected for pure elements because of the oxidation state of the deposits. Even though no deliberate oxygen was introduced in the vacuum deposition chamber, O/Ti ratios indicate that Ti is present as TiO₂. Ir is also present as IrO₂ in the thinner coating, 2 µg/cm², while metallic Ir dominates in the 10 µg/cm² samples. Because of overlapping of binding energies for carbon and ruthenium, deconvolution of the Ru high resolution spectra is very complex. Nonetheless, because of the key role that ruthenium plays as an OER catalyst component, a rigorous in-depth methodology was developed to determine the real surface concentration of ruthenium and its valence state. Based on the atomic concentrations of Ru, O, and oxidized C, we believe that Ru may be present as organo-metallic compounds through Ru-O-C bonds for both 2 and 10 µg/cm² on Pt-NSTF.

2. Ti – Ir OER Catalyst

The purpose of this series was to explore the influence of the combination of one OER-active (Ir, 1 - 2 µg/cm²) and one supportive, OER-inactive component (Ti, 2 - 4 µg/cm²). The results obtained suggested that the properties of these two elements are additive. OER activity improves with the Ir content. The OER activity improves further when the catalyst is made in the presence of oxygen. This improvement is more prominent at higher potentials. However, both the polarization curves as well as the intrinsic ORR activity are lower due to the Ti coverage of the ORR catalyst (Pt).

Transmission electron microscopy (TEM) results from Oak Ridge National Laboratory reveals that both Ti and Ir are clearly observed on the Pt surface as a thin layer. A Ti/Ir “nanocrystalline” layer is observed on the surface of Pt “cap” and ~50 nm down the sides of the Pt/NSTF ORR catalyst. The Ti/Ir layer is ~4-5 nm thick. In high resolution XPS, these samples show an unusual Ir spectral feature that appears only when Ti and Ir are deposited on the same catalyst. This feature will be a subject of further investigation.

3. Ti – Ir – Ru – Ox OER Catalyst

The purpose of this series was to explore the combination of the model catalysts where all the components are present. The primary variable here was the flux of oxygen during the sputter deposition. The most interesting finding in this series was that the presence of oxygen during deposition correlates with changes in fuel cell performance rather than with the OER activity or stability. Based on XPS, the presence of oxygen during the catalyst deposition decreases the amount of sputtered Ti, most probably due to the oxide buildup on the surface of the Ti target.

TEM imaging showed a thin, continuous layer of Ti, Ru and Ir was present on the surface of the Pt/NSTF “cap” and on the surface of the Pt coating along the sides of the coated NSTF whiskers. However, no individual particles were seen. The ~2 nm thick layer is crystalline, contains Ti, Ir, and Ru and is primarily on the “cap” surface. The amount of Ru in the surface layer is greater than either Ti or Ir, in agreement with XPS data for the same samples. Oxygen was also detected, indicating the possible presence of oxides.

4. Ir – Ru – Ox OER Catalyst

Based on the evaluation of the single component OER catalysts as well as the negative impact of Ti on the fuel cell performance, further effort on the project...
focused on the binary composition of Ir and Ru. The ratio of Ru:Ir was varied from 3:1 to 1:3 w/w (85–38 Ru at%), keeping the total OER added PGM loading at 2 µg/cm², the level defined by the milestone for year one. In addition, the same catalysts were deposited in the presence of oxygen. All catalysts achieved the milestone OER activity at 1.45 V and some at 1.5 V (Figure 3). Samples prepared with oxygen during the deposition process behaved the same way. As such the binary Ru–Ir catalyst composition has been chosen for future studies aimed at achieving different morphologies.

Task 2: Anode Catalysts with Low Oxygen Reduction Reaction Activity

This task is based on the notion that HOR as a facile reaction can proceed with practically unchanged rate when a Pt catalyst gets passivated by additives such as tantalum [6]. The rate of the ORR, a much more demanding reaction, on the other hand, decreases much more rapidly [7]. The effort in this task is still in the beginning phase. A series of Pt₁₋ₓ(Ta₂O₅)ₓ coatings on NSTF whiskers grown on glassy carbon disks for HOR was prepared. A series of Pt₁₋ₓ(Ta₂O₅)ₓ catalysts deposited on NSTF-whiskers grown on glassy carbon disks for HOR was produced. As expected, the presence of significant amounts of Ta₂O₅ decreases the exchange current densities for HOR decrease by only a small amount (Figure 4).

Conclusions and Future Directions

- Integrated OER/ORR catalyst systems with 2 µg/cm² of additional PGM achieved the first year milestone for OER activity of 1 mA/cm² at 1.45 V, with no impact on the ORR.
- Exploring the space around the components (Ru, Ir, Ti) of the model OER durable catalyst in real PEM fuel cell environment provided a direction for the future synthetic efforts which will be based around combinations of Ru + Ir.
- Having established the inherent activities of the OER catalyst, future catalyst evaluation protocols will focus on more realistic startup–shutdown test conditions, including cell reversal.

**FY 2010 Publications/Presentations**


**References**

V.E.7 Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

Bryan Pivovar (Primary Contact), Shyam Kocha, Huyen Dinh, Lin Simpson, Chai Engrtrakul, Arrelaine Dameron, Tim Olson, KC Neyerlin, Svitolana Pylypenko, Justin Bult, Brian Larsen, Jeremy Leong
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Project Start Date: July 20, 2009
Project End Date: 2013

Objectives
• Produce novel catalysts based on extended Pt surfaces with increased activity and durability.
• Further increase mass activity of extended surface catalysts.
• Effectively incorporate extended Pt catalysts into more traditional dispersed electrodes for improved mass transport/water management.
• Demonstrate and validate models for catalysts and electrodes based on extended surfaces.

Technical Barriers
This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) Durability (of catalysts and membrane electrode assemblies)
(B) Cost (of catalysts and membrane electrode assemblies)
(C) Performance (of catalysts and membrane electrode assemblies)
(D) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets
This project is synthesizing novel extended surface Pt catalysts and will be incorporating these catalysts into thick, dispersed electrodes. The project has targets outlined in the Multi-Year Research, Development and Demonstration Plan for both electrocatalysts for transportation applications (Table 3.4.12) and membrane electrode assemblies (MEAs) (Table 3.4.13). A summary of these targets is presented in Table 1.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2010/2015 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM Total Content</td>
<td>g/kW rated in stack</td>
<td>0.3/0.2</td>
</tr>
<tr>
<td>PGM Total Loading</td>
<td>mg PGM/cm² electrode area</td>
<td>0.3/0.2</td>
</tr>
<tr>
<td>PGM Cost</td>
<td>$/kW @ $15/g</td>
<td>8/6</td>
</tr>
<tr>
<td>Electrochemical Area Loss</td>
<td>%</td>
<td>&lt;40%/&lt;40%</td>
</tr>
<tr>
<td>Mass Activity</td>
<td>A/mg-Pt @ 900mV</td>
<td>0.44/0.44</td>
</tr>
<tr>
<td>Specific Activity</td>
<td>µA/cm²-Pt @ 900 mV</td>
<td>720/720</td>
</tr>
<tr>
<td>Durability with Cycling ≤80°C</td>
<td>Hours</td>
<td>5,000/5,000</td>
</tr>
<tr>
<td>Unassisted Start from Low Temperature</td>
<td>°C</td>
<td>-40°C/-40°C</td>
</tr>
<tr>
<td>Thermal Cyclability in Presence of Condensed Water</td>
<td>Yes/Yes</td>
<td></td>
</tr>
</tbody>
</table>

PGM = platinum group metal; RH = relative humidity

Accomplishments
• Synthesized novel extended surface Pt catalysts using Cu nanowires and spontaneous galvanic
displacement (SGD). These materials advance our team’s earlier work in the area of Ag and Se nanowires as templates [1]. Cu-based systems offer potential advantages as Pt-Cu alloys have been found to yield materials with greatly enhanced specific activity [2]. Preliminary results have shown significantly enhanced specific activity of these structures compared to traditional Pt catalysts.

- Demonstrated for the first time continuous, conformal coating of Pt on carbon nanotubes (CNTs). CNTs offer the potential of high conductivity and low corrosion compared to other support materials. Demonstrated control of Pt layer thickness by deposition time.
- Investigated vertically aligned CNTs growth and Pt deposition by several techniques. Optimized growth parameters to allow a wide range of tube lengths and packing densities providing tunable substrates for deposition.

Introduction

Pt remains a primary limitation for the widespread commercialization of fuel cell vehicles. To date, approaches looking to replace Pt with a non-PGM have met with limited success. “Thrifting” of Pt (i.e., ultralow Pt loadings) seems to be the most likely (near-term) option for meeting cost, performance and durability targets. Typical Pt catalysts for fuel cell applications are small nanoparticles (such as cubo-octahedron) that have high surface areas, and therefore significant fractions of Pt atoms are surface accessible. This makes sense as one would want as many Pt atoms on the surface as possible. However, catalytic activity and durability of extended surfaces can outweigh the surface area advantages of smaller particles, particularly if these advantages can be maintained at thin wall thickness, as highlighted by the promising work done on nanostructured thin film catalysts based on Pt or Pt alloys at 3M [3] and Pt and Pt alloy nanotubes UC Riverside [1]. The synthesis of catalysts with high mass activity and the effective implementation of these catalysts in high-performance, durable and robust MEAs will help enable fuel cell commercialization on a significant scale.

Approach

Our approach involves synthesizing novel catalyst particles using either a nanostructured support material such as CNTs, metal oxide nanoparticles, or perylene red nanowhiskers; or a sacrificial metal template. Pt is deposited on these materials either through vapor deposition (including sputtering and atomic layer deposition [ALD]) or solution deposition (including galvanic displacement). Our goal is to produce nanostructures with thin, continuous films of Pt as similar structures have shown high catalytic activity and durability. The materials synthesized are characterized by several techniques with a strong focus on microscopy and electrochemistry. To date, extended surface catalysts have been demonstrated in traditional, thick catalyst layers that include Nafton® and have been shown to exhibit good tolerance to a wide range of operating conditions including cold-start. The novel catalysts produced in this project will be implemented in thick, dispersed electrodes to investigate the production of high-performance, robust electrodes from these materials. Modeling will be used in support of our catalyst synthesis studies and our electrode studies, extending established models involving wetting of Pt on supports, simulating electrode architecture, and evaluating criteria that impact electrode performance.

Results

We have investigated a number of substrates for their potential application as supports for extended surface Pt hosts. Our results with CNTs have focused on two approaches: CNT mats, where mats are drop cast onto substrates prior to Pt deposition; and vertically aligned CNTs. Based on the high surface tension of Pt and the tendency of numerous Pt/CNT catalysts reported to form isolated particles, we expected difficulty in getting CNTs to conformally coat with Pt. Our early studies resulted in the first reported continuously coated CNTs. These materials, an example of which is shown in Figure 1, obtained from Pt-sputtered CNT mats, demonstrated the potential of CNTs as hosts for continuous thin films of Pt and resulted in an early project milestone being accomplished. Through systematic studies of deposition time we were able to obtain target Pt thickness of ~2 nm, such as that estimated from Figure 1 from comparisons of coated regions of CNTs to uncoated regions highlighted by the measurements within Figure 1.

Vertically aligned CNTs were investigated as they resulted in an increased materials yield on a geometric area basis compared to the drop cast CNT mats. As part of this project vertically aligned CNTs were for the first time synthesized at NREL. In the area of vertically aligned CNT synthesis, we performed tests to investigate reproducibility of our methods both from sample to sample and within a sample. These studies focused on Fe-catalyst deposition for vertically aligned carbon nanotubes (VACNTs) and involved sputtering, ALD, and electrochemical deposition. We also modified synthesis conditions to include water assisted deposition. We now have a wider materials set for study and a better appreciation for the variables controlling VACNT formation. We also isolated that it is largely reproducibility of the Fe-based catalyst used for VACNT growth that is the principal step leading to
reproducibility issues between samples. The use of ALD allows for better reproducibility than what was obtained using other techniques. Figure 2 and Table 2 summarize the impact of temperature on the growth conditions presented and give examples of the different VACNTs that we have synthesized and how by controlling specific parameters (in this case temperature) we produce materials with specific properties.

In the area of Pt deposition, our studies have shown that VACNTs have very heterogeneous coatings of Pt regardless of deposition technique, although ALD provides slightly better uniformity than sputtering in most cases. Because ALD is a step-by-step process that offers the potential for very thin, conformal coatings we had hoped for much more uniform coatings using ALD. Of particular issue is the slow nucleation process of Pt on CNTs, as reflected in Figure 3a, which shows the Pt composition at the bottom, middle and top of 20 micron VACNTs. Pt deposition on the surface takes over 100 cycles before significant nucleation takes place. The resultant particles either tend to have exceptionally thick coatings or discrete particles using the approaches we have investigated and are strongly dependent on their location along the CNTs. In order to investigate the nucleation process we have performed a number of pretreatments to the CNTs including oxygen plasma, Ar plasma, and trimethylaluminum (TMA). Of these three pretreatments, only the TMA pretreatment showed an enhancement in nucleation rate. Even with this increased nucleation, the sample still showed a strong dependence on position Figure 3b. With further increases in nucleation rate it is possible that ALD will yield the target structures we are striving for, so continued effort will be placed on investigation of nucleation rates using ALD.

**TABLE 2.** Effect of Synthesis Temperature on the Length and Width of VACNTs

<table>
<thead>
<tr>
<th>Synthesis Temperature (°C)</th>
<th>Approx. Width (nm)</th>
<th>Approx. Length (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>30</td>
<td>3-5</td>
</tr>
<tr>
<td>725</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>750</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>775</td>
<td>15</td>
<td>115</td>
</tr>
<tr>
<td>800</td>
<td>12</td>
<td>87</td>
</tr>
</tbody>
</table>

**FIGURE 1.** Transmission Electron Microscopy of Multiwalled Drop Cast CNT Mats with Pt Sputter Deposited

**FIGURE 2.** (left): VACNT Synthesized at 700°C; (right): VACNT synthesized at 775°C
In the area of metal template synthesis and SGD, we have focused on Cu nanowires followed by subsequent displacement by Pt. There are only a few reports of Cu nanowire synthesis in the literature and the reported procedures have taken many hours with limited yields. We have developed a microwave-assisted wet chemical approach that takes only 15 minutes and greatly increases our yield of materials, examples of the materials generated are shown in Figure 4. These nanowires add to the Ag and Se nanowires that have already been demonstrated as templates for spontaneous galvanic displacement by our project subcontractor UC Riverside [1]. Cu offers potential advantages over Ag and Se because it has been shown to lead to improved activity when used in alloys with Pt [2]. We have examined a limited materials set after galvanic displacement and have found improvements in specific activity when compared to traditional materials (~6x improvement). Our studies in this area are in the preliminary stages and will continue with a focus on mass activity and durability.

**Conclusions and Future Directions**

We have demonstrated for the first time conformal Pt coatings on CNTs, and Pt nanostructures from Cu nanowires. We have performed controlled growth of CNTs. We have investigated Pt ALD, sputtering, SGD and other solution based routes as Pt deposition techniques. Future work, broken down by topical area, includes:

- **Templates/Cores**
  - Further advancement of Cu-based nano-templates.
  - Development of short, less dense VACNTs that are analogous to the 3M nano-structured thin-film whiskers.
  - Investigation of metal oxide supports.

- **Pt Deposition**
  - Continued investigation of sputtering onto CNT mats in order to increase heterogeneity and yield.
  - ALD studies investigating the effect of adhesion layers and processing conditions on Pt nucleation and growth.
  - Optimization of SGD displacement process, resultant structures/composition, and electrochemical performance and durability.

- **Electrode Studies**
  - Electrochemical screening (specific and mass activity) of novel catalysts.
  - Incorporation of highest performing catalysts into electrode studies.
  - MEA fabrication and fuel cell testing of novel catalysts.
• Modeling
  – Advancement of models and correlation of experimental data with models involving Pt wetting on surfaces, electrode structure and performance.

FY 2010 Publications/Presentations


References


V.E.8 Nanosegregated Cathode Alloy Catalysts with Ultra-Low Platinum Loading

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Project Start Date:  September 2009
Project End Date:  September 2012

Objectives

- Fundamental understanding of the oxygen reduction reaction on multimetallic PtM (M = Co, Ni, Fe, Mn, Cr, V, and Ti) and PtM1N2 (M1 = Co or Ni; N2 = Fe, Mn, Cr, V, and Ti) materials.
- Develop highly-efficient, durable, nanosegregated Pt-skin PtM and PtM1N2 catalysts with ultra low Pt content.
- Find relationships between activity/stability of well-characterized bulk alloys and real nanoparticles (NPs).
- Develop novel chemical and physical methods for synthesis of monodispersed PtM and PtM1N2 alloy NPs and thin metal films.
- Resolve electronic/atomic structure and segregation profile of PtM and PtM,N2 systems.
- Resolve composition effects of PtM and PtM1,N2 systems.
- Demonstrate mass activity and stability improvement of PtM and PtM1,N2 alloy NPs.
- Use computational methods as the basis to form any predictive ability for tailoring binary and ternary systems to have desirable reactivity and durability properties.

Technical Barriers

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

(B) Cost
- Reduce precious metal loading of catalysts.
- Increase the specific and mass activities of catalysts.
- Increase the durability/stability of catalysts with cycling.
- Test and characterize catalysts.

Technical Targets

This project is conducting fundamental studies of the oxygen reduction reaction on Pt-based PtM binary and PtM1,N2 catalysts. Insights gained from these studies will be applied toward the design and synthesis of highly-efficient, durable, nanosegregated Pt-skin catalysts with ultra low Pt content that meet or exceed the following DOE 2015 targets:

- Specific activity @0.9 V Ir-free: 720 mA/cm²
- Mass activity @0.9 V: 0.44 A/mgPt
- Platinum group metal total content: 0.2 g/kW
- Total loading: 0.2 mg/cm²
- Catalyst support loss: <30%
- Durability with cycling (80°C): 5,000 hrs

Accomplishments

- Synthesized wide range of bi/multi-metallic NPs with controlled size and composition by colloidal organic solvo-thermal approach.
- Resolved particle size effect for bimetallic NPs: optimal size is found to be 5 nm with activity (1.5 A/mgPt) that exceeds the DOE 2015 targets.
- Established post-synthesis routes for altering surface/adsorption and catalytic properties:
  - Acid treatment for removal of non-precious metal atoms and optimal annealing temperature to create the most active (1.4 A/mgPt) segregation profiles for bimetallic PtM NPs.
  - Performed composition optimization of bimetallic PtM catalysts.
  - Established activity (stability) trends for bimetallic NPs.
- Confirmed that ternary alloys could provide additional tunability towards activity and stability.
Introduction

In the quest to make the proton exchange membrane fuel cell (PEMFC) a competitive force, one of the major limitations is to reduce the significant overpotential for the oxygen reduction reaction (ORR) and minimize dissolution of the cathode catalysts. Here, we report a progress for Fiscal Year (FY) 2010 in experimental and theoretical studies to addressing the importance of alloying Pt with 3d elements (M= Ni, Co, Fe etc.) in order to form catalytically active materials with so-called nanosegregated profile [1] and to minimize the amount of Pt. We have demonstrated that the nanosegregated surfaces are superior in both: exceptional catalytic activity for the ORR and higher stability of Pt surface atoms.

Approach

To address the challenges that are listed as the DOE targets for the Fuel Cells sub-program we rely on our materials-by-design approach [2,3]. This involves four major steps: (i) advanced synthesis of novel nanoscale materials, which enables control of their size and composition; (ii) characterization of atomic and electronic properties by ex situ and in situ surface characterization techniques and theoretical methods; (iii) resolving the surface electronic and crystal structures at atomic/molecular level that govern efficient kinetics of the ORR; and (iv) synthesis/fabrication of the highly efficient nanoscale materials, which are guided by the fundamental understanding of structure-function relationships.

Results

The Crystallite Size Effect for Pt₃M Catalysts: The crystallite/particle size effect is the variation in reaction rate or selectivity with characteristic dimension of metallic catalysts, while the structure sensitivity refers to the dependence of reaction rate or selectivity on the geometry of the surface. Hence a structure sensitive reaction is expected to exhibit a crystallite size effect. This has been confirmed for the ORR on Pt, i.e., the ORR is strongly affected by the particle size of Pt NPs supported on carbon [4]. In order to systematically explore this effect for Pt alloys we have established novel colloidal organic solvo-thermal routes for synthesis of monodisperse Pt₃M NPs with controlled size ranging from 3 to 9 nm in diameter. We have found that the particle size effect also applies for the ORR on Pt₃M NPs [5]. As summarized in Figure 1 for 3-9 nm Pt₃Co NPs, while specific activity increases with the particle size, i.e., from 2-4 mA/cm², respectively, the optimal mass activity is obtained for ~5 nm NPs. Both the specific activity (3 mA/cm²) as well as the mass activity (1.6 A/mgₚt) of the ORR on 5 nm Pt₃Co NPs significantly exceeds the DOE targets of 0.72 mA/cm² and 0.44 A/mgₚt.

Temperature-Induced Segregation towards the Nanosegregated Materials: The term nanosegregated materials has been coined to describe the formation of oscillatory concentration profile with 100% Pt in the first layer, counterbalanced by depletion of Pt in the second layer, which is followed by enrichment of Pt in the third layer [1]. Surface segregation was confirmed experimentally and theoretically for the bulk Pt₃M single and polycrystalline surfaces, but not for corresponding NPs. Given that the highest activity that has ever been observed on cathode catalyst was obtained on
Pt<sub>3</sub>Ni(111) electrode, with a specific activity 90-fold higher than the state-of-the-art Pt/C catalysts [1], it has been of paramount importance to develop preparation method that would allow the design of the PtM NPs with nanosegregated-like catalytic properties.

For that reason the temperature annealing effect on Pt-alloy NPs was explored. The results are summarized in Figure 2 for the monodisperse and homogeneous 4.5 nm Pt<sub>3</sub>Co/carbon catalyst synthesized by solvo-thermal route and then treated at various temperatures, ranging from 300 to 800°C. No obvious size or morphology change was observed for the catalysts annealed up to 400-500°C (Figure 2a). Particle sintering appeared for the catalyst annealed at the temperatures higher than 500°C, which is evident at 800°C (Figure 2b). The X-ray diffraction (XRD) analysis showed single crystal phase for all thermally annealed NPs, confirming the homogeneous alloy composition. This exclusion allowed exploration of the intrinsic effect of thermal annealing on the catalytic performance of the catalyst. Figure 2e and ref. [6] show that, without significant particle sintering, the specific activity increase of almost 1 mA/cm<sup>2</sup> was obtained for the nanoparticles pre-treated at 400°C. If compared to the state-of-the-art Pt/carbon catalyst, 3-fold activity enhancement for the ORR is reached on this catalyst. In turn, this may imply that the surface segregation may have happened with Pt<sub>3</sub>M NPs even at the moderate 400-500°C temperatures.

Due to experimental limitations in resolving the concentration profile of the very first atomic layers for nanoscale materials, we used Monte Carlo simulations to probe formation of the Pt-skin for 5 nm Pt<sub>3</sub>Co NP at the optimal temperature. Figures 2c and 2d reveal that the resultant Pt concentrations are 99 at% in the outermost surface layer, 44 at% in the second sub-surface layer, and 92 at% in the third sub-surface layer, suggesting that 400°C would induce formation of the nanosegregated structure. As shown in Figure 2e, the descending trend in specific surface area for different annealing temperatures is followed by ascending trend in specific activities. In turn, volcano-like shape is observed for mass activity vs. annealing temperature. It is important to point out that the activities presented here are much higher than those reported in the literature for PtCo alloy catalysts prepared by conventional co-precipitation or impregnation methods [7]. This suggests that the solvo-thermal synthesis brings high level of control of the crucial parameters such as homogenous distribution of particle size and composition profiles, which indeed lead to formation of nanosegregated-like properties.

Composition Effects—Tailoring of Nanosegregated Layers: Having established the optimal particle size of Pt<sub>3</sub>M NPs and the most favorable annealing temperature for the formation of nanosegregated-like materials, the next step was to establish the most favorable composition of PtM NPs. To unravel this complex issue we relied on the advanced solvo-thermal methods to synthesize Pt<sub>x</sub>Ni<sub>y</sub> NPs with altered 3:1, 1:1, 1:2 and 1:3 atomic ratios. In order to avoid the particle size effect, the size of all NPs was controlled to be 5 nm. Due to surface chemistry of the 3d elements under PEMFC-related conditions, the NPs were pretreated in acid solution to remove surface Ni atoms and to form the so-called skeleton-like surface structure (Figure 3). As summarized in ref. [8], the highest specific (4.0 mA/cm<sup>2</sup>) and mass (1.5 A/mgPt) activities for the ORR are observed on NPs having 1:1 Pt to Ni atomic ratio. This result differs from the most active concentration profile (3:1 Pt/Ni atomic ratio) previously observed on the extended Pt<sub>3</sub>M surfaces [8]. The resolution of this disparity is obtained by utilizing energy-dispersive X-ray (EDX) spectroscopy; i.e, EDX
showed that acid pretreatment transforms PtNi NPs into Pt skeleton structure with ca. 25% Ni.

Further modification and altering of the activity and stability of PtNi NPs was obtained by subsequent annealing at 400°C. This treatment allowed relaxation of low-coordinated surface atoms and the formation of the core (PtNi)/shell (2 atomic Pt layers) structure depicted in Figure 3. The XRD analyses revealed that the core/shell-like NPs are homogenous having a face-centered cubic pattern with the decrease of lattice constant due to the alloying of Pt with Ni. The core/shell PtNi NPs have unique activity for the ORR, i.e., 1 mA/cm² at 0.95 V (!) as well as a promising stability (PtNi/Pt NPs do not suffer from the decay in activity or surface area after 30,000 cycles between 0.5 to 1.1 V).

Electrocatalytic Trends for Ternary Systems:
Organic colloidal solvo-thermal approach was developed to synthesize Pt-based PtM₁N₂ (NM = Fe, Co, and/or Ni) ternary alloys in order to understand fundamental differences between bimetallic and ternary systems, Figure 4. It is expected that addition of the third 3d element would induce additional level in altering of the catalytic activity for binary systems. Currently, there is no fundamental correlation between the addition of two 3d elements and induced change of electronic/adsorption/catalytic properties of the nanosegregated materials. The preliminary results (summarized in Figures 4a-d) are encouraging, given that PtCoNi NPs show specific (5 mA/cm²) and mass (2 A/mg) activity that exceed the corresponding bimetallic systems and the DOE 2015 targets. In turn, this indicates that ternary alloys could provide additional tunability towards the activity and stability of Pt-based alloys. We strongly believe, therefore, that our material-by-design approach will enable further enhancement of the catalytic properties with breakthrough performance for the cathode catalysts in PEMFCs.

Conclusions and Future Directions
- PtM and PtM₁N₂ NP cathode catalysts obtained from the organic solvo-thermal synthesis exhibit superior activity and stability than those prepared by the conventional methods. The optimal particle size, annealing temperature, and alloy composition of the PtM NPs are determined.
Significant mass activity and durability improvements are obtained for PtM and PtM,N₂ NPs. Advanced theoretical modeling (density functional theory, Monte Carlo) methods are developed for resolving nanosegregated structures. Understanding of the ternary alloy catalysts is yet to be addressed.

In collaboration with industrial partners, fabrication and testing in a membrane electrode assembly of the most promising catalysts is planned as well as patenting of the novel synthetic routes developed in this project.

**FY 2010 Publications/Presentations**


Electrochemical Soc. 217th Meeting Vancouver, Canada, April 2010.

References


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Project Start Date: July 1, 2009
Project End Date: September 30, 2013
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Objectives

Developing high-performance fuel cell electrocatalysts for the oxygen reduction reaction (ORR) comprising contiguous Pt monolayer (ML) on stable, inexpensive metal or alloy:

- Nanoparticles (NP)
- Nanorods
- Nanowires
- Carbon nanotubes (CNT)

Technical Barriers

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

- Durability
- Cost
- Performance

Introduction

The last decade has seen considerable advances made in fuel cell electrocatalysis yielding improved electrocatalysts, and increasing our understanding of the kinetics of the ORR along with affording significant advances in theoretical treatments. However, some technological difficulties that hamper the automotive applications of fuel cells have not been removed. It is generally accepted that there is an optimal size for the...
ORR where the balance between the effects of increasing the surface area and the adverse effect of small particles oxidation are met.

**Approach**

The awareness of a complex influence of the nanoparticle size and shape on the catalyst’s activity has been growing, but a clear description was not available. We examined the effects the thickness of the Pt shell, lattice mismatch, and particle size on specific and mass activities from the changes in effective surface area and activity for oxygen reduction induced by stepwise Pt ML depositions on Pd and Pd₃Co nanoparticle. We find significant weakening of binding energy of oxygen (BE-O) on the (111) facet compared to the extended surface due to nanoscale induced in-plane lattice contraction. Because the ORR rate on Pt is desorption limited, lowering BE-O enhances the ORR activity. Thus, the high coordination (111) facets are most conducive to the ORR on nanoparticles. In addition, they are less prone to dissolution than low-coordinated edges, defects, and less close-packed facets.

Therefore, smooth, lattice contracted (111) like surface structures are needed to achieve durable high ORR activity. Based on our understanding of the effect of shape, size and composition of nanoparticles on the kinetics of the ORR, we have studied Pt monolayers on surfaces having predominantly highly coordinated atoms that exist on nanorods, nanowires, smooth nanoparticles, hollow Pd spheres, single crystalline nanoparticles with predominantly (111) facets. We have studied hollow Pt electrocatalyst to optimize the nature and size of templates, deposition process and the size of hollow with respect to activity and stability. We will also study design and synthesis of, what we call, the second generation core-shell catalysts particularly using a sub-surface core modification.

**Results**

**Pd Nanorods, Nanowires as Supports**

The structural sensitivity of the ORR on Pt is now established for nanoparticles catalysts. The activity decreases in the sequence for the (111) > (100) > (110) oriented facets. The nanorods and nanowires with smooth surfaces present attractive option because they can be tailored to increase surface fraction of atoms of the most ORR active facets and decrease low coordination sites. Syntheses of nanorods and nanowires were carried out using chemical and electrochemical deposition. In both cases enhanced reaction kinetics was observed. This is the first report on electrochemical deposition of nanowires. The results will be reported soon. They are quite promising; given the better Pd utilization and a direct formation at the carbon surfaces that provides electrolyte access to a major part of the catalysts' surface and thus its the best utilization. Figure 1 shows the scanning transmission electron microscope (STEM) image of carbon supported Pd nanowires synthesized using a chemical procedure and polarization curves for a Pt₉/Pd/C catalysts. Their specific and mass activities for Pt monolayers on Pd nanorods are given in Table 1, while for nanowires are 641 μA/cm² and 1.01 A/cm², respectively. The results are preliminary, and indicate broad possibilities for improvements.

**Smooth, or Smooth and Hollow, Pd Nanoparticles**

Smooth Pd nanoparticles can be obtained by removing the low coordination support atoms (at edge and kink sites), which are places where OH strongly adsorbs and the dissolution first occurs can increase the catalyst's stability and activity without particle size growth. Several cycles of bromide adsorption and subsequent reductive desorption removes the low-
coordination atoms from Pd surfaces. The morphologies of the Pd nanoparticles before and after the bromide treatment show that the sharp edges appearing in most of the particles in the Pd/C can be hardly observed after the bromide treatment, resulting into a rounded-shape nanoparticles, much more uniform particle size distribution. The latter indicates a pronounced Ostwald ripening effect. The effect of the Br- treatment of a Pd surface causes an increased activity and stability of a Pt/Pd/C catalyst having \( \text{i}_{\text{on}} = 1.21 \, \text{A/mg Pt} \) and \( \text{i}_{\text{p}} = 0.78 \, \text{mA/cm}^2 \) that surpasses commercial Pt/C catalysts by 5 times in mass activity. A negligible change in \( \text{E}_{\text{1/2}} \) after 10,000 potential cycles indicates a high stability of a Pt monolayer on a smooth Pd surface.

**Hollow Pt Nanoparticle Catalysts**

We explored whether hollow can induce a needed lattice contraction as a no-cost, trouble-free core. Using Ni nanoparticles as dissoluble template, we produced compact Pt hollow nanospheres. Excellent durability was found: no loss after 10,000 potential sweep cycles between 0.65-1.05 V, and in severe pulse potential cycle test, 30 s alternatively at 0.65 and 1.05 V, sustainable Pt mass activity of 0.58 mA g\(^{-1}\) was achieved, exceeding the DOE target of 0.44 mA g\(^{-1}\) for platinum group metals. In another test, no further loss was confirmed after additional 7,000 potential cycles that last more than 200 hours. The enhancement over solid Pt nanoparticles (45% Pt/C, 3.2 nm) is six-fold after 100-hour durability test.

As shown in the STEM images (Figure 2), compact single grain nanospheres with 3-12 nm in diameter and 1-2 nm in shell thickness were found after durability test. Electron and X-ray diffraction measurements revealed up to 2% average lattice contraction compared to Pt lattice constant of 0.3923 nm. The density functional theory (DFT) calculation for solid and hollow Pt nanoparticles manifests a trend that the lattice contraction with a subsequent weakening of oxygen binding energies relative to that of Pt(111) is greater for hollow than for solid nanoparticles, independent of particle size. In addition to lattice contraction, we found significantly smoother surface on hollow particles. Both effects led to high sustainable ORR activity not achieved previously.

**Conclusions and Future Directions**

- Smooth surfaces, with highly-coordinated atoms, are suitable to support a Pt ML that yield very active catalysts.
- Pd nanowires were synthesized. Their thickness needs to be reduced and removal of surfactants simplified to obtain an excellent catalyst with a Pt ML.
- Sub-surface ML modification of cores is very promising; it opens up numerous possibilities for design of catalysts.
- Hollow Pd and Pt nanoparticles are very attractive for further studies.
- Initial difficulties with refractory metal alloys and metallization of CNTs are being resolved; the results are encouraging (not shown here).

Future studies will focus on:

1. Improve synthesis of Pd nanorods, nanowires, and Pd hollow NPs. (BNL, MIT, JMFC)
2. Improve metallization and catalysation of CNTs, oxides, nitrides. (JMFC, MIT, BNL)
3. Pd-Nb alloy NPs; start the work on Pd-W NPs and Pd-V. (BNL, MIT)
4. Scale-up of selected catalysts up to 20 grams. (JMFC, BNL)
5. MEA fabrication and tests.

**Special Recognitions & Awards/Patents Issued**


3. Three patents issued in 2010
   - 7,704,919 Electro catalysts having gold monolayers on platinum nanoparticle cores, and uses thereof
   - 7,704,918 Synthesis of metal-metal oxide catalysts and electrocatalysts using a metal cation adsorption/reduction and adatom replacement by more noble ones
   - 7,691,780 Platinum- and platinum alloy-coated palladium and palladium alloy particles and uses thereof

4. Three patent applications in 2010
   - 20100177462 Platinum-Based Electro catalysts Synthesized by Depositing Contiguous Adlayers on Carbon Nanostructures
   - 20100099012 Electrocatalyst Synthesized by Depositing a Contiguous Metal Adlayer on Transition Metal Nanostructures
   - 20100097742 Electrodes Synthesized from Carbon Nanostructures Coated with a Smooth and Conformal Metal Adlayer

**FY 2010 Publications/Presentations**


V.E.10  The Science and Engineering of Durable Ultralow PGM Catalysts

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Project Start Date:  October, 2009
Project End Date:  October, 2014

Objectives

• Development of durable, high mass activity platinum group metal (PGM) cathode catalysts enabling lower cost fuel cells.
• Elucidation of the fundamental relationships between PGM catalyst shape, particle size and activity to help design better catalysts.
• Optimization of the cathode electrode layer to maximize the performance of PGM catalysts – improving fuel cell performance and lowering cost.
• Understanding the performance degradation mechanisms of high mass activity cathode catalysts – provide insights to better catalyst design.
• Development and testing of fuel cells using ultra-low loading high-activity PGM catalysts – validation of advanced concepts.

Technical Barriers

This project addresses the following technical barriers from Section 3.4 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability: PGM catalysts durability goals have not been achieved for transportation and stationary systems.
(B) Cost: The amount of expensive PGM catalyst currently required in fuel cell stacks does not meet cost targets for transportation and stationary systems.
(C) Performance: The performance of PGM catalysts at required loadings to meet cost targets does not meet the current targets.

The technical targets for catalyst loading are indicated in Table 1. These targets were formulated with the assumption that fuel cell durability and impurity tolerance would not be impacted by the decreased Pt loadings used in the fuel cells.

Technical Targets

Table 1. Technical Targets: Electrocatalysts for Transportation Applications (Extracted from Table 3.4.12. Technical Plan April 27, 2007)

<table>
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<th>Characteristic</th>
<th>Units</th>
<th>2005 Status</th>
<th>Stack Targets</th>
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<td>Stack 2010</td>
<td>2015</td>
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<td>PGM total content (both electrodes)</td>
<td>g/kW rated</td>
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<td>1.1</td>
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<td></td>
<td>mg PGM/cm² electrode area</td>
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Accomplishments

• New nanowires supports for low PGM catalysts developed.
• Polypyrrole nanowire supports developed using electrosynthesis.
• Ultra-low loading Pt layers successfully deposited by radio frequency magnetron sputtering.
• Pt dispersion onto differing supports studied by scanning electron microscopy (SEM) and X-ray diffraction.
• Theoretical density functional theory modeling commenced.
• Single-cell fuel cell testing of new low-PGM catalysts commenced.

Introduction

Minimizing the quantity of Pt group metals used in proton exchange membrane fuel cells is
one of the remaining grand challenges for fuel cell commercialization. Tremendous progress has been achieved over the last two decades in decreasing the Pt loading required for efficient fuel cell performance. Prior work at Los Alamos has led to a twenty-fold reduction in the amount of Pt required for good fuel cell performance at acceptable power densities. Unfortunately, the fluctuations in the price of Pt represent a substantial barrier to the economics of widespread fuel cell use. Durability and impurity tolerance are also challenges that are tightly coupled to fuel cell Pt electrode loading. Traditional approaches to decreasing the amount of Pt required for good performance include:

- Increasing mass activity by decreasing Pt particle size by supporting on carbon.
- Alloy formulation Pt-Co, Pt-Cr alloys to improve mass activity.
- Increasing Pt utilization by optimization of electronic and ionic contact of the Pt particles.
- Improving conductivity of the electronic and ionic conducting constituents of the membrane electrode assembly.
- Improving reactant to and product mass transport away from the electroactive sites. Recent novel approaches include the nanoengineering of core shell catalysts and Pt particles of unusual geometries such as nanowires/whiskers.

The success of the aforementioned approaches has been great; however further advances using such approaches may be reaching a number of limitations. In the case of decreasing particle size, a peak in mass activity is observed around 2.5 nm Pt particle size due to a steady decrease in the area specific catalytic activity for oxygen reduction when the quasi-spherical particle size decreases below threshold bulk values in the ~10 nm range. The mass activity continues to improve due to an inverse linear relationship between particle surface area and particle volume (mass). The decrease in area specific activity overwhelms the increase in surface area for a given mass for Pt particle sizes between 2 and 3 nm. Durability also suffers as the difference in positive free energy between the nanoparticle and a bulk crystal also increases with decreasing particle size. The energetic destabilization of the Pt particles with decreasing size makes them more susceptible to oxidation, dissolution/re-precipitation and grain growth via Oswald ripening processes. Long-term fuel cell durability testing, cyclic voltammetry and thermodynamic measurements confirm this behavior.

**Approach**

Our approach to new PGM catalyst design is multi-tiered. We are designing new low platinum loading catalysts on novel support materials to improve fuel cell performance. Novel PGM shapes; nanoparticles, nanotubes and nanowires are being synthesized in a variety of sizes. We are using contemporary theoretical modeling and advanced computational methods to understand and engineer the new catalysts. We are also modeling and designing appropriate catalyst architectures to maximize the performance of our novel catalysts. Catalyst-support interactions and their effects on durability and mass activity are also investigated. We study and test the performance of the catalysts in electrochemical cells, single-cell fuel cells and fuel cell stacks. The new catalysts are extensively characterized before and after fuel cell operation.

**Results**

**Activation of Pyrograf and Bulk Chemical Deposition of Polypyrrole with Light and Heavy Deposits**

Low-cost Pyrograf III carbon nanofibers (Applied Sciences Inc.) were “activated” with concentrated nitric acid to impart surface functionality. The hydrophilic surface moieties provided relatively stable aqueous suspensions and purportedly improved the adhesion and uniformity of polypyrrole depositions. For bulk chemical depositions of polypyrrole, appropriate amounts of pyrrole were added to roughly 2 mg/cm² aqueous Pyrograf suspensions and stirred briskly. After at least 10 minutes, ammonium persulfate was then added to catalyze the polymerization. The suspensions quickly flocculated to a degree commensurate with the pyrrole addition. The PPy-coated nanofiber products were filter rinsed with deionized water.

**Activated Pyrograf with Ti and Pt Depositions**

To form thin and uniform carbon nanofiber films, dilute aqueous suspensions of activated Pyrograf were filter cast onto hydrophilic microporous filter membranes (Millipore HVLP). The hydrophilic nature of the filter was crucial for achieving an equal flow throughout and hence an even amount of material accumulation. After thorough drying, the thin film coated filters were loaded into a multi-target sputtering system (Model 2400, High Tech Services, Inc.) equipped with 15 cm titanium and platinum targets. The Ti target was first sputter cleaned for 15 min with 500 W radio frequency power under 8 mTorr of argon and then the filter samples were sputter coated with the Ti for 12 min at 50 W. The Ti-coated samples were removed from the sputtering chamber for analysis and to allow air-induced formation of oxides to avoid possible alloying with the subsequent Pt deposition. Later, the samples were reintroduced into the sputtering system. After sputter cleaning for 10 min at 300 W radio frequency power, Pt was deposited on the samples for 3 min at 50 W in
8 mTorr argon for a target deposition of 0.05 mg Pt/cm². Subsequent analyses with X-ray fluorescence (XRF) were used to verify platinum loadings. The Pt-catalyzed Ti-coated Pyrograf films were applied to vacuum-table-dried Nafion® NRE212 membranes by hot-pressing the nanofiber coated filters under high-pressure (15 MPa) at 130°C for 3 min. Despite the pressure, the full depth of the film did not always transfer. In this example, XRF indicated that a nanofiber layer corresponding to 0.042 of the original 0.05 mg Pt/cm² adhered to the membrane. The 5 cm² active area fuel cell was completed with the use of an ELAT® SSE 2.22 carbon cloth gas diffusion layer (GDL) backing the nanofiber cathode and a Nafion®-impregnated Pt catalyzed carbon cloth ELAT® electrode on the anode side (ELAT® materials originally supplied by E-Tek). The cloths and catalyzed membrane were assembled loose, cell compression was relied upon to provide the necessary interfacial continuity.

Activated Multi-Walled Carbon Nanotubes (MWCNTs) and Pt Deposition

MWCNTs (Nanostructured and Amorphous Materials Inc.) were activated in a similar manner as the Pyrograf, although the MWCNTs were not as easily suspended. Well-dispersed aqueous suspensions could only be obtained using high dilutions and the direct insertion of a high-power ultrasonic horn (Branson Sonifier 450) into the mixture to break up agglomerates. When filter cast, these suspensions provided highly uniform thin films. Platinum deposition, catalyzed membrane preparation and the remaining fuel cell components were similar to the above Pt/Ti/Pyrograf cell, except that an even higher pressure (20 MPa) was used to obtain a similar transfer effectiveness corresponding to a loading of 0.044 mg Pt/cm².

Fibron Carbon Supports and Pt Deposition

An aqueous nanofiber polypyrrole dispersion (PPC-10-1-01 from Fibron Technologies, Inc.) was further diluted and filter cast as above to form a uniform thin film. Pt was sputter coated for loadings of 0.05 mg Pt/cm². Even though the catalyzed nanofiber polypyrrole Fibron film was hot-pressed to the membrane at the higher pressure (20 MPa), only 0.035 equivalents of the 0.05 mg Pt/cm² Fibron film transferred to the membrane. The remaining fuel cell aspects of this particular Fibron-based cell were the same as above. An improved fuel cell environment for the nanofiber catalyst layer and a simpler cell fabrication process was achieved by eliminating the problematic step of hot-pressing the nanofiber film to the membrane. This was accomplished by directly filter casting the nanofiber suspension onto the GDL. Since the surface of a carbon cloth GDL varies substantially in topography and porosity around the weaves, much more uniform microporous layer-coated carbon paper GDL materials were used instead. In the filter casting process, the Nafion®-coated GDL was first soaked with methanol to promote wetting of the full structure before the aqueous suspension was introduced. An SGL 30 DC carbon paper gas diffusion layer was first coated with 0.18 mg Nafion®/cm². A dilute suspension of Fibron nanofiber polypyrrole was filter cast onto the GDL. After drying, the nanofiber-coated GDL was sputter coated with 0.05 mg Pt/cm². For the remaining fuel cell components, SGL 30 DC was painted with a 2:1 Pt/C:Nafion® ink with a 0.05 mg Pt/cm² loading to serve as the anode and Nafion® NRE 212 was used for the membrane. The fuel cell was assembled with loose components. In this configuration, the cathode interfaces superficially consisted of Nafion® membrane/Pt-coated polypyrrole/Nafion® recast/GDLmicroporous layer. After compression, significant intermingling of these layers probably occurred.

Fuel Cell Testing

The 5 cm² fuel cells were tested at 80°C with hydrogen/air pressures of 30/30 psig (285/285 kPa) and reactant humidifiers operating at 80°C. High air-flow stoichiometries (up to 4 x stoichiometry at 1 A/cm²) and/or sub-saturated air humidification conditions were required to obtain stable operation of the flooding-prone cathode nanofiber structures. Elevated cell resistances in the polarization curves occurred due to the relatively dry operating conditions and the corresponding improvements in performance and high-frequency resistance on the return (upward) voltage scan. Due to the precarious balance between excessively dry and flooding, performance of these nanofiber-based fuel cells are much more sensitive to operating conditions than conventional electrodes. High charge transfer resistances were also observed due to the lack of ionomer penetration into the nano-composite electrodes.

Electrochemical Synthesis of Polypyrrole Nanowires

Our alternative support material studies include the development of low Pt loading catalysts on polypyrrole nanowires [1-4]. Using electrochemical synthesis methods, we were able to grow polypyrrole nanowires on a carbon paper GDL using template molecules such as heparin and starch. With this new approach we can achieve a high surface area structure that may lead to a higher oxygen reduction reaction catalytic activity with lower Pt loadings.

Electrochemical synthesis was carried out in an aqueous solution containing 0.2 M pyrrole, 0.40 wt% heparin sodium salt and 0.07 M LiClO₄ by applying potential square waves between 0.300 V (2 s) and 0.850 V (8 s) for 1,200 s at room temperature. Potentials
measured vs. Ag/AgCl (3.5 M KCl) reference electrode. Without the use of templating agents, a low surface area dendritic structure results (Figure 1).

In order to increase the surface area in the polypyrrole film, we first used heparin as a template molecule during the polypyrrole electropolymerization process on a glassy-carbon electrode while applying cyclic multipotential steps. As shown in Figure 2, the presence of heparin results in polypyrrole/heparin nanowires with a much higher surface area than the polypyrrole dendrite structure. After the use of heparin as a template molecule proved to be effective for the formation of a nanowire structure, we obtained a similar result on a carbon paper GDL, so it could be used as a new high surface area gas diffusion electrode (GDE) in a fuel cell configuration. By studying different variables such as pyrrole/heparin ratio and deposition time, the electropolymerization process was optimized so we one can control the diameter and length of the nanowires as desired.

While heparin worked very well as a proof of concept template molecule we immediately searched for a low-cost replacement since heparin is an expensive prescription drug used as a blood thinner. As a result of our search for an alternative template molecule, we found that starch is a very good candidate as is shown in Figure 3. Additionally, starch has the advantage of being inexpensive, easy to find and environmentally benign. Moreover, as in the case of heparin, we found that the tuning of different variables such as pyrrole/starch ratio and deposition time allows controlling the diameter and length of the nanowires.

We are currently investigating Pt deposition by RF magnetron sputtering and by electrochemical deposition. After the optimization of the electrochemical synthesis of the Pt coated polypyrrole/starch nanowires is completed, fuel cell test studies will be carried out in order to obtain performance and stability data for the new GDE. Additionally, the structure will be also prepared on a glassy carbon disk electrode and rotating ring disk electrode studies will be performed to determine the catalytic activity of the Pt coated polypyrrole/starch nanowires.

Conclusions and Future Directions

- Pt catalysts can be deposited uniformly on a variety of nanowire supports using radio frequency magnetron sputtering.
• New oriented polypyrrole nanowire catalyst supports were developed for fuel cell cathode use.
• Novel supported Pt catalysts require optimization of the electrode layer.
• Oxygen reduction activity as a function of loading will be probed by rotating disk electrode electrochemical methods.
• Support stability will be studied using cyclic voltammetry and post testing materials characterization.
• Mechanism of the nucleation and growth of PGM on the supports will also be studied.

References
V.E.11 Molecular-Scale, Three-Dimensional Non-Platinum Group Metal Electrodes for Catalysis of Fuel Cell Reactions

Objectives

1. Demonstrate that non-platinum group metal catalysts can be used for oxygen reduction in polymer-coated electrode structures based on polyelectrolyte membranes. (Year 1)

2. Incorporate catalysts into polymer binders of composite electrodes for the construction of membrane electrode assemblies (MEAs) to demonstrate that this is an effective matrix for testing of new catalysts. (Year 2)

3. Demonstrate that the three-dimensional structure of polymer-coated electrocatalyst layers can offset slower kinetics of the catalyst centers when compared with two-dimensional platinum or non-platinum catalysts. (Year 3)

4. Demonstrate that significant stability of the matrix is possible. (Year 3)

5. Demonstrate the design, synthesis and scale up of new catalysts capable of performance that is superior to platinum group metals. (Year 4)

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:

(C) Performance
(E) System Thermal and Water Management
(B) Cost
(A) Durability

Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst – 300 A/cm³
- Cost <$3/kW
- Durability >5,000 hours (>120°C)
- Electrochemical area loss <40%
- Electrochemical support loss <30 mV after 100 hrs @ 1.2 V

Accomplishments

- Developed electrochemical screening methods for new catalysts using classical electrochemical methods.
- Developed synthetic methods to prepare new catalysts.
- Developed modeling procedures for prediction of catalyst activity on a molecular level.
- Modified polymer synthesis methods to provide attachment of catalysts to polymers.
- Undertaken preliminary study of polymer ink formulation for non-Nafion® binders for composite electrode fabrication for MEAs.

Introduction.

Although proton exchange membrane (PEM) fuel cells are relatively efficient energy conversion devices
(−50%), there still remains considerable interest in improving the performance while reducing the cost. An area of study that can lead to greater efficiencies while reducing costs is that of the electrocatalysts and particularly the catalysts used for oxygen reduction where the sluggish kinetics leads to inefficient conversion of the energy to heat rather than electricity. The heat generation imposes extra costs due to system complexity to handle both heat and water management. The use of platinum and other platinum group metal catalysts adds further expense. There therefore is considerable interest in developing alternative catalysts that are less expensive and also more efficient. Gasteiger and co-workers [1] have provided a very thorough review of the benchmark activities required for Pt, Pt-alloy and non-Pt catalysts for oxygen reduction and describes in detail different approaches to catalysis of this important reaction.

Methods have been reported to prepare non-precious metal catalysts that involve a curious procedure whereby a rather complicated molecule such as a metal porphyrin or a complex such as iron phanethroline is adsorbed on carbon and then heated to over 800°C to form the catalyst [2-5]. In some cases the carbon support is treated with nitrogenous compounds at high temperature followed by addition of metal ions such as Fe or Co. Although the resulting electrodes are often highly porous with very high surface areas the resulting catalyst layers on the electrode surface are two-dimensional in nature. With these non-platinum catalyst structures the kinetics of oxygen reduction are much less rapid than commercially available platinum on carbon electrode. It is thought that the density of the non-platinum catalytic sites is insufficient to sustain the desired reaction. With the porphyrin catalysts, for example, their poor solubility results in strong adsorption on to the carbon support and insufficient loading of catalyst as well as possible deactivation of the metal center. Since it has been shown by Heller [6], for example, that the copper laccase enzyme obtained from biological sources is capable of supporting current densities for oxygen reduction of 0.5 mA/cm² at a planar carbon electrode with a polarization of only 70 mV, it appears that nature has evolved a catalyst that can outperform platinum. Electrode structures are desired which can allow incorporation of such catalytic species into MEAs, which increase in the surface concentration of the electrocatalysts and which allow the activity of the catalyst to be retained while it is incorporated into the PEM fuel cell engineering platform.

Approach

Homogeneous redox catalysis has been the center of considerable academic attention for several decades now. A recent review by Saveant [7] provides an extensive overview of the topic and includes methods of tethering catalysts close to the electrode surface. These methods suggest ways to incorporate into fuel cell MEAs electrocatalysts that mimic the enzyme catalyst centers and may lead to better performance at reduced cost. Figure 1(a) shows a schematic of a gas diffusion electrode structure typically used in a PEM fuel cell. The electrode usually consists of catalyst nanoparticles (e.g. Pt) dispersed on carbon support particles bound together by a polymeric ionomer material (e.g. Nafton®) on a current collector such as a gas diffusion layer (GDL) which is electronically conductive. The polymer therefore acts as a binder to hold the electrode together and as an electrolyte to transport hydrogen ions to and from the electrode surface. This structure has been designed to optimize the transport of electrons, hydrogen ions, substrate and product to and from the catalyst surface and generally the overall thickness of the electrode layer is about 10 μm. A thicker electrode introduces mass transport limitations that degrade performance. The right hand side of Figure 1(a) shows a schematic blow up of the surface of the electrode where the polymer binder layer is used to bind homogeneous catalysts close to but not right on the surface. This structure allows the use of a variety of catalysts some of which are listed in Figure 1(a) and could be used to tether even an enzyme catalyst such as the copper laccase structure shown in Figure 1(b) or an oxygen binding catalyst such that shown in Figure 1(c). It has been shown (see reference [7] and references therein) that the optimum thickness of the polymer layer can be up to 500 nm thick which would be equivalent to about 100 monolayers of the catalyst on the electrode surface. This thickness of the polymer layer on the electrode particle surface represents little if any increase of the overall thickness of the gas diffusion electrode and hence it is possible to greatly increase the areal density of catalysts on the electrode without increasing the electrode thickness, a concern that was well described by Gasteiger et al. [1].

The operation of the polymer-tethered catalyst layer can appear puzzling to some and the reader is referred to reference [7] for further details. Suffice to say here is that the electrons are transferred from the surface of the current collector by means of an electron hopping mechanism between redox centers as well as by movement of the polymer tethered catalyst back and forth towards the electrode. Therefore the polymer in addition to binding the catalyst must also provide the means to transport protons and ions which can neutralize the charging of the polymer layer. This charging process may indeed be a rate determining step but so also may be the rate of diffusion of the oxygen into the layer or the actual rate of reaction of the catalyst with the substrate and the subsequent dissociation rate of the catalyst and product. In this the catalyst is no different from a metal surface catalyst. What is very different about this approach is that the catalyst center
is effectively a homogeneous catalyst and it may be approached from all directions by the substrate. This provides a geometric advantage for the catalyst center over a surface bound center and can provide an increase in catalytic activity of an order of magnitude or more. This effect combined with the multilayer effect can provide up to three orders of magnitude increase purely due to geometric effects on a molecular scale that hold the potential to make up for the large catalyst area and potentially slower intrinsic kinetics.

The third and most important advantage of the approach is that the catalyst functions essentially as a homogeneous catalyst that can be thoroughly characterized in solution. This makes design and synthesis of the catalysts much more straightforward since the can be studied without resort to surface analysis techniques and to the invocation of surface effects that are poorly understood. Thus, catalysts can be designed from first-principles based on well-known chemistry and physics. The structures of the catalytic centers are understood since the catalysts are synthesized and characterized by classical electrochemical methods in solution thereby avoiding some of the difficulties that have arisen from surface bound catalysts. The catalysts are then incorporated into polymers for coating on electrode surfaces and again the behavior can be characterized by simple electrochemical methods prior to incorporating the polymer-bound catalysts into composite electrodes for MEAs. This last step is critical for the project and represents the Go/No-Go decision point that allows the flow of more efficient catalysts into the PEM fuel cell platform for practical use.

Results

Figure 2 illustrates the process of catalyst screening and incorporation into polymers using classical cyclic voltammetry techniques. Figure 2(a) shows the voltammetric response of a representative iron porphyrin complex (Fe(III)/TMPyP) which is soluble in aqueous perchloric acid solution due to the quaternized pyridinium groups. The Fe(III)/Fe(II) redox couple is shown to be a chemically and electrochemically reversible couple under nitrogen (blue line) indicating fast electron transfer between the carbon electrode and the iron complex. Upon saturation of the solution with oxygen the red curve is observed which shows the increase of reduction current due to reaction of the Fe(II) complex with oxygen. The extent of the increase in current is dependent upon the relative concentration of catalyst and substrate and the sweep rate used to perform
the experiment. From measurements such as these it is possible to actually determine the rate constants of the catalytic reactions [7]. The corresponding copper complex was also active for catalysis of the oxygen reduction reaction (ORR). A point to note here is that these complexes show some stability in acid at least kinetically. Many complexes are immediately decomposed by acid and these results show that the instability can be mitigated. Whether this will be long enough to be useful in a fuel cell remains to be seen.

Figure 2(b) shows the voltammery of a catalyst which has been attached to a polymer and the polymer layer coated on a carbon electrode. In this case the catalyst is a rhodium Cp* organometallic complex which has carbon-metal bonds that are not susceptible to acid cleavage. The left hand voltammograms show the response of the catalyst in two cases. One is with a thin layer of polymer (B) and the other is with a thick layer (A). Integration of the current peaks gives the charge due to the catalyst and hence one can calculate the density of catalyst sites on the electrode. The peak shapes are symmetrical and characteristic of a thin layer of reactant on the electrode surface. These shapes vary with the sweep rate and from such experiments it is possible to estimate the rate of polymer charging [8] as well as diffusion rates through the polymer layer. The voltammogram on the right hand side of Figure 2(b) shows the effect of the addition of a substrate molecule which is reduced by the catalyst. One can see in this case a small increase in the reduction current and a reduction in the height of the oxidation current peak which indicates a reaction occurs between catalyst and substrate but the small increase in reduction current indicates a slow reaction. In this case comparison with the behavior of the catalyst in solution shows that the activity of the catalyst is reduced and this was attributed to low availability of hydrogen ions for the reaction in the polymer matrix that was used. This illustrates the importance of the polymer properties in providing for transport of protons to the site of the reaction. The polymer used in this case was not a polyelectrolyte with no ion transport functionalities. For future work in this project it will be important to choose polymer matrices with this capability and for this use will be made of
polymers from the high temperature membrane project funded by the Department of Energy [9].

These initial results from simple electrochemical experiments demonstrate the importance of the polymer structure that is used to tether the catalysts to the electrode. Preparation of Pt-catalyst MEA electrodes with polymers other than Nafion® is shown in Figure 3 to illustrate this point. The break-in current of a Nafion® electrode is compared with that of an electrode prepared with a polyether polysulfone binder electrolyte. The cartoons on the right hand side of Figure 3(a) represent what is thought to be happening. During break-in the Nafion® polymer is mobile enough to move close to the surface and provide adequate contact. The polyether polysulfone is a stiff polymer and is unable to move close to the electrode surface and hence the break-in is very poor. Figure 3(b) shows polarization curves for three different polymer binders. Once again there is a distinct correlation between the flexibility of the polymer backbone or side chain and the performance in an MEA. These results emphasize the importance of polymer structure on the ability to fabricate a workable MEA electrode and hence attention to polymer structure and properties is critical to the success of this project. In order to demonstrate the feasibility of MEA fabrication readily available catalysts will be selected for incorporation into the polymers. The presence of the catalysts will alter the properties of the polymers and hence considerable experimentation will be required to determine the best formulations and fabrication procedures. This is best done with easily obtainable catalytic centers.

Figure 4 illustrates some syntheses of copper complexes which will be examined for catalytic activity using the classical electrochemical procedures. These are related to complexes already described by Gewirth et al. [10]. In addition to synthesis and characterization experimentally these complexes will also be modeled by molecular calculation to compare theory and experiment. Validation of the modeling procedure by such experiments will allow new catalysts to be

![Figure 3](image-url)

**FIGURE 3.** Effect of Polymer Structure on MEA Performance  (a) Comparison of break-in of MEA electrodes prepared with Nafion® and polyether polysulfone; (b) Comparison of polarization curves of MEAs prepared with different polymer binders in the gas diffusion electrode.
Future Directions

- Increase screening rates of available catalysts to select promising candidates that are stable to acid.
- Develop quantitative measurements of catalytic activity in solution and in polymer-solvent mixtures that are representative of an MEA electrode environment.
- Develop synthetic procedures for attachment of catalysts to polymer binders.
- Continue to explore the properties required of polymer binders to facilitate fabrication of MEAs and study how the presence of catalytic centers changes these properties.
- Design and prepare new catalysts.
- Develop and validate molecular modeling techniques.

Conclusions

Conclusions

- Classical electrochemical methods can be used to characterize the catalytic activity of homogeneous ORR catalysts.
- The structure of the polymer matrix must be designed to provide adequate charge and mass transport to the catalyst centers.
- The polymer binder properties are critical for MEA fabrication.

Conclusions and Future Directions

FIGURE 4. Synthetic Routes under Development to Two Types of Copper Catalysts
FY 2010 Publications/Presentations


References


6. Soukharev, V., Mano, N. & Heller, A. A four-electron O-2-electroreduction biocatalyst superior to platinum and a biofuel cell operating at 0.88 V. *Journal of the American Chemical Society* 126, 8368-8369 (2004).


V.F.1 CIRRUS: Cell Ice Regulation & Removal Upon Start-Up

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Contract Number: DE-FG56-07GO17014

Subcontractors:
• W.L. Gore & Associates, Elkton, MD
• SGL Carbon, Meitingen, Germany
• University of Delaware, Newark, DE

Project Start Date: July 1, 2007
Project End Date: June 30, 2010

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 repeatable achievement of 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) Water Transport within the Stack
(G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

Nuvera is demonstrating the ability to meet 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. The hardware platform initially used in this work was Nuvera’s Andromeda™ fuel cell, designed in 2005, with an active area of 360 cm² and a rating current density of 1.0 A/cm². In the previous reporting period it was shown that Andromeda is capable of starting from -20°C in 30 sec to 50% of its rated power respecting an energy budget of 5 MJ. This report presents the progress obtained in proving the reliability of the startup procedure identified and the durability of a stack subjected to such protocol.

Though the work on Andromeda has been successful at -20°C, the intrinsically high thermal mass of the stack limits the ability to lower even further the starting temperature and it imposes the removal of the coolant during freeze operation even at -20°C.

Thus a stack redesign was required to study startability from extreme temperatures (-40°C) and allow operations at -20°C with resident coolant that dramatically simplify the fuel cell balance of plant.

This new stack, Orion™ (active area 250 cm², rating current density 2 A/cm²), became available last year, and it has been used as the stack platform for this project since the third quarter of 2009.

Accomplishments

- The reliability of the selected startup procedure (from -20°C) was proven through 200 freeze starts performed on Andromeda.
- The diagnostic run on samples subjected to 200 freeze starts did not show significant degradation of fuel cell materials.
- Orion prototypes demonstrated performance (0.6 V @ 2 A/cm²) matching design expectations.
- The Orion stack was successfully started from -20°C with resident coolant, achieving the DOE targets of time to 50% power within the energy budget.
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 (third and fourth quarters of 2007, completed) Nuvera surveyed the status of the art on the topic and set up the enabling tools (test infrastructure and modeling capabilities). In the Selection phase (2008, completed) Nuvera used these tools to select a proper freeze start strategy to meet the DOE requirements and a set of materials to enable the successful execution of the test. In the Qualification phase (2009, completed) Nuvera assessed performance stability of the combined material set and operating methods 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) drove the identification of improvements of materials, strategy and stack architecture. Finally, the effectiveness of these actions is being verified in the Validation phase (first and second quarters of 2010) in which the most advanced configuration is tested to quantify the improvements achieved.

Results

In 2009 Nuvera set up a test campaign that consisted of repeating the same startup protocol 200 times on an Andromeda stack. As stated before, the objectives were to prove the reliability of the procedure and measure the degradation of the materials to understand the main area of improvement and development. The test was made possible through the automation of a test stand with integrated climatic chamber (performed in 2008) that allowed five startups per day, significantly accelerating the testing process. The results proved the robustness of the protocol as it can be seen in Figure 1. In fact, all the startups were successful and even though in some cases the stack didn’t reach exactly the 50% of rated power after 30 sec (50% of 0.664 W/cm²), overall the performance was above the 50% target with no decreasing trend over time. Some voltage degradation was noticed along the course of the test but the measurement of the stack resistance proved the decrease in voltage over time can be almost entirely attributed to a progressive loss of compressive load. This issue has been addressed in the Orion stack by implementing a compression system that provides a better control of the compressive load.

In two different situations (after 100 and 200 cycles) the stack was opened and material samples were extracted for analysis at Gore and SGL labs. The investigation was focused on detecting the typical freeze related decay mechanisms identified during the Freeze Workshop held at Nuvera in early 2009. Even though some evidence of degradation occurred, none of these could be related directly to freezing. This finding indicates that the combination of the procedures applied and the materials used did not experience accelerated degradation with respect normal operation of the fuel cell, at least after 200 repetitions. A summary table describing the decay modes investigated, the diagnostic techniques used and the results found is reported in Figure 2 with some pictures illustrating the findings.

Over the course of the year several prototypes of the Orion stack have been assembled to stabilize the hardware and achieve the performance targets. The
The proven high power density of the stack helps to reduce its thermal mass because it decreases the number of cells that are needed to obtain the rated power. Furthermore, the stack hardware is lighter, which leads to a lower intrinsic thermal mass, and the cooling compartment is smaller, which results in lower overall mass of coolant that is resident during the startup phase. The tests run on Orion highlighted the effectiveness of the design actions described above. A dedicated coolant loop was built to supply an Orion stack with an anti-freezing cooling fluid (mixture of water and ethylene glycol) and such loop was installed on a portable rack that allowed freezing the stack and the coolant system as a whole. The startup performed on this setup was successful as shown in Figure 4 where the Orion stack was able to start from -20°C and in 28 seconds it reached the 50% of rated power (50% of 1.2 W/cm²). The total energy spent to purge the stack during the shutdown phase and the subsequent startup was calculated at 2.937 MJ, which is less that the DOE target of 5 MJ.

**Conclusions and Future Directions**

Nuvera will focus the remaining months of the project on exploring the capability of Orion to start from
extreme temperatures approaching -40°C. Preliminary tests conducted at -30°C seem to confirm the advantage of a reduced thermal mass but more investigation is needed.

For the future Nuvera recognizes the need to study the impact of different pre-conditions on the ability to start from sub-freezing temperature. For this purpose Nuvera implemented a technique to monitor the high frequency resistance of the stack during operation, which is recognized by the fuel cell community as a good indicator of the state of hydration of the membrane, the effectiveness of the purging procedure applied, and the likelihood of a successful startup.

Finally the work done in CIRRUS has proven that the temperature over the surface of the membrane electrode assembly is far from being uniform during the startup and the knowledge of the temperature gradients as a function of time might be an interesting area of study to drive the optimization of materials and procedures.

**FY 2010 Publications/Presentations**

1. September 2009 - Billerica, MA, Detroit, MI (via conference call) - FreedomCar Review.
V.G.1 Development and Demonstration of a New-Generation High Efficiency 10-kW Stationary Fuel Cell System

Technical Targets

Work under the project is aimed at developing novel fuel processing, polymer electrolyte membrane (PEM) fuel cell technologies and integration strategies in order to make progress toward achieving DOE targets for stationary PEM fuel cell power systems for year 2011. These targets and project progress are shown in Table 1.

TABLE 1. DOE Targets vs. Project Achievements

<table>
<thead>
<tr>
<th>Metric</th>
<th>2009 Project Status</th>
<th>2010 Project Achievement</th>
<th>2011 DOE Target1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical efficiency at rated power</td>
<td>System not built</td>
<td>32.6%</td>
<td>40%</td>
</tr>
<tr>
<td>CHP energy efficiency</td>
<td>System not built</td>
<td>60.8%</td>
<td>80%</td>
</tr>
<tr>
<td>Degradation with cycling2</td>
<td>2.5%/1,000 hours of fuel cell stack</td>
<td>0.85%/1,000 hours on fuel cell stack</td>
<td>&lt;0.25%/1,000 hours3</td>
</tr>
<tr>
<td>Hydrogen generator not built</td>
<td>TBD-testing underway</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating lifetime</td>
<td>Hydrogen generator not built</td>
<td>832 hours on hydrogen generator</td>
<td>40,000 hours</td>
</tr>
<tr>
<td></td>
<td>3,500 hours on fuel cell stack</td>
<td>7,000 hours on fuel cell stack</td>
<td></td>
</tr>
<tr>
<td>CHP purpose-built fuel cell system not tested</td>
<td>1,000 hours on fuel cell system</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TBD – To be determined
1 Complete DOE table 3.4.4 found at http://www1.eere.energy.gov/hydrogenandfuelcells/mppdfs/fuel_cells.pdf.
2 Percentage presented as per 1,000 hours given that total test data are less than lifetime target.
3 Equivalent to <10% after 40,000 hours durability target.

Other challenges being addressed under the project are:
• Cost reduction by the simplification of balance-of-plant (BOP) components and development of an adsorption enhanced reforming fuel processor.
• Reduced startup time by improved thermal management design.

Accomplishments
• Successful commissioning of an integrated prototype in a laboratory setting.
Automated fuel processor combustor startup and safety shutdowns implemented.
Continuous (24 hours/day) test operation capability established.
53.4% gross electrical efficiency on integrated fuel cell subsystem.
32.6% electrical efficiency demonstrated on integrated CHP prototype system.
9.3 kW of waste heat recovered.
Continuous production of ~95% purity hydrogen on separate bench-scale adsorption enhanced reforming test rig:
- No materials degradation indicated
- >10,000 regeneration cycles achieved
Over 7,000 hours on separate test fuel cell stack with ~6% performance degradation:
- ~3x improvement from previous year
Operational hours on integrated CHP prototype system detailed in Table 2.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot-Idle¹</td>
<td>2,164</td>
</tr>
<tr>
<td>Pure Hydrogen Production</td>
<td>832</td>
</tr>
<tr>
<td>Power Production</td>
<td>396</td>
</tr>
<tr>
<td>Maximum Continuous Unattended Hydrogen Production</td>
<td>206</td>
</tr>
</tbody>
</table>

¹ Reformer combustor hot (700°C) only without synthesis gas or power production occurring.

Introduction

The development of highly efficient and cost-effective clean energy solutions is not without challenge. Hydrogen fuel cell technologies are expected to become a significant player in reducing our dependence on imported fossil fuels and curb the further accumulation of greenhouse gases and criteria pollutants. Fuel cells can be used in many applications, including but not limited to stationary primary and backup power, portable power and motive power (automobiles, motorcycles, aircraft, etc.).

This project is focused on the design, fabrication and field demonstration of a stationary CHP system that will provide multi-dwelling residential and light commercial end-users with on-site generated electrical and heating needs. The proposed technology addresses DOE targets by using PEM fuel cell stacks as they have been proven to achieve high efficiency, greater durability and lower costs than competing fuel cell technologies.

An integrated hydrogen generator employs an optimized steam methane reformer (SMR) to achieve high fuel to hydrogen output, along with the recovery and utilization of heat from waste streams to address DOE's combined efficiency (electricity plus useful heat) target of greater than 80%.

In parallel to the development of an SMR-based fuel processor, IE has collaborated with California State Polytechnic University, Pomona to research an alternate hydrogen generation method called adsorption enhanced reforming (AER). According to process simulations done at Sandia National Laboratories in 2008, AER promises up to 40% CHP system electrical efficiency when integrated into the as-designed, open-architecture (pure hydrogen interface between the fuel cell and hydrogen generator) prototype unit now operating in our laboratory.

Approach

The approach to achieving the project’s 40% electrical efficiency target is incremental and based on, (1) optimization of the SMR plus fuel cell architecture and (2) the development of an 80% or greater thermally efficient AER hydrogen generator that can “plug and play” into the same SMR plus fuel cell hydrogen feed interface. The SMR plus fuel cell optimization work will rely on allowing slightly less than 100% hydrogen to enter the fuel cell (99%, balance inert) which will translate into only a small efficiency penalty to the fuel cell, but has the advantage of increased hydrogen recovery from the hydrogen generation process whereby its thermal efficiency can be boosted from 70% up to as much as 73%. Preliminary process simulations indicate that this approach can increase the overall CHP system electrical efficiency from its current status of 32.6% to approximately 36%.

An AER hydrogen generator produces a fuel cell feed stream similar to the optimized SMR plus fuel cell system approach but requires operation at 500°C versus 900°C. This means less energy is required for hydrocarbon conversion by the AER approach making the technology more thermally efficient than SMR. Predictive models have indicated that hydrogen generation efficiencies of up to 85% can be achieved with the AER technology compared to 70%-73% attainable by SMR. The multiplier between the AER hydrogen generator and the fuel cell efficiencies, less 12% for the parasitic power requirements to run the CHP system (0.85 x 0.55 -0.12), would result in an electrical efficiency of approximately 41%. Furthermore, since with AER, hydrocarbon reforming and carbon dioxide adsorption occur simultaneously, an additional purification step is eliminated thereby reducing system complexity and costs.
Results

During Fiscal Year (FY) 2009, the integrated CHP system was designed. This last year (FY 2010) marked the construction and testing of the CHP prototype comprised of 23 modular subsystems including water delivery and recovery, fuel delivery, controller and power management, air delivery, safety, chassis, purification, reformer, fuel cell and enabling sub-subsystems. Each subsystem underwent independent bench testing and validation prior to being installed on the overall CHP system. After all subsystems were installed onto the CHP unit, the system went through a cold commissioning phase to check the functionality of electrical components, pressure test vessels and piping and validate the controller system under cold-gas flow conditions. Subsequently, the unit was hot commissioned over a one month period where combustor startup and reforming behaviors were initiated and observed. The pre-commissioning prototype is shown in Figure 1.

After commissioning, the unit was operated first during normal day shifts until the controller safety shutdown sequence and test facility alarms were automated. In March, the unit ran unattended 24 hours/day and achieved its longest continuous run of 31 days while operating in some combination of hot-idle, reforming, pure hydrogen production or electrical production mode(s). A comprehensive set of tests were conducted to evaluate system load versus hydrocarbon conversion in the reformer, fuel cell gross and net efficiency, peak system efficiency and useful heat recovery as a function of cooling water inlet temperature. Conversion ranged from 77%-89% depending on conditions. A summary of other test results are presented in Table 3.

![Figure 1. CHP Prototype in Test Station](image)

<table>
<thead>
<tr>
<th>CHP Technical Accomplishments</th>
<th>Expected Initial Performance @ 10kW</th>
<th>Achieved@11kW</th>
<th>Expected Target With Optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Hydrogen Produced (SLPM)</td>
<td>135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Gas Fed to Reformer (SLPM)</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Gas Fed to Combustor (SLPM)</td>
<td>6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen Fed to Combustor (Proxy for PSA off-gas) (SLPM)</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fraction of Natural Gas Power Converted to Pure Hydrogen*</td>
<td>72%</td>
<td>68.2%</td>
<td>73.5%</td>
</tr>
<tr>
<td>Fuel cell Gross power (W)</td>
<td>11540</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen Consumed by Fuel Cell (SLPM)</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gross Efficiency of Fuel Cell</td>
<td>53%</td>
<td>53.4%</td>
<td>✔ 55%</td>
</tr>
<tr>
<td>Fuel cell parasitic power (W)</td>
<td>720</td>
<td>620</td>
<td>✔ 600</td>
</tr>
<tr>
<td>Hydrogen production parasitic power (W)</td>
<td>850</td>
<td>610</td>
<td>700</td>
</tr>
<tr>
<td>Percentage of DC Power Available to Customer</td>
<td>89.4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>End-to-End Electrical Efficiency (Electricity Out / LHV Fuels In)</td>
<td>33.2%</td>
<td>32.6%</td>
<td>36.2%</td>
</tr>
<tr>
<td>Thermal Power Recovered from Hydrogen Generator (W)**</td>
<td>4200</td>
<td>2732**</td>
<td>✔ 5000</td>
</tr>
<tr>
<td>Thermal Power Recovered from Fuel Cell (W)</td>
<td>4200</td>
<td>6640</td>
<td>5000</td>
</tr>
<tr>
<td>End-to-End Thermal Efficiency</td>
<td>30.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Combined Heat and Power Efficiency</td>
<td>61.1%</td>
<td>60.8%</td>
<td>&gt;71.5%</td>
</tr>
</tbody>
</table>
As represented by check marks in Table 3, four initial performance milestones were achieved during functional validation testing. These data were collected from a sub-optimized prototype. The highest recorded electrical efficiency was 32.6% (natural gas compression parasitic power demand not factored in) with a combined CHP efficiency of 60.8%. Optimization steps, including but not limited to, returning pressure swing adsorption (PSA) exhaust gas to the reformer combustor, replacement of an existing flue heat exchanger with a larger one, improved insulation and operating the reformer at higher temperatures will be carried out in the coming months. Performance estimates for an optimized SMR plus fuel cell system architecture based on the aforementioned steps are shown in the far right column of Table 3. These estimates are lower than DOE targets due largely to the input energy requirement of reforming at ~900°C and associated heat losses. To address this gap, IE continues to develop strategies to advance AER and AER fuel cell/FC interface technologies that could meet these targets in a real commercial system.

The prototype startup times from stone cold (20°C) to full electrical production, referred to as “cold start” ranged from 4-6 hours. The hot start time defined as the period from which the fuel processor was in “hot-idle” (combustor fired only maintaining the reactor without reforming near 700°C) to full electrical production was approximately one hour. To date, the CHP prototype has undergone 29 cold starts/ stops, and nine hot starts/stops without degradation in mechanical integrity and/ or catastrophic failure such as a sudden loss of pressure while operating.

Work on AER was conducted in collaboration with California State Polytechnic University, Pomona under the direction of Professor Dr. Mingheng Li. A four-tube (2” diameter by 48” long each) reactor was designed, constructed and tested from the middle of last year through March of 2010. The experimental rig produced hydrogen continuously by reforming in one tube for 30 seconds and then switching to an adjacent tube that would reform for the next 30 seconds. As there were four tubes in total, each tube, while not reforming would undergo 90 seconds of regeneration (desorption of undesired reaction products in preparation for the next 30 second reforming step). Tests were done using ethanol, liquefied petroleum gas (LPG) and methane as the feed. Regeneration was done with a simulated fuel cell cathode exhaust gas (oxygen reduced air with water vapor) to emulate process conditions that the AER fuel processor would see when fully integrated into a CHP system. The reactor beds were packed with a mixture of Ceria impregnated hydrocarbon reforming catalyst and potassium-promoted hydrotalcite carbon monoxide/ dioxide adsorption pellets. Experimental conditions are shown in Table 4.

<table>
<thead>
<tr>
<th>Primary Experimental Parameters</th>
<th>Range of Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed Temperature</td>
<td>475°C to 550°C</td>
</tr>
<tr>
<td>Feed Rate</td>
<td>0.01 to 0.03 mol/min</td>
</tr>
<tr>
<td>Steam/Carbon Ratio</td>
<td>2 to 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Supplementary Experimental Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Source</td>
<td>Ethanol, LPG, Methane</td>
</tr>
<tr>
<td>Cycle Time</td>
<td>72, 96, 120, 144, and 168 seconds</td>
</tr>
<tr>
<td>Tubes in Cycle</td>
<td>Three tubes or four tubes</td>
</tr>
<tr>
<td>Steam Clean Time</td>
<td>10 and 20 seconds</td>
</tr>
</tbody>
</table>

During the testing phase, more than 350 hours of hydrogen production were logged with each reactor tube having been subjected to roughly 10,000 reforming-regeneration cycles. We did not observe any decrease in hydrocarbon conversion (80-90% depending on process settings) or materials degradation as commonly found throughout the literature regarding prior art.

The sample data represented in Figure 2 show a steady flow of product gas (~96% H₂, ~4% balance being a mixture of CO, CO₂, N₂ and CH₄). Of the ~4% balance, CO which is known to poison PEM fuel cells exists at the sub-100 parts per million (PPM) level. While this amount is too much for use in these fuel cells, a passive device can be used in conjunction with AER to convert this CO back to CH₄ prior to entering the stack; CH₄ is harmless to the stack. The CO₂ in the stream is also at the sub-100 PPM level.

In parallel to the design, construction and testing of the AER rig, process models were developed using HYSYS software. With inputs setting the operating temperature at 500°C, pressure at 60 psig and steam to carbon ratio of 2:1, the model predicted a reformer gas outlet equilibrium concentration of 2.56% CH₄, 79.2% H₂ and 18.15% H₂O. After condensing out the water downstream of the reformer, the concentration becomes...
3.24% CH₄ and 96.76% H₂. These modeled predictions are consistent with the experimental data.

**Conclusions and Future Directions**

Progress during project year three was marked by the construction and validation testing of a CHP prototype in IE’s laboratory. Over 350 hours of electrical production were logged whereby 32.6% system electrical efficiency was achieved. More than 2,100 hot hours and 29 start/stop thermal cycles were carried out.

Continuous production of near fuel cell grade hydrogen has been achieved with a bench-scale AER rig. Over 10,000 process cycles were logged without signs of materials (reforming and adsorbent pellets) degradation.

The coming year will focus on PSA retrofit engineering, system-wide optimization and field demonstration.

Major tasks/direction going forward:

- PSA retrofit engineering.
- System repackaging, pre-deployment testing and optimization.
- Six-month field demonstration in the United Kingdom (Chalvey, Slough).

**FY 2010 Publications/Presentations**


V.G.2 Development of a Low Cost 3-10 kW Tubular SOFC Power System

Objectives

The goal of the 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 remote and micro-CHP (mCHP) platforms to allow short and longer term market penetrations.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell 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 desired product while also demonstrating required life and efficiency targets through multi-level testing.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2011 Goal</th>
<th>2010 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Efficiency</td>
<td>%</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Combined Heat and Power Efficiency</td>
<td>%</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>Durability @&lt;10% Rated Power Degradation</td>
<td>hours</td>
<td>40,000</td>
<td>7,000</td>
</tr>
<tr>
<td>Cost Start-Up Time</td>
<td>minutes</td>
<td>&lt;30</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Transient Response (from 10-90%)</td>
<td>seconds</td>
<td>&lt;3</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Cost</td>
<td>$/kWe</td>
<td>$750</td>
<td>$729 (estimate on volume)</td>
</tr>
</tbody>
</table>

Accomplishments

- Passed “Go/No-Go” test by achieving 0.7%/1,000 hr degradation (goal <2%) over 1,500 hr testing.
- Have demonstrated a 24% increase in power density enabling 33% reduction in stack volume and 15% reduction in stack weight.
- Operated over 5,000 hrs at an ambient temperature of over 45°C.
- Have received $1.1M in Italian government funding to match DOE development funds for mCHP units.

Introduction

Achieving combined heat and power goals of over 40% net electrical efficiency and over 85% total energy efficiency are goals of the DOE 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) cost reducing cell manufacture, (3) increasing stack and system efficiency,
(4) prototype system testing, and (5) integration into a mCHP platform. This phase of the project will make a major drive toward the DOE’s goals set forth for 2012 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 heat removal and 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, significant progress was achieved in improving the power of each individual tube. Figure 1 shows that power progression since the 2009 yearly review. During 2009 the average of all cells tested operating at 800°C was a little over 200 mW/cm². In early 2010 that value was increased to approximately 550 mW/cm² or over 150% at the same operating temperature of 800°C. The operating temperature of the cell was then lowered by 50°C and the peak power was just below 500 mW/cm², again a greater than 100% improvement. Later in the fiscal year further enhancements were made in the cathode layer and the manufacturing process to apply that layer allowing a peak power of 615 mW/cm² at 750°C. Further testing is ongoing and the anticipation is that these same powers will be achievable at 700°C. The advantages of these power enhancements is straightforward as to less tubes resulting in less cost but the reduction in temperature further exacerbates the improvements by allowing for less insulation which is less cost and size of the overall unit.

Gains were not only realized in peak power per tube but also power per tube at normal operating points. Figure 2 shows the power density at 0.7 V operating voltage which is more near the average operating point of a generator. As can be seen, at the start of the DOE program each tube could only achieve 72 mW/cm² while prior to last years annual merit review the value had increased to 339 mW/cm². Since the 2009 review the power at 0.7 V operation has further been enhanced to 421 mW/cm² or an additional 24%. This achievement allows for a reduction in almost a quarter of the cell count which represents a sizable overall cost of the unit while maintaining an efficiency of a generator at or above 40% (net power/lower heating value). This also represents a sizable volume and weight reduction which can not be overlooked when considering shipping costs and installation difficulties for these smaller units by field personnel.

Power enhancements and size and weight reductions themselves are not enough to make for a commercially viable product. A sizable determination of the long-term acceptance of this product is its performance stability resulting in a lower overall cost of electricity and cost of ownership. Recognizing this to be the case Acumentrics worked with the DOE to develop a mid-project “Go/No-Go” milestone to demonstrate that the stability of the stack can achieve a goal of less than 2%/1,000 hr degradation. Figure 3 shows the results of that test over the first 1,500 hrs of its operation. The 1 kW unit was nominally operated near 600 W and achieved 0.7%/1,000 hr degradation passing the milestone with less than half the allowable limit. This unit was also tested for over 5,000 hr total operation showing comparable stability numbers which have proven its viability to be placed in a number of remote power applications. These applications will be further tested in the coming year and may prove to be viable test sites and a starting point for a market transformation project.

In addition to cell power and stability enhancements, there have been...
a number of improvements in the generator performance and cost reduction. One of the most significant generator cost reductions has come with improvements in the high-temperature recuperator used to pre-heat the incoming air utilizing the exhaust gas from the fuel cell stack. The goal of this device is to be as small, least expensive, and as efficient as possible while having a low pressure drop and lifetime that matches or exceeds that of the stack. Figure 4 shows the advancement in that device over the last year of development. The initial device was 300 in$^3$ in volume and nearly 18 lbs in weight. The latest generation has been reduced to a third of the volume or 100 in$^3$ and less than 4 lbs in total weight. Long term this results in less cost since the weight reduction has primarily come from the utilization of less metal and thereby reducing the material cost component of the overall device. Novell brazing techniques allowing for manufacture of the device with these thinner materials while maintaining the quality needed for the product.

**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.

- Passed “Go/No-Go” test by achieving $0.7\% / 1,000$ hr degradation (goal $<2\%$) over $1,500$ hr testing.
- Have demonstrated a $24\%$ increase in power density enabling $33\%$ reduction in stack volume and $15\%$ reduction in stack weight.
- Operated over $5,000$ hrs at an ambient temperature of over $45°C$.
- Have received $1.1$M in Italian government funding to match DOE development funds for mCHP units.

Moving forward, the advances made in cell power will be tested for longer durations to assure the achievability of lifetime goals. Further testing will demonstrate not only stability at steady-state operation but also consider thermal cycling for product platforms with less stringent operating hour requirements but more stringent cyclic duty. Work will also continue into resolving thermal management issues now that significantly higher power is being achieved in a smaller volume. Further work into the reduction of weight and cost of the metallic recuperator will be performed to meet the long-term product goals.
FY 2010 Publications/Presentations

Objectives

- To design and produce an advanced prototype proton exchange membrane (PEM) fuel cell system with the following features:
  - 5 kW net electric output.
  - Flexible-fuel capable—liquefied petroleum gas (LPG), natural gas, ethanol.
  - Reduce material and production cost and increase system and stack durability.
  - Increase electrical efficiency over the existing GenSys 5U48 design.
  - Increase total system 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).
  - $400/kW fuel cell stack cost (direct hydrogen).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) Performance  
(B) Cost  
(A) Durability

Technical Targets

Integrated Stationary PEM Fuel Cell Power Systems (5-250 kW) Operating on Reformate

This project conducted fundamental analysis and demonstration of fuel flexible (ethanol/LPG) CHP integrated system. Results of the 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 at <10% rated power degradation: 40,000 hours
- Cost at 2,000 units/year: $750/kWe
- Performance (target values adjusted to account for LPG-fueled system)  
  - Electrical efficiency at rated power: 38.5%  
  - CHP efficiency at rated power: 78.5%

Accomplishments

- Completed the analytical and design work necessary for the prototype system, received a “go” decision from DOE for the next phase of the project.
- Completed the fabrication and assembly of the prototype system and began system integration testing.
- Achieved system material cost reduction of 53 percent (in production quantities) when compared to prior year’s system material cost roll-up.

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
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 is not only advancing the state-of-the-art of PEM fuel cell technologies, but also established an integrated, low-cost, flexible-fuel reformer for on-site fuel cell power generation. These achievements, in turn, helped to enable commercialization of the technology by improving economic feasibility and providing multiple fuel options for a variety of commercial applications. This project included the design, manufacture, test and field demonstration of a CHP, grid-connected fuel cell system. The resulting system advanced the state-of-the-art toward the DOE's program objectives of increased durability, reduced cost and improved efficiency.

Approach

- Concept Development (100% complete)
  - Go/No-Go: Concept design review
- System Definition (100% complete)
  - Go/No-Go: System interface review
- System Integration (100% complete)
  - Go/No-Go: Field readiness review
- Prototype Field Demonstration (85% complete)
  - Construction Engineering Research Laboratory unit demonstration rolled into 7A project using commercial GenSys unit.
  - Demonstration currently being conducted at Union College Beuth House, Schenectady, NY, using commercial GenSys unit.
- Project Closeout (90% complete)

Results

Demonstration

Plug Power installed a GenSys Blue high-temperature PEM fuel cell system at Union College Beuth House in Schenectady, NY. This includes field readiness design, build, shipping, installation, commissioning, demonstration, decommissioning, site restoration and public/end user education. The system continues to run, logging 1,436 hours since commissioning, and is continually evaluated.

Stack Sourcing

The original project intent was to leverage Plug Power’s supply chain and knowledge gained during Topic 3.1 work activities at Warner Robins Air Force Base (which led to development of the “Rev 3” membrane electrode assembly, MEA), and expand to a fuel cell stack solution capable of meeting both DOE objectives and those required for productization.

Based on preliminary work on the TeleCOOP project, Plug Power and Ballard proceeded to collaborate. However, stack integration complications occurred with the commercially available Ballard MK-1500 series stack design and DOE goals were not met. These complications included: high pressure drop posing issues finding applicable balance-of-plant components, high differential pressure posing issues in controllability of the system, and system efficiency and turndown capability being negatively impacted by the stack design.

Improvements made by 3M in durability and cost, and leveraging the production design MEA, confirmed the viability of a Plug Power/3M stack solution from a material cost and superior system design perspective.

Stack Sourcing Pressure Drop

The commercially available stack had up to 3.5x the pressure drop of the Plug Power stack design. The higher pressure drop required for the water management method led to lower system efficiency and difficulty finding components to supply the required reactants. Low power efficiency was also affected due to “differential pressure floor.”

Stack Sourcing Efficiency Impacts

The efficiency impact of the commercially available stack negated any potential gains it had in cost and durability. The GenSys 6U48 product advantage over incumbent technology is based on superior efficiency leading to op-ex savings. The commercially available stack was not a viable solution for a GenSys product and did not show a path to meeting DOE objectives.

Low-Temperature PEM for CHP Applications

Using a low-temperature PEM system in a CHP application has been studied for both the maximum heat recovery and maximum output temperature based on the existing design. 8,200 W (28,250 BTU/hr) are available at a temperature of 65°C (150°F) and the maximum outlet temperature of 77°C (170°F) is possible with 5,050 W available. Further improvements in quality of heat are possible at the expense of electrical efficiency and Plug Power is investigating the viability of a low-temperature CHP system based on the GenSys system architecture.

System Material Cost

Material cost of the GenSys system has been reduced by 63 percent due to design activities related to this project. Fuel cell stack material costs were reduced 59 percent and an additional 15 percent cost reduction is expected once the design is fully tooled.
Reliability Improvements Startup Sequencing

In an effort to combat carbon corrosion on the MEA during H2/air front propagation at start-up, various system controls approaches were studied. Results of these tests proved that a controls and isolation solution existed that was much less costly than an MEA materials solution. This allowed reduction in MEA loading, leading to a lower overall cost.

Reliability Improvements Cathode Humidification

Several different types of cathode humidifiers were studied with the goal of reducing part cost while maintaining a high cathode saturation for increased stack life. The outcome from these tests resulted in qualification of a part that was approximately 50 percent of the cost of the incumbent, with improved levels of humidification across the operating range.

Conclusions and Future Directions

The Union College unit will be decommissioned in the summer of 2011. Due to significant system advancements, DOE has agreed to close out the 7C project and roll the Construction Engineering Research Laboratory contract obligations into the 7A project. Under the 7A project Plug Power will provide data to the Construction Engineering Research Laboratory from one of the 20 systems to be installed at Warner Robins Air Force Base in Georgia.

FY 2010 Publications/Presentations

V.G.4 Research and Development for Off-Road Fuel Cell Applications

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Technical Advisor: Walt Podolski
Phone: (630) 252-7558
E-mail: podolski@anl.gov

Contract Number: DE-FC36-04G014303

Subcontractors:
• The Toro Company, Bloomington, MN
• University of California, Davis, CA (UC Davis)

Project Start Date: August, 2007
Project End Date: September, 2011

Objectives

• Develop a proton exchange membrane (PEM) fuel cell system to operate in off-road applications.
• Established comprehensive set of PEM fuel cell system requirements for turf and grounds maintenance vehicles.
• Evaluate air-filtration technologies for off-road applications.
• Shock and vibration testing in the lab and field.
• Fully integrate prototype PEM fuel cell system in a Toro® Workman® e2065 – series utility vehicle for field trials.
• Fully integrate second generation PEM fuel cell system in a Toro® Mid-Duty Electric (MDE) light-duty maintenance truck.
• Conduct field trials utilizing two vehicles at various venues.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

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® Model e2065 lawn tractor equipped to operate on direct current (DC) voltages, 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® Model e2065 light-duty maintenance truck.
• Installed a 2nd generation IdaTech Liquid Fueled Fuel Cell System in a Toro® Workman® model MDE light-duty maintenance truck.
• Completed field trials with two vehicles.

Introduction

Nearly no practical work has been performed by the fuel cell industry, 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, ammonia, 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.

Results

An IdaTech Liquid Fueled Fuel Cell System was assembled, tested at IdaTech, delivered to UC Davis and demonstrated at UC Davis. Initial shock and vibration testing was completed at UC Davis followed by field trials at River's Edge golf course and The High Desert Museum, Wildlife and Living History. Accelerometers were mounted in the rear compartment next to the fuel cell system for all shock and vibration testing. The field trial results indicate the rear of the vehicle sustains higher shock g-forces than the front with the maximum recorded shock of 117 g-forces. The vibration results show that the terrain provides input vibrations in the range of 1 to 20 Hz at 2 to 3 g-forces and that the vehicle does not sustain any vibration amplitudes greater than 1 g-force.

Toro® determined that the IdaTech FCS 3000 fuel cell system matched the operational requirements of the Workman® Model e2065. As a result, a Toro® Workman® Model e2065 light-duty maintenance truck was received and retrofitted to house an IdaTech FCS 3000 fuel cell system. The model e2065 unit was designated test vehicle-one (TV-1).

Three fuel cell systems were assembled and all three passed operational testing. One fuel cell system, while sitting next to the vehicle, was used to charge the batteries. After successfully demonstrating that the fuel cell system could charge the batteries, the fuel cell system 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 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:

- System run time = 318 hrs
- Total fuel feed = 474 liters

A second vehicle, designated TV-2, was procured from Toro® which Toro® has designated 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 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 system for maintenance. Onboard data acquisition was added with data collection every 10 seconds on a memory card. The fuel cell system installed in TV-2 is shown in Figure 3. The second vehicle was deployed at The High Desert Museum (HDM) Wildlife and Living History south of Bend, Oregon. This field trial differed in that the terrain was flatter, the operators more educated and the vehicle accumulated more operating hours. The vehicle is
shown in front of the HDM in Figure 4. TV-2 has accumulated the following statistics:

System run time = 368 hrs
Total fuel feed = 315 liters
Total energy = 149 kW-hrs
Total thermal cycles = 63

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 contacted the Etrix Group Inc., a local electronic design company, to consolidate the needed functions onto one board.

Conclusions and Future Directions

Overall the prototype vehicle project was a great success making significant progress toward manufacturing of a green vehicle for golf course and parks and recreation maintenance vehicles with potential for liquid fuelled fuel cell powered vehicles in industrial settings. Operation at two test venues 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.

The two test units have completed filed trials and are in the process of being disposed.

Work on air filtration (Task 3) has been restarted due to Donaldson’s decision to cease fuel cell filter production and support. The objective is to evaluate commercially available air filters for off-road applications. The work has just commenced with UC Davis.
Objectives

- Understand the role of cathode electrocatalyst degradation in the long-term loss of polymer electrolyte membrane fuel cell (PEMFC) performance,
- Establish dominant catalyst and electrode degradation mechanisms,
- Identify key properties of catalysts and catalyst supports that influence and determine their degradation rates,
- Quantify the effect of cell operating conditions, load profiles, and type of electrocatalyst on the performance degradation, and
- Determine operating conditions and catalyst types/structures that will mitigate performance loss and allow PEMFC systems to achieve the DOE lifetime targets.

Technical Barriers

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

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is conducting fundamental studies of platinum-based PEMFC cathode electrocatalyst degradation mechanisms. Insights gained from these studies can be applied toward the definition of operating conditions to extend PEMFC lifetimes and to the development of cathode electrocatalyst materials that meet the following DOE 2015 electrocatalyst durability targets with voltage cycling:

- 5,000 hours (<80°C) and 2,000 hours (>80°C),
- <40% loss of initial catalytic mass activity, and
- <30 mV loss at 0.8 A/cm²

Accomplishments

- Prepared Ketjen carbon-supported Pt nano-particle electrocatalysts (Pt/C) of varying particle size and incorporated these electrocatalysts into the cathodes of membrane-electrode assemblies (MEAs).
- Quantified Pt/C catalyst oxygen reduction reaction (ORR) activity, electrochemically-active surface area (ECA), and performance losses in a fuel cell as a function of initial Pt particle size and cell parameters (relative humidity, temperature, upper potential limit, and cycling protocol).
- Developed a kinetic Monte Carlo (KMC) code to predict Pt nano-particle evolution under fuel cell conditions.
- Determined Pt particle size and particle size distribution evolution during potential cycling as a function of initial Pt particle size (1.9, 3.2, 5.7, and 9.1 nm) during potential cycling in an aqueous environment, using anomalous small-angle X-ray scattering.

Introduction

One of the primary challenges facing the development of PEMFCs for automotive and stationary power applications is the durability of the fuel cell materials. Though significant progress has been made toward achieving the technical target of 5,000 operating hours, particularly for non-conventional catalysts...
architectures, the durability status for conventional stacks is considerably shorter than 5,000 hours [1-3]. Typical degradation rates for constant load conditions are 25-40 µV/h and can be an order of magnitude higher when operating under non-steady-state conditions prevalent in the automotive application, including load and start-stop cycling and extended time at open circuit [3]. The observed degradation under these conditions has reversible and irreversible components with one of the most dominant contributors to irreversible degradation being loss of cathode oxygen reduction reaction activity. The subjects of this project are the irreversible losses in PEMFC performance, as these are the most challenging in terms of mitigation strategies. Specifically, this project focuses on cathode catalyst degradation, because the degradation of this component has the most profound impact on cell performance. The project’s primary focus is elucidation of the effects of catalyst and support physicochemical properties and cell operating conditions on the rates and mechanisms of cathode catalyst degradation, with a secondary focus on the impact of catalyst degradation on the transport properties of the cathode.

Approach

The project approach is to perform systematic cell degradation tests, in situ and ex situ structural characterization of the catalysts, fundamental out-of-cell studies, and theoretical modeling to identify the degradation modes and factors contributing to cathode catalyst degradation. The catalysts to be studied are benchmark Pt on carbon supports with varying properties, Pt alloys with varying oxophilicity, and three classes of Pt catalysts having the highest reported oxygen reduction activity. Specifically, our approach is to utilize accelerated stress tests of MEAs containing various catalysts and supports and in situ and ex situ dissolution, microscopic, structural, and chemical characterization of these catalysts. To elucidate the effect of particle size, we will systematically vary the particle size of Pt and one Pt alloy on a standard support. To elucidate the effect of catalyst type and catalyst oxophilicity, we will study four classes of catalysts: Pt, Pt alloys, acid-leached alloys, and core-shell catalysts with approximately the same particle size and particle size distributions. To elucidate support effects, we will study Pt on carbon supports with systematically varied surface area, pore size, and relative proportions of micro- and mesopores. In addition, to study the role of carbon degradation in ECA loss we will assess the effect of surface area of carbon exposed to the electrolyte and Pt contact area with the carbon using a series of Pt/C catalysts with differing Pt loading. We will also determine the effects of catalyst precursor impurities on degradation rates by post-synthesis doping of a Pt/C catalyst with varying levels of precursor impurities (e.g., Cl, Na, K, and F).

The results of the experimental efforts will feed into coupled models at various levels of complexity from atomic-level, ab initio oxidation and dissolution calculations, to catalyst degradation models, to cell kinetic and transport models. The modeling effort will also define the experiments necessary to complete the cell model. The project can be categorized into three broad and coupled tasks: (1) MEA studies utilizing accelerated stress test protocols, on-line electrochemical diagnostics, and post-test microscopic and X-ray scattering characterization, (2) mechanistic and physicochemical property studies using aqueous electrochemistry, X-ray spectroscopy/scattering, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and in situ TEM, and quartz crystal microbalance measurements, and (3) model development, verification, and implementation. All of these techniques have been demonstrated to provide important and complementary information regarding catalyst degradation mechanisms.

Results

To establish the background for studies of advanced classes of catalysts, our initial studies have focused on determining the effects of cell operating parameters and initial Pt particle size on cell performance and performance degradation. Catalysts were prepared containing 40 wt% Pt nano-particles with a mean diameter of 1.9 nm on high-surface-area Ketjen black carbon support (Pt/C). This material was heat treated to form catalysts with mean particle sizes of 3.2, 7.1, and 12.7 nm, respectively. These catalysts were studied in an aqueous electrochemical environment (0.1 M HClO₄ electrolyte) using anomalous small angle X-ray scattering, to determine the evolution of Pt particle size and particle size distribution as a function of potential cycling using the DOE cycling protocol (0.6 V to 1.0 V triangle wave; 50 mV/s). These catalysts were also incorporated into the cathodes of MEAs and subjected to the DOE cycling protocol in the fuel cell environment. Cell diagnostics of cathode catalyst ECA, ORR mass activity, and air and oxygen polarization curves were performed after 1,000, 3,000, 5,000, and 10,000 voltage cycles. Studies were also performed on the effect of various fuel cell operating parameters (relative humidity [RH], temperature, cycling profile, and upper potential limit) on the degradation of the cathode electrocatalyst performance on membrane-electrode assemblies containing the 3.2 nm Pt/C as the cathode catalyst. The results of these initial studies are summarized below.

Summary of MEA and aqueous cell particle size study results:

- Cycling to 1.0 V has minimal impact on ECA and oxygen reduction reaction mass activity of catalysts
with large initial particle size (7.1 and 12.7 nm; see Figure 1).

- Cycling to 1.0 V degrades the ORR mass activity of catalysts with small initial particle size (1.9 and 3.2 nm) toward that of larger particles (7.1 and 12.7 nm).
- Beginning of life fuel cell performance of MEAs with smaller cathode catalyst particle size (1.9 nm and 3.2 nm) is highest, but voltage cycling degrades performance to below that of MEAs with larger initial particle size (7.1 nm and 12.7 nm).
- MEAs with larger cathode catalyst particles (7.1 nm and 12.7 nm) show minimal performance degradation over 10,000 voltage cycles.
- Particles of \( \sim 3 \) nm show growth and narrowing of distribution over 1,750 potential cycles in aqueous electrolyte (Figure 2-top).
- Particles of \( \sim 12 \) nm show no growth or change in distribution over 1,750 potential cycles in aqueous environment (Figure 2-bottom).
- Anomalous small angle X-ray scattering shows that the mean particle diameter of \( \sim 3 \) nm catalyst grows by \( \sim 0.1 \) nm over 1,750 cycles, with the majority of particle growth occurring during the first 900 cycles in aqueous environment.
- Potential cycling causes Pt catalysts of 2.4 to 5.7 nm initial size to evolve to identical specific surface areas, independent of initial particle size.

Summary of MEA parametric study results (Figure 3):

- Increasing the upper limit of voltage cycling from 0.95 V to 1.05 V increases cathode catalyst ECA loss and ORR mass activity loss.
In addition to causing a loss of ECA, cycling to high potentials (1.05 V) increases cathode transport losses.

- Low anode/cathode inlet RH decreases cathode catalyst degradation (30% RH versus 100% RH).
- Increased cell temperature increases cathode catalyst degradation (90ºC versus 80ºC).

These studies on Pt/C provide the background for ongoing studies of platinum alloy (e.g., Pt₃Co/C) cathode electrocatalyst degradation modes.

In the modeling tasks of the project, a KMC model has been developed that can predict Pt nano-particle evolution under fuel cell conditions. As a first step of the validity of this tool, the evolution of a 3.1 nm Pt particle from a spherical particle with random atomic orientation to its thermodynamic equilibrium structure in vacuum at 300 K was determined. As shown in Figure 4, the KMC tool correctly predicts the evolution of the particle to a cubo-octahedra structure, as observed experimentally. This model is being further developed to follow the shape and structure evolution of Pt alloy nano-particles and the changes in the nano-particles in the fuel cell environment due to various processes, such as dissolution and surface migration of atoms. This KMC tool will enable the identification of the causes of the stability/instability of nano-particle alloys in the fuel cell environment and to identify properties and mechanisms that control degradation.

**Conclusions and Future Directions**

The following interim conclusions can be made from our initial studies of the degradation of baseline Pt/C electrocatalysts:

- Initial fuel cell performance increases with decreasing cathode electrocatalyst mean Pt particle size, however degradation of performance with potential cycling increases with decreasing particle size.

- Potential cycling (0.4 to 1.0 V; 50 mV/s) causes Pt catalysts of <∼4 nm initial mean diameter to evolve to specific surface areas comparable to those of 7-12 nm particles (20-30 m²/g).

- Performance degradation with potential cycling can be attributed to increased rates and extent of ECA loss with decreasing Pt particle size for electrocatalysts with mean Pt particle sizes <∼4 nm.

- Extent of loss of ∼3 nm Pt nano-particle cathode electrocatalyst performance, caused by loss of ECA, increases with increasing cell temperature, increasing RH, and increasing upper limit of potential cycling.

The immediate future direction of the experimental portion of the project is to complete characterization of the Pt/C class of catalysts, including acquiring additional data needed for the nano-particle degradation modeling effort, such as Pt dissolution rates and extent of oxidation as a function of potential. Immediate future work on advanced catalysts will focus on characterization of platinum-cobalt alloy nano-particles of varying initial particle size.

**Future Directions**

- Characterize Pt dissolution as a function of particle size for Pt and Pt₃Co.

- Determine effect of temperature on Pt dissolution rates for “benchmark” Pt/C catalyst (3.2 nm mean diameter).

- Determine ORR activity of Pt₃Co/C catalysts of varying particle size and evolution of activity with potential cycling.

- Quantify Pt₃Co catalyst performance loss in a fuel cell as a function of initial particle size and cell parameters.

- Extend KMC code development to alloy nano-particles.

- Model aqueous cell and MEA mean particle size and particle size distribution evolution with cycling.
• Develop model for Pt nano-particle voltammetry, including states of oxide as a function of potential to predict Pt dissolution rates.
• Synthesize and characterize nano-particles of advanced Pt alloy electrocatalysts (e.g., Pt₃Sc and Pt₃Y).

**FY 2010 Publications/Presentations**


**References**


V.H.2 Durability Improvements Through Degradation Mechanism Studies

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Start Date: October 2009
Project End Date: 2013

Objectives

- Identification and delineation of individual component degradation mechanisms.
- Explore Nafion® structure and correlate different electrode structure to fuel cell tests:
  - Understand impact of structure electrode on durability and performance.
  - Define different production methods (especially solvents) on electrode structure.
- Quantify influence of operating environment on different component degradation.
- Make degradation measurements of components and component interfaces.
- Elucidation of component interactions, interfaces, operating conditions on cell degradation.
- Develop individual degradation models of all fuel cell components.
- Development and public dissemination of an integrated model of cell degradation.
- Development of advanced in situ and ex situ characterization techniques for analysis of fuel cell component degradation.
- Develop methods to mitigate degradation of components.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) Durability
(B) Cost

Technical Targets

- Transportation Durability: 5,000 hours (with cycling)
  - Estimated start/stop cycles: 17,000
  - Estimated frozen cycles: 1,650
  - Estimated load cycles: 1,200,000
- Stationary Durability: 40,000 hours
  - Survivability: Stationary -35°C to 40°C
- Cost ($25/kWe)

Accomplishments

- Characterization of particle size growth after freeze operation and comparison to drive cycle operation data.
- Measurements of effect of catalytic ink solvent on electrode layer durability:
  - Comparison of electrochemical surface area (ECSA) and mass activity on performance durability.
  - Measurement of mass transport changes in electrode.
  - Characterization of polymer dispersion and electrode structure by small angle neutron scattering (SANS) and nuclear magnetic resonance (NMR).
- Measured water profile changes after severe catalyst corrosion.
- In situ carbon corrosion measurements separating catalyst support, gas diffusion layer (GDL), microporous layer (MPL), and GDL substrate.

**Introduction**

The durability of polymer electrolyte membrane (PEM) fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications. Although there has been recent progress in improving durability, further improvements are needed to meet the commercialization targets. Past improvements have largely been made possible because of the fundamental understanding of the underlying degradation mechanisms. By investigating component and cell degradation modes, defining the fundamental degradation mechanisms of components and component interactions, new materials can be designed to improve durability. Various factors have been shown to affect the useful life of PEM fuel cells [1-4]. Other issues arise from component optimization. Operational conditions (such as impurities in either the fuel and oxidant streams), cell environment, temperature (including subfreezing exposure), pressure, current, voltage, etc., or transient versus continuous operation, including start-up and shutdown procedures), represent other factors that can affect cell performance and durability.

To achieve a deeper understanding of PEM fuel cell durability and component degradation mechanisms, we have assembled a multi-institutional and multi-disciplinary team with significant experience investigating these phenomena. This team is headed by LANL and includes three other national laboratories (Argonne National Laboratory, Lawrence Berkeley National Laboratory and Oak Ridge National Laboratory), a university (University of New Mexico), a membrane/ionomer supplier (Ion Power), and a stack integrator (Ballard Power Systems).

**Approach**

Our approach to understanding durability and degradation mechanisms within fuel cells is structured in three areas: fuel cell testing (life testing, accelerated stress tests [ASTs], ex situ aging), characterization of component properties, and modeling (component aging and integrated degradation modeling). 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 fuel cell degradation and to develop and employ materials that will overcome durability limitations in fuel cell systems. This work is also being coordinated with other funded projects examining durability through a DOE Durability Working Group, and through a US Fuel Cell Council task force on durability.

**Results**

One of the major degradation issues involves the electrocatalyst, and has been studied in some detail [1] yet is not completely understood, nor have the durability issues been fully solved. The cost of the noble metal used in the catalyst makes this a crucial area that requires improvement in durability. For example, Pt particle size has been observed to increase especially during power cycling. Post-characterization of the cathode catalyst by techniques such as transmission electron microscopy (TEM) and X-ray diffraction (XRD) show particle size growth and particle agglomeration. An example of the change in platinum particle size distribution is shown in Figure 1a for operation with the US06 drive cycle.

Similarly, other types of operation show similar Pt particle degradation such as operation at freezing temperatures as shown in Figure 1b. This analysis shows that cathode catalyst coarsening observed over 2,000 hours of drive cycle operation is similar to a short period of operation with freeze cycles. The catalyst particle size is observed to rapidly increase compared with life testing at a constant potential. Also, the degree of particle size growth is dependent upon the amount of water in the system, with operation at 100% relative humidity (RH) showing a higher degree of particle growth (5.0 nm) compared to operation at 50% RH (4.2 nm), compared with an initial average particle size of 2.2 nm. This particle growth is attributed to dissolution and re-precipitation. In addition to the particle size growth, a change in the particle size distribution is occurring, as evidenced by the bi-modal shape observed especially with the 100% RH testing, observed at ~8 nm. This is evidence of particle coalescence, as particle growth by dissolution and re-precipitation should not show a change in the shape in the distribution. A short period of operation with freeze cycles shows a similar cathode catalyst coarsening (see Figure 1b). During freeze operation, significant coarsening of Pt on cathode was observed (from ~2.2 nm to ~4.2 nm) for both tested cells, no difference was observed in the Pt sizes and distributions between the two cells, however this Pt particle growth occurred in only a few hundred hours of operation but with the sub-freezing operation. Figure 2 shows TEM of how the electrocatalyst and the catalyst layer changes during
Movement of Pt is observed from cathode to the cathode/membrane interface. Increased Pt agglomeration is observed near interface (0.2-0.4 µm). Pt-particles are observed across the remaining 47 µm to anode side however, no Pt particles are observed within 3 µm of cathode. Pt particles are also found in the center of the membrane, noting that Pt particles are observed continuously/homogeneously across the membrane starting ~3 µm from cathode, with a nominal Pt particle size ~15 nm diameter. Pt particles are found across membrane up to anode/membrane interface, where the Pt “plates” the anode surface.

The main metrics for analysis of electrocatalyst durability have been ECSA, mass activity, and performance as measured by polarization curves. Post characterization by TEM and XRD has been most widely used to determine the particle size growth. Comparing mass activity and ECSA as a function of particle size can show a good correlation [1,5,6]. This correlation appears to be true for catalysts in certain types of MEAs. However in other types, the correlation can be poor, or even non-existent. An excellent example of this is shown by the polarization performance curves as a function of potential cycles in Figures 3a and 3b and the corresponding ECSA shown in Figures 4a and 4b. This work done by Christina Johnston and Yu Seung Kim at LANL explores the effect of different solvents on the electrode structure performance and durability. Electrodes made from water-based catalytic inks show rapid performance degradation, whereas electrodes made from catalytic inks based on glycerol, show virtually no performance loss. This examination was for identical cathode catalysts.

However, the lack of performance loss appears to not be associated with the catalytic surface area, as in Figure 4a vs. Figure 4b, the loss in catalyst surface area is essentially identical. For the case of electrodes made from a glycerol-based catalytic ink, there is essentially no
To meet commercialization targets, improvements in durability are still required. Catalyst and electrode durability remains a primary degradation mode; catalyst particle growth occurs with potential cycling and with freeze testing/cycling. ASTs are used to rapidly evaluate component degradation, however the results such as ECSA and mass activity are sometimes easy to correlate, and sometimes difficult to correlate. Correlation of the results appears to depend upon the electrode layer structure, and the fabrication process used to produce the electrode. Tests which were developed to accelerate single components also affect the performance in other areas. Examples of this are tests to examine losses due to catalyst degradation and kinetics losses and also lead to losses in mass transport.

**Conclusions**

Future Directions

- Fuel Cell Durability Testing and Performance Evaluation
  - Elucidation of single component degradation mechanisms:
    - Electrocatalyst, catalyst support, membrane, ionomer, MEA, GDL, metal bipolar plate, carbon bipolar plate, and seals.
  - Elucidation of multi-component degradation mechanisms.
  - Parametric aging studies:
    - Temperature, RH, transients (potential cycling), and shut-down/start-up,
  - Fuel cell testing on mixed MEAs:
    - Mixed Nafion®/hydrocarbon membranes and ionomer.
    - Characterization of Nafion® within aged electrode films.
  - Evaluation of water/Nafion® dispersions tendency to create weaker electrode structures.
- Fuel Cell Component Characterization
- SANS of electrode layers.
- XRD and TEM: higher crystallinity in aged electrodes.
- Neutron reflectivity measurements of swelling of Nafion® films on carbon substrates.
- NMR characterization of aged fuel cell components (membrane, catalyst and GDL).
- Development of in situ analytical techniques:
  - In situ Raman and infrared.
  - Effect of film-forming properties on the electrode/membrane interface by X-ray tomography and scanning electron microscopy.

Fuel Cell Degradation Modeling
- Development of models for alternating current impedance data; heliox and 100% O2 experiments.
- Model membrane degradation:
  - Effect of mechanical loads on chemical degradation.
  - Effect of chemical degradation on mechanical properties.
  - Mechanical failure of the membrane due to RH cycling.
- Model corrosion of the graphite and metallic bipolar plate.
- Improve model for electrocatalyst degradation and catalyst support carbon corrosion:
  - Account for Pt band formation.
  - Model Pt agglomeration due to carbon corrosion.
  - Carbon oxidation due to potential cycling, startup/shutdown, and fuel starvation.
  - Effect of support loss on ECSA.
- Model effect of GDL/MPL degradation:
  - Improve transport model to account for measurable properties such as surface energies, internal contact angles, pore size distributions.
  - Model effects of sealants and gaskets including impact of degradation products.

FY 2010 Publications/Presentations

References
V.H.3 Durability of Low Platinum Fuel Cells Operating at High Power Density

Objectives

- The objective of this project is to study and identify strategies to assure durability of fuel cells designed to meet DOE 2015 cost targets.
- Develop a practical understanding of the degradation mechanisms impacting durability of fuel cells with low platinum loading (≤0.2 mg/cm²) operating at high power density (≥1.0 W/cm²).
- Develop approaches for improving the durability of low-loaded, high-power stack designs.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost

Technical Targets

<table>
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¹ Cost assessment of Nuvera's architecture by Directed Technologies, Inc. based on their DOE-sponsored Design for Manufacturing and Assembly model [1] and comparing the results to an updated “Industry” estimate. 0.60 V/cell @2.0 A/cm² were obtained at 0.5 mg/cm² platinum loading on Orion stack by Nuvera.
² Demonstrated under power profile specific-to-fork truck applications in material handling market at total platinum loading of 0.5 mg/cm².
³ Demonstrated in 360-cm² stack by Nuvera in New European Driving Cycle power profile at platinum loading of 0.50 mg/cm².
⁴ Demonstrated in 250 cm² stack by Nuvera - 0.60 V/cell @ 2.0 A/cm².

Accomplishments

- Nuvera completed system analysis specific to high-power operation and its impact on the process conditions throughout the active area of the fuel cell stack. The results informed the experimental design for the combined test cycles, or new stress tests (NSTs), based on rated current density (RCD) of 1, 2 and 3 A/cm² and respective constant power turn down.
- New single-cell, open flowfield hardware capable of high RCD was developed and validated over the planned range of experimental operating conditions.
- Catalyst-coated membranes (CCMs) with two levels of platinum loadings (0.45 and 0.2 mg/cm²) were selected and the higher loaded material was procured and characterized at the beginning of life (BOL) in Nuvera 360-cm² cells and LANL 50-cm² hardware throughout the range of operating conditions. The CCM proved promising to allow increased operating temperature with sub-saturated inlet gasses at appropriate gas stoichiometries as targeted by the automotive system map presented by ANL [2]. An accelerated stress test (AST) campaign on the selected material set has started at LANL.
- ANL performance model was calibrated for the open flowfield, and the resulting modeling polarization curves matched Nuvera experimental BOL data, completing the ground work for further development of the durability model.
Introduction

Understanding and improving the durability of cost-competitive fuel cell stacks is imperative to successful deployment of the technology. Stacks will need to operate well beyond today's state-of-the-art rated power density with very low platinum loading in order to achieve the cost targets set forth by DOE ($15/kW) and ultimately be competitive with incumbent technologies. Little-to-no study of durability factors has been carried out in this area of design and operation. The industry today is focusing mostly on reduced platinum loading as it heads for the DOE target point of 0.2 mg/cm² platinum and 1.0 W/cm² power density. As demonstrated through DOE-sponsored cost modeling, this point falls short of the corresponding $15/kW stack cost target for 2015.

Approach

Nuvera proposes an accelerated cost-reduction path focused on substantially increasing power density to address non-platinum group metal material costs as well as platinum. Understanding the largely unstudied factors affecting stack durability under these high power conditions is the focus of the present project. Of specific interest is the impact of combining low platinum loading with high power density operation, as this offers the best chance of achieving long-term cost targets. The team effort will be divided into two activities: modeling and experiments.

Results

Development efforts were focused on the detailed design, procurement and validation of single cell with open flowfield (SCOF) hardware. Nuvera’s patent pending design, shown in Figure 1, allows operation at high current density, flexible selection of the flowfield design, simulation of stack-level temperature gradients as well as an isothermal profile, control and uniformity of compression over the active area apart from sealing, and current distribution measurement.

Material sets A and B were selected for the project in standard and custom platinum loadings with advice from leading CCM developer W.L. Gore. Anode electrode 584.05 loaded at 0.05 mg/cm², membrane M815 at 15 microns thickness, and cathode electrode C580.4 loaded at 0.4 mgPt/cm² comprise the benchmark CCM A. Custom cathode electrode C580.15 is being procured by W.L. Gore for the CCM B, preserving the same anode electrode structure and membrane as in CCM A and resulting in total platinum loading of 0.2 mg/cm² in material set B. All cells are assembled with gas diffusion media produced by W.L. Gore.

Material set A was received in 50-cm² format for the ASTs and in 360-cm² format for the NSTs and characterized for the BOL polarization curve, sensitivities to relative humidity, temperature, and cathode stoichiometry. Data obtained both at Nuvera and Gore demonstrated capabilities of M815 to increase the window of operating temperatures using sub-saturated inputs to the cell provided specific stack operating conditions are maintained. Electrochemical impedance spectroscopy and other diagnostic data obtained on material A both at LANL and Nuvera showed expected cell low initial resistivity and other metrics to be monitored in the test campaign.

In the experimental campaign we focused only on those ASTs which provide direct input to the durability model and can be compared to the fuel cell tests under load protocols (NSTs). ASTs will focus on the electrocatalyst stability at cycling potential defined in B1 protocol by the DOE. Additional AST B1* will be conducted with a lower range of cycling potential than B1 to correspond to the cell voltage achieved in Nuvera large-area cell at 2.0 A/cm². We will also focus on the membrane mechanical stability defined in the B4 protocol by the DOE.

The NST protocols focused on the combined power cycles at the different current densities were proposed, discussed and agreed among Nuvera, LANL and ANL. Three groups of NSTs are defined as following: N1 is the group of sensitivity tests aimed at evaluating the addition of electrical current on the ASTs, N2 is a group of combined humidity and load cycles derived from the protocol recommended by the Fuel Cell Technical Team (FCTT), and N3 is a group of combined city/highway drive cycles accounting for system conditions and implications.
The test plan is designed along three parameter vectors: total Pt loading, current density and the flowfield architecture (graphite single cell with land and channel, SCOF and stack). The latter parameter doesn’t represent a quantified metric, however, is chosen to maximize applicability of the test results across the industry. The schematics of the experimental design space is shown in Figure 2.

N3A-X protocols were evaluated in Nuvera 360-cm² cell stacks for performance and stability over several hundred hours. On-going N3A-2 durability test on material set A in an eight-cell stack is currently passing 600 hours with the cell voltage decay stabilizing below 10 μV/hr/cell at 1 and 2 A/cm² current density, shown in Figure 3.

A two-dimensional fuel cell performance model was established at ANL and initial assessment against

<table>
<thead>
<tr>
<th>AST</th>
<th>NST</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>N1A-2</td>
<td>Benchmarking+Electrocatalyst cycle stability with and without current $B1^*$ potential limits equivalent to N1A-2</td>
</tr>
<tr>
<td>B1*</td>
<td>N1A-2</td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>N1B-2</td>
<td>Membrane mechanical stability with and without current</td>
</tr>
<tr>
<td>N2A-1</td>
<td>N2A-2</td>
<td>N2A-3</td>
</tr>
<tr>
<td>N3A-2</td>
<td>N3A-3</td>
<td>Combined city/highway drive cycle over range of RCD/ICD</td>
</tr>
</tbody>
</table>

$^*$ mid-current point added based on FCTT recommendations
the BOL data was completed. The model accounts for:

a) a seven-layer cell architecture, including both anode
and cathode flowfields, gas diffusion and catalyst layers;

b) temperature, current, potential, relative humidity,
and species distribution; and

c) anode/cathode counter-flow, cathode/coolant co-flow. Modeling results were
calibrated with the polarization curves from 360- and
250-cm² area cell stacks.

Polarization curves resulting from modeling effort
are plotted in Figure 4 overlaying experimental data at
BOL on 360-cm² area cells with 18-micron membrane
and 0.5 mg/cm² total Pt loading electrodes, representing
Nuvera’s internal benchmark MEAs.

Conclusions and Future Directions

The work completed in the first nine months of
the project has concluded the preparatory phase of the
experimental and modeling scope. All partners agreed
to the detailed experimental test plan of ASTs and NSTs
going forward. Preliminary qualification of CCM A in

Nuvera 360-cm² area stacks proved the feasibility of
using this material set for the project and helped establish
essential aging parameters towards understanding
degradation mechanisms and durability model
development. In the next period work will focus on:

• Delivery to and validation of SCOF at LANL.

• Completing ASTs on CCMs A and B and analysis of
test results by the partners.

• Analysis of the ANL model’s sensitivities to metrics
recorded in the ASTs.

• Beginning the NST campaign on SCOF both at
LANL and Nuvera.

• Continuing the NST campaign in the large-format
cells in short stacks and benchmarking the results
between SCOF and large area cells.

• Publishing the degradation model framework and
further model validation.

Special Recognitions & Awards/Patents Issued

1. B.S.Lunt Variable load fuel cell. Patent pending
Application #61319522, 03/31/2010.

FY 2010 Publications/Presentations

Southfield, MI.

2. B.Lunt -High Power Density Test Fixture, Small Fuel
Cells Conference, April 13, 2010, Cambridge, MA.

3. S.Blanchet, SPIRE, 2010 DOE Annual Merit Review,

References

1. B.James et al, Mass Production Cost Estimation
for Direct H2 PEM Fuel Cell Systems for Automotive

**V.H.4 Improved Accelerated Stress Tests Based on Fuel Cell Vehicle Data**

**Objectives**

- Correlate real-world operating conditions to cell degradation.
- Correlate existing DOE accelerated stress tests (ASTs) to degradation.
- Assess degradation modes between real-world operating conditions and existing DOE ASTs.
- Recommend modified ASTs that more accurately gauge in situ component behavior.
- Identify life-limiting mechanisms not addressed by current DOE ASTs and recommend new ASTs.

**Technical Barriers**

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

(A) Durability

(C) Performance

**Accomplishments**

- Fleet performance and operating cycle analyses complete.
- Correlation of platinum decay in real-world operation and lab AST complete.
- Lab ASTs for platinum degradation complete.
- Lab ASTs for carbon support corrosion complete.
- Lab ASTs for membrane mechanical degradation complete.

**Project Approach**

UTC will lead a top-tier team of industry and national laboratory participants to update and improve DOE's ASTs for hydrogen fuel cells. This in-depth investigation will focus on critical fuel cell components (e.g., membrane electrode assemblies, MEAs) whose durability represents barriers for widespread commercialization of hydrogen fuel cell technology. UTC has access to MEA materials that have accrued significant load time under real-world conditions in a PureMotion® 120 power plant used in transit buses. These materials are referred to as end-of-life (EOL) components. Advanced characterization techniques are used to evaluate degradation mode progress using these critical cell components extracted from both bus power plants and corresponding materials tested using the DOE ASTs. These techniques will also be applied to samples at beginning-of-life (BOL) to serve as a baseline. These comparisons will advise the progress of the various failure modes that these critical components are subjected to, such as membrane degradation, catalyst support corrosion, platinum group metal dissolution, and others. Gaps in the existing ASTs to predict the degradation observed in the field in terms of these modes will be outlined. Using these gaps, new ASTs will be recommended and tested to better reflect the degradation modes seen in field operation. Also, BOL components will be degraded in a test vehicle at UTC designed to accelerate the bus field operation.

**Results**

**Fleet Durability Growth**

Before reviewing the progress on each of the individual tasks, some perspective on the role of the
DOE program in improving proton exchange membrane fuel cell durability is helpful. UTC’s approach to achieve the durability targets consists of three aspects. First, UTC is analyzing its fleet operation cycle for critical factors that accelerate performance decay and materials degradation. Second, sub-scale ASTs are performed at LANL using DOE protocols. Third, UTC is implementing its accelerated life test (ALT) article to simulate real-world degradation with selected accelerated conditions identified from the data analysis. Data collected from detailed teardown analyses of aged components from these three elements are incorporated in physics-based numerical models for materials and performance decay.

**Task 1.1 - Fleet Data Analysis**

The first aspect of this analysis is to characterize the performance decay among the various buses in the field. Figure 1 shows the stack performance decay observed in the various bus vehicles. The 2010 fleet leaders are currently still in service with over 6,000-7,000 hours of operation. The 2008 fleet leader failed after ~2,850 hours of field service as a result of hydrogen cross-over and exhibited an overall decay of ~5-6 µV/hr. The second aspect of the fleet data analysis is to identify the key components of the field operating cycle that can be correlated to the degradation of key components (e.g. MEAs). Figure 2 shows the fleet operating cycle that is typically seen in any given hour of operation. Such a cycle imposes ~100 load cycles per hour with about ~30% time spent at an idle condition. As seen in Figure 2, the required power draw (green trace) is instantly manifested in the fuel cell voltage response (blue trace). At a high level, this indicates that the fuel cell is exposed to the bus power draw directly, and that the hybridizing batteries on-board mainly serve to recover energy during braking. Thus, the imposed cycle on the fuel cell is aggressive and represents very realistic conditions from both a fleet and light-duty vehicle perspective.

**Task 1.2 – EOL Stack Diagnostic Testing**

For the current DOE project, since the 2010 fleet leaders are currently still in service and not yet available, the stacks from the 2008 fleet leader were chosen for detailed diagnostics and post-mortem analyses. Cells were extracted from the stack for comparison between BOL and EOL. Although characteristics associated with all four DOE ASTs with targeted mechanisms (namely, catalyst decay, carbon corrosion, membrane mechanical and membrane chemical decay) have been investigated, only the result pertinent to platinum group metal (PGM) decay is reported here. Results associated with other
mechanisms will be reported in future reports. Figure 3 shows performance decay of cells from the 2008 fleet leader stack. It can be seen that after ~2,850 hrs of field operation, the voltage decay is ~15 mV at 0.2 A/cm².

**Task 1.3 – EOL Stack Teardown Analysis**

The stacks were torn down and cells extracted for detailed analysis. Four areas of the cell (air inlet and outlet, fuel inlet and outlet) were subjected to detailed analysis using a variety of ex situ techniques that include cyclic voltammetry to study Pt electrochemical surface area (ECA), X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques for Pt particle size and distribution. ECA results obtained from the 2008 fleet leader cell using cyclic voltammetry (2,850 hrs) are shown in Figure 4, which also include baseline (BOL) ECA data. At BOL, both anode and cathode catalysts had ECA of ~80 m²/g. After 2,850 h, the average ECAs of anode and cathode are ~50 m²/g and ~28 m²/g, respectively. Assuming that only ~70% of Pt surface area is ionically contacted by cyclic voltammetry, the Pt particle sizes can be estimated based on Pt theoretical density which are also shown in Figure 4 (in red).

![Baseline and Air Inlet - 2850 hr TEM Images](image)

**FIGURE 5.** TEM Cathode Catalyst Images for Baseline and 2,850 h Catalyst Samples from Air Inlet Region

**TABLE 1.** Status of all AST Testing (Performed by LANL)

<table>
<thead>
<tr>
<th>Component</th>
<th>Decay Mechanism</th>
<th>DOE AST Protocol</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Pt dissolution-sintering (PGM decay)</td>
<td>0.6 – 1.0 V cycle in H₂/N₂</td>
<td>- Completed</td>
</tr>
<tr>
<td></td>
<td>Support corrosion</td>
<td>1.2 V hold in H₂/N₂</td>
<td>- Completed, data under review</td>
</tr>
<tr>
<td>Membrane</td>
<td>Mechanical degradation</td>
<td>Relative humidity cycling (0% to 90°C dew point) in air/air</td>
<td>- Completed</td>
</tr>
<tr>
<td></td>
<td>Chemical degradation</td>
<td>Open circuit voltage hold in H₂/air</td>
<td>- Post-mortem in progress</td>
</tr>
</tbody>
</table>

**Task 1.4 – High-Resolution TEM Analysis**

PGM catalyst decay was also investigated using TEM techniques. Analysis on BOL and EOL MEAs were performed at ORNL. Images obtained from baseline and 2008 fleet leader samples are shown in Figure 5.
is clear from these images that Pt particle coarsening has occurred. ECA measurements and TEM analysis of the catalyst at the air inlet are in qualitative agreement.

**Task 2 - Lab-World Degradation - DOE ASTs**

All lab DOE ASTs are performed at LANL on a BOL MEA used in a UTC 2008 fleet leader. Table 1 summarizes the status of all sub-scale AST testing.

### PGM Decay AST

Catalyst AST testing has been completed on the BOL MEA. The ECA and voltage loss are shown in Figure 6. It has been concluded that surface area, voltage and mass activity loss after 50,000 cycles at 0.6-1.0 V is ~37%, ~5 mV and ~20%, respectively. Comparison between these results and the DOE 2012 targets for catalyst is shown in Table 2. Post-mortem analyses on the AST-degraded electrodes are ongoing.

<table>
<thead>
<tr>
<th>Observed at 30,000 Cycles</th>
<th>DOE Target at 30,000 Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>~37% ECA loss</td>
<td>&lt;40% loss of initial area</td>
</tr>
<tr>
<td>~5 mV loss @ 0.8 A/cm²</td>
<td>&lt;30 mV loss @ 0.8 A/cm²</td>
</tr>
<tr>
<td>~20% loss of mass activity</td>
<td>&lt;40% loss of activity</td>
</tr>
</tbody>
</table>

**Membrane Mechanical Degradation AST**

Lab DOE AST for membrane mechanical degradation has also been performed on the BOL MEA used in a UTC 2008 fleet leader. Tested under the DOE relative humidity cycling protocol, the membrane endured ~5,500 cycles before significant cross-over was observed. Cross-over current, shorting resistance, and teardown analysis on the degraded MEA are currently underway and will be reported in the future.
degradation will be performed in the third quarter in 2010.

- ALT: Test vehicle has been facilitated.
- Next Step: Correlate real-world degradation to lab tested degradation for carbon corrosion and membrane mechanical/chemical degradation. Complete testing BOL materials using ALT test vehicle.

**FY 2010 Publications/Presentations**

2. “IMPROVED AST's BASED ON FCV DATA” presentation to DOE Annual Merit Review meeting June 8, 2010.
V.H.5 Accelerated Testing Validation

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⁴ Ballard Power Systems, Burnaby, BC, Canada
⁵ Ion Power, New Castle, DE

Project Start Date: October 2009
Project End Date: 2013

Objectives

- Correlation of the component lifetimes measured in an accelerated stress test (AST) to “real-world” behavior of that component.
- Validation of existing component specific ASTs for electrocatalysts, catalyst supports and membranes (mechanical and chemical degradation).
- Development of new ASTs for gas diffusion layers (GDLs) and bipolar plates.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost

Technical Targets

Cost and durability are the major challenges to fuel cell commercialization. ASTs enable the rapid screening of fuel cell materials and are critical in meeting the long life times required for stationary and automotive environments. Moreover these ASTs can also help predict the lifetime of the various components in “real-world” applications.

- Transportation Durability: 5,000 hours (with cycling)
  - Estimated Start/Stop cycles: 17,000
  - Estimated Frozen cycles: 1650
  - Estimated Load cycles: 1,200,000
- Stationary Durability: 40,000 hours
  - Survivability: Stationary -35°C to 40°C
- Cost ($25/kWe)

Accomplishments

- Performed all four DOE Fuel Cell Tech Team recommended ASTs on baseline GORE™ membrane electrode assemblies (MEAs) at two different loadings and on two different membrane types
- Ballard manufactured and supplied LANL the MEAs that went into the P5 and HD6 bus stacks.
- ORNL manufactured and supplied metal nitrided bipolar pate materials for AST testing.
- Characterized Pt particle size in the catalyst layer before and after ASTs using X-ray diffraction.

Introduction

The durability of polymer electrolyte membrane (PEM) fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications [1]. Commercial viability depends on improving the durability of fuel cell components to increase the system reliability and to reduce system lifetime costs by reducing the stack replacement frequency. The need for ASTs can be quickly understood given the target lives for fuel cell systems: 5,000 hours (~7 months) for automotive, and 40,000 hrs (~4.6 years) for stationary systems. Thus testing methods that enable more rapid screening of individual components to determine their durability characteristics, such as off-line environmental testing, are needed for evaluating new component durability in
a reasonable turn-around time. This allows proposed improvements in a component to be evaluated rapidly and independently, subsequently allowing rapid advancement in PEM fuel cell durability. These tests are also crucial to developers in order to make sure that they do not sacrifice durability while making improvements in costs (e.g. lower platinum group metal loading) and performance (e.g. thinner membrane or a GDL with better water management properties).

DOE has suggested AST protocols for use in evaluating materials, but only for the catalyst layer (electrocatalyst and support), and for the membrane [2,3]. The USFCC has also suggested AST protocols for the same materials [4]. While these protocols have concentrated on the catalyst, catalyst support and membrane materials, to date, no accelerated degradation protocols have been suggested for GDL materials or MPL layers, bipolar plates or seals. In spite of recent advances in AST development, a main portion, which is deficient, is the quantitative correlation between the results of a given fuel cell AST and the degradation rate or life in an operating fuel cell.

**Approach**

A main desired outcome of this task is the correlation of the component lifetimes measured in an AST to in situ behavior of that component in “real-world” situations. This requires testing of components via ASTs and in operating fuel cells, and delineating the various component contributions to the overall cell degradation. This will primarily be performed by using a simplified one-dimensional model that takes into account the different component contributions like membrane ionic conductivity, cathode catalyst layer kinetic losses and mass transport losses (catalyst layer and GDL) to the overall losses observed in operating cells [5]. This project will then attempt to correlate the performance losses observed due to a particular component in “real-world” situations with the degradation in AST metrics of that component. The correlation between AST and life data if state-of-the-art materials are used, in essence gives one data point. Thus, for a reasonable correlation to be made, materials with different life spans will be utilized. This relies on the expertise of the suppliers as partners in the project. This work is also being coordinated with other funded projects examining durability through a DOE Durability Working Group, and through a USFCC task force on durability.

**Results**

GORE™ Primea® MEAs sandwiched between two SGL SigracetTM 24BC GDLs were used as the baseline MEAs for AST testing in a single serpentine flow field. The testing was performed in accordance with the published Fuel Cell Tech Team protocols [6]. The results from the potential cycling AST are illustrated in Figure 1, which shows the degradation in electrochemical surface area (ECSA) and performance as a function of the number of potential cycles. There is reasonable agreement in the ECSA and performance loss targets with the lower loaded (0.2 mg-Pt/cm²@ cathode) MEA showing a 40% loss in ECSA after 12,500 cycles and a 30 mV loss in performance after 15,500 cycles. Moreover, the higher loaded (0.4 mg-Pt/cm²@ cathode) MEA exhibited better durability with the 40% ECSA loss target occurring after 20,000 cycles. Figure 2 illustrates the impedance of an MEA before and after the potential cycling test. The Nyquist plot clearly shows two semi-circles with the low frequency semi-circle corresponding to mass transport losses and the high frequency semi-circle corresponding to kinetic losses. It is seen that the potential cycling not only introduces a significant increase in the charge transfer resistance, but it also results in an increase in the mass transport losses. This result indicates that the upper potential for the cycling that is presently 1.0 V may need to be lowered in order to avoid any carbon corrosion and make this test truly representative of the electro-catalyst alone.

Performance degradation due to catalyst support corrosion during a 1.2 V constant potential hold is
illustrated in Figure 3. It is seen that two identical MEAs showed very similar performance losses indicating the excellent reproducibility of the tests. Figure 3a shows that by doubling the cathode catalyst loading to 0.4 mg-Pt/cm², the loss of ECSA can be delayed significantly. The target 40% ECSA loss is reached after 61 hours instead of 29 hours. Figure 3b confirms that this translates to a slower loss of performance at 1.5 A/cm². However, the 30 mV target for this metric is still passed within the first ≈12 hours. This illustrates that there is significant loss in performance due to mass transport losses that is not captured in the ECSA measurements and therefore the ECSA metric may not be very relevant for this constant potential hold AST.

The main metrics for analysis of electrocatalyst durability have been ECSA, mass activity, and performance as measured by the kinetic region of polarization curves. Post characterization by transmission electron microscopy and X-ray diffraction (XRD) has been most widely used to determine the particle size growth. As shown in Figure 4, comparing mass activity (MA) and ECSA as a function of particle size (determined by XRD) can show a good correlation. Here, the fresh cathode catalyst had a spherical particle size of 2.7 nm that grew to ≈6.5 nm after 30,000 potential cycles and to ≈10 nm after 200 hours of 1.2 V potential hold. Although the mechanism of Pt particle growth is expected to be completely different in these two tests, it is important to note that the average Pt particle size can be used as an excellent marker to track performance loss in both “real-world” and AST testing of PEM fuel cells.

Conclusions and Future Directions

The ASTs performed on baseline GORE™ materials showed excellent repeatability for both the catalyst layer...
and membrane. Potential cycling led to an increase in the Pt particle size at the cathode that correlated well with catalyst MA and ECSA loss. The catalyst cycling was however found to cause some mass transport losses that may be associated with carbon corrosion. Constant potential holds led to a dramatic increase in catalyst particle size and an associated thinning of the catalyst layer that were consistent with both mass transport and kinetic losses observed in fuel cell performance. The GORE™ 510 catalyst layer had reasonably good Pt catalyst stability but poor carbon corrosion resistance. The durability of the catalyst and the support increased with increasing loading. The GORE-SELECT™ 720 and N212 membranes had excellent mechanical stability and met the DOE AST targets. The following work will be carried out in the coming years of this project in order to validate existing ASTs and recommend new ASTs.

- **AST Testing**
  - Perform ASTs on the Ballard-supplied materials.
  - Perform ASTs on materials with differing durability supplied by Ion Power.
  - Develop ASTs for ORNL supplied bipolar plate materials.
  - Develop ASTs for GDLs/microporous layers.

- **“Real-World” Testing**
  - Perform simulated automotive drive cycle testing on selected materials with differing durability.
  - Study effect of operating conditions (stressors) like temperature, pressure and relative humidity on drive cycle testing.
  - Analyze the performance data from two different Ballard bus stacks.

- **Characterization of Materials**
  - In situ characterization of catalyst activity, membrane crossover and shorting resistance, and mass transport limitations as a function of AST and “real-world” testing.
  - Ex situ characterization of catalyst particle size distribution, layer thickness, membrane thickness, and GDL hydrophobicity as a function of AST and “real-world” testing.

- Correlation of AST to “Real-World” Data
  - Modeling of fuel cell performance data to provide component specific degradation rates.
  - Statistical correlation of performance degradation with physical properties in both AST and “Real-world” data.

### FY 2010 Publications/Presentations


### References

V.H.6 Development of Micro-Structural Mitigation Strategies for PEM Fuel Cells: Morphological Simulations and Experimental Approaches

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Contract Number: DE-EE0000466

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- University of New Mexico, Albuquerque, NM (P. Atanassov)

Project Start Date: January 1, 2010
Project End Date: March 31, 2013

Objectives

- Identify/verify catalyst degradation mechanisms:
  - Pt dissolution, transport/plating.
  - Carbon-support oxidation and corrosion.
  - Ionomeric thinning and conductivity loss.
  - Mechanism coupling, feedback, and acceleration.
- Correlate catalyst performance/catalyst structural change as a function of:
  - Unit cell operational conditions.
  - Catalyst layer morphology and composition.
  - Gas diffusion layer (GDL) properties.

- Develop kinetic and material models for catalyst layer aging:
  - Macro-level unit cell degradation model.
  - Micro-scale catalyst layer degradation model.
  - Molecular dynamics degradation model of the platinum/carbon/ionomer interface.
- Develop mitigation strategies for catalyst degradation through modification of:
  - Operational conditions.
  - Component structural morphologies/compositions.

Technical Barriers

This project addresses the following technical barriers of the DOE Fuel Cell Technologies Program Multi-year Research, Development, and Demonstration Plan. This plan can be accessed at http://www.eere.energy.gov/hydrogenandfuelcells/mypp/.

(A) Durability
- Pt catalyst and Pt catalyst layers degradation:
  - Effect of structure and composition
  - Effect of operational conditions

(B) Performance:
- Effect of cathode catalyst structure and composition

(C) Cost (indirectly)

Technical Targets

This project is conducting fundamental studies of Pt/carbon catalyst degradation mechanisms and degradation rates which will be correlated with unit cell operational conditions and catalyst layer structure and composition. Furthermore, forward predictive micro- and macro- models for cathode performance and degradation will be developed. Design curves that will be generated both through model simulations and experimental work will enable membrane electrode assembly (MEA) designers to optimize performance, durability, and indirectly cost towards the 2015 stack targets for fuel cell commercialization [1]:

- Durability: 5,000/40,000 hrs (2015 transportation/2011 stationary application target)
  - Electrocatalyst support loss <30 mV after 100 hrs @ 1.2 V
  - Electrochemically active surface area (ECSA) loss <40%
• Cost: $15/kWₑ
  – Platinum group metal total loading: 0.2 mg

**Approach**

A dual path approach is taken in this project:

1. Development of models at the molecular, micro-structural, and macro homogeneous scales that include the degradation effects related to platinum dissolution/transport/plating, carbon surface oxidation/corrosion, and ionomer thickening/conductivity loss. These models will provide the ability to study the effects of composition, the morphological design, and the operational window on catalyst degradation via simulated accelerated stress testing (AST). The design curves generated in each scale of the modeling work will enable the development of mitigation strategies through trade-off analysis.

2. Development of key operational and catalyst/catalyst layer structural degradation design curves through AST coupled with ‘state-of-the-art’ in situ/ex situ characterizations techniques. This allows the correlation of performance loss with structural changes measured within the MEA. The experimentally collected design curves will enable the identification of mitigation strategies through MEA property trade-off analysis; as well it will provide validation data for the various levels of degradation models described above.

**Accomplishments**

The following was accomplished during the first two quarters:

• The Discrete Macro-model was further developed to include a description of catalyst layer composition and structure (Agglomerate Model) with inputs for platinum loading, the catalyst compositional weight ratios, platinum particle size, utilization (or ECSA), material densities, and layer thickness. A comparison of Discrete and Agglomerate Model simulations showed that predicted performance is very sensitive to the choice of the catalyst model. The Agglomerate Model, which at the present time does not include liquid water, is able to capture mass transport losses at high current density suggesting that both the presence of liquid water and the catalyst structure have an effect on mass transport losses (Figure 1).

• Simulated design curves of the effect of performance on ionomer cathode loading reveals optimal performance at ~30% for the baseline MEA in agreement with experimental results (Figure 2).

• The methodology and diagnostic techniques for MEA characterization have been down-selected in order to establish an efficient and extensive characterization protocol.

• Key operational and structural stressors have been identified and prioritized for AST based on their effect on the degradation rates.

• The DOE catalyst AST and the Ballard Standard AST protocols were evaluated using a reference MEA in order to understand and compare their impact on catalyst layer degradation. The major differences between the two protocols are the cathode environment, cycle profile and frequency, and the upper potential voltage limit shown in Table 1. The performance losses from the two different protocols at the end of the test (Figures 3 and 4) are very similar and consistent with
predominately kinetic changes for both ASTs as shown by the voltage loss, EPSA and mass activity changes. At high current density the performance losses increase indicating some contribution of non-kinetic related losses that is somewhat larger for the BPS AST. The post-mortem analysis revealed that both the membrane and cathode thicknesses did not change under both protocols, while differences were observed in the average Pt crystallite size and Pt migration into the membrane. A larger average Pt crystallite size was observed in the MEA subjected to the DOE protocol due to re-deposition of Pt at the catalyst layer/membrane interface under N₂ conditions at the cathode. Under a simulated air cathode environment, a Pt band was observed in the membrane which does not form when N₂ is used.

**TABLE 1. AST Protocols**

<table>
<thead>
<tr>
<th>Attributes</th>
<th>DOE AST</th>
<th>Ballard AST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adapted for BPS</td>
<td>Hardware</td>
</tr>
<tr>
<td>Cycle Profile</td>
<td>Triangular Wave</td>
<td>Square Wave</td>
</tr>
<tr>
<td></td>
<td>0.6 V to 1.0 V, 50 mV/s</td>
<td>0.6 V (30 s) to 1.2 V (60 s)</td>
</tr>
<tr>
<td>Time/Cycle</td>
<td>16 s</td>
<td>90 s</td>
</tr>
<tr>
<td>Number of Cycles</td>
<td>30,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Total Cycling Time</td>
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<td>125 hours</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
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<tr>
<td>RH Anode/Cathode</td>
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<td>100% / 100%</td>
</tr>
<tr>
<td>Fuel/Oxidant</td>
<td>H₂ 4,450 sccm N₂ 9,000 sccm</td>
<td>H₂ 4,450 sccm 21% O₂/N₂ 9,000 sccm</td>
</tr>
<tr>
<td>Pressure</td>
<td>5 psig</td>
<td>5 psig</td>
</tr>
</tbody>
</table>

**Future Directions**

The 2010/2011 anticipated work and accomplishments are expected to be:

- Expanded macro-level model that captures the compositional-based effects with an extended range of the validation data (both operationally and compositionally).
- Modeled molecular features/characteristics of the Pt/C/ionomer interface.
- Expanded Micro-structural and Macro-homogenous Models that include a liquid water description.
- Measured performance degradation rates for different carbon supports, ionomer content, and Pt/C ratios.
- Measured performance degradation rates as a function of upper potential limit for Pt supported on a mid-range and low surface area carbon black.

**FY 2010 Publications/Presentations**

2. Presentation to the Fuel Cell Tech Team (January 13, 2010).
3. 2010 Annual Merit Review Poster Presentation (June 8, 2010).
References

V.I.1 Diesel-Fueled SOFC System for Class 7/Class 8 On-Highway Truck Auxiliary Power

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) reformate.
• 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 Fuel Cell 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. 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% (25%) (lower heating value basis)
• Cycle capability: 150 cycles (10 cycles)
• Durability: 20,000 hours (1,500 hours)
• Start-up time: 15-30 min (60 min)

Accomplishments

Developed:

• Low-cost balance-of-plant (BOP) concepts and compatible systems designs.
• Identified low-cost, high-volume components for BOP systems.
• Demonstrated efficient SOFC output power conditioning.
• Demonstrated SOFC control strategies and tuning methods.

Demonstrated:

• Operation meeting SOFC APU requirements on commercial ULSD fuel.
• SOFC system operations on dry CPOX reformate.
• Successful start-up and shut-down of SOFC APU system without inert gas purge.

The SOFC APU demonstration was carried out at the Cummins Power Generation (CPG) facility in Minneapolis, Minnesota on February 26, 2010. The demonstration was successfully completed on February 27, 2010 including the necessary steady-state, transient, and peak power operation tests. Table 1 lists the results against project objectives.
TABLE 1. Results Against Project Objectives

<table>
<thead>
<tr>
<th>Objective</th>
<th>Target</th>
<th>Demonstrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation on Liquid Fuel</td>
<td>ULSD</td>
<td>ULSD</td>
</tr>
<tr>
<td>Average Power (Net DC)</td>
<td>1,100 Watts</td>
<td></td>
</tr>
<tr>
<td>Average Power (Net AC)</td>
<td>820 Watts</td>
<td></td>
</tr>
<tr>
<td>Combined Heat and Power (CHP)</td>
<td>&gt;4 kWatts</td>
<td></td>
</tr>
<tr>
<td>Peak Power (Net DC)</td>
<td>1,250 Watts</td>
<td></td>
</tr>
<tr>
<td>Specific Power (Net DC)</td>
<td>17 W/kg</td>
<td>9 W/kg</td>
</tr>
<tr>
<td>Power Density</td>
<td>8 W/L</td>
<td>3 W/L</td>
</tr>
<tr>
<td>Start-up Time (Cold)</td>
<td>1 hour</td>
<td>1 hour</td>
</tr>
<tr>
<td>Efficiency @ Rated Power</td>
<td>25% lower heating value</td>
<td>11% lower heating value</td>
</tr>
<tr>
<td>In-Vehicle Demonstration</td>
<td>Operation on a Class 8 Truck</td>
<td>Operation on Truck Hardware in Lab</td>
</tr>
</tbody>
</table>

DC - direct current; AC - alternating current

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 provide heating for both cabin and engine.

This project was directed at designing, building and demonstrating a ULSD-fueled SOFC APU installed in an on-highway truck to supply AC power for cabin loads, engine heating, and battery charging during rest periods.

Approach

The plan to complete the objectives of the project included identifying the overall truck system performance, power electronics, heating, battery, fuel cell system, and fuel cell hot zone requirements.

The APU design used 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 was to have been accomplished by modifications to a pre-existing 250 W SOFC module. CPG was 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 built the hot modules, including stacks, reformers, heat exchangers, tail-gas combustors and insulation packages.

Results

Since last year’s report, we fabricated and tested two generations of complete SOFC modules and operated those 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 was 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 used 66 tubes, each Ø10x135 mm. The first round of modules were delivered to CPG in the third quarter of Fiscal Year (FY) 2009, the second round used for the demonstration in the first quarter of FY 2010.

In FY 2009, Protonex began testing subscale stacks on liquid fuels to determine proper set-points for the fuel processor and cathode air flow to enable reliable startup and shutdown 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.

CPG completed the BOP air delivery system fabrication for the four module fuel cell system. The system includes one cathode air blower, one CPOX air boost blower, four cathode flow control valves, four anode control valves, eight air mass flow sensors. The system achieved the required flow characteristics for the modules. CPG utilized low-cost automotive components in this fuel cell development application to prove a reduced cost bill of materials.

CPG revised the power electronics topology to eliminate the DC-DC boost. The revised topology was simpler and provided an overall efficiency improvement of 3-4%.

Identified and tested a group of inexpensive waste heat recovery exchanger designs that provide the required cab heating with an effectiveness of ≥95% and pressure drop of <2” water over the required range of operating conditions. 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.

The final demonstration occurred on February 26th, 2010 (Figure 1) with the results shown in Table 1. The key performance parameters are:
1. Operation meeting SOFC APU requirements on commercial ULSD fuel.
2. SOFC systems operating on dry CPOX reformate.
3. Successful start-up and shut-down of SOFC APU system without inert gas purge.
4. AC power output sufficient to operate 12,000 BTU air conditioning system.

The test consisted of heating each module individually for convenient monitoring, and allowing the entire system to achieve a steady state. Note that the system is capable of starting all modules simultaneously if desired. The steady-state DC power production was 1,500 W gross with approximately 580 W of parasitic losses for a net production of 1,120 W. A peak power loading of 1,680 W with a net output of 1,225 W was recorded for 10 minutes higher peak loading of the modules is possible, the peak loading was not limited by inherent module capability, rather it was limited by the thermal balance. Future systems could be designed for higher firing rates and power production with moderate design modifications to the heat exchangers, fuel feed system and thermal insulation package.

After the peak loading, the system continued in steady-state DC power operation for 10 hours, simulating the rest period over which a Class 7/8 APU would operate. At the end of this time the power output was 1,490 W gross and 1,110 W net.

The system was then transitioned to AC loading for 1.5 hours. The AC loading required the modules to be connected in series electrically; thus forcing the same current through all modules and reducing total power by 5%. The larger change in parasitic losses was due to the inverter efficiency of ~85%. The power produced during this period is shown in Figure 2, 1,460 W gross and 820 W net at the end of the test. This allowed the air conditioning, lighting and additional DC loading thus simulating a truck “hotel” load to all operate simultaneously from power generated by the SOFC sub-system.

Conclusions and Future Directions

Summary

- During FY 2010 the project fabricated and delivered the second generation of SOFC modules with significantly improved performance and stability. These modules were demonstrated and characterized on both hydrogen and reformed liquid fuels.
- Demonstrated the viability of a dry CPOX approach at the stack and module level.
- Built and tested two complete 4-module sets for testing.
- Completed conceptual design of higher-power (~1 kWe) module.
- Completed SOFC APU unit fabrication and demonstration.
- Project work completed in the second quarter of FY 2010

Discussion

At the conclusion of the SOFC APU project the technology may be seen to be approaching the necessary requirements for creating successful commercial implementation(s) in mobile power markets in the five-to ten-year range.
Key technical obstacles for commercial implementation were addressed in this project:

- Diesel fuel reforming without water (including sulfur handling): The Protonex module demonstrated short-term operation on commercial ULSD without supplementary water or water recycling under controlled oxygen-to-carbon ratio conditions.
- Cost: The implementation of low-cost automotive control components was demonstrated through novel adaptations to achieve required accuracy and resolution. Stereolithography components demonstrated potential for cost-effective integration of multiple functions in tooled components.
- Performance: The APU power unit demonstrated the potential to produce required mission levels of power generation from a package envelope comparable to current production APU products.

Durability and efficiency are two areas that require additional development to reach commercial requirements. Observed levels of stack degradation during this project are recognized to be inadequate to support a commercial product and are the object of ongoing development at Protonex.

Observed system efficiency, while comparable to small diesel gensets operating at light-load conditions, needs improvement to maximize economic benefits. Observed efficiency was negatively impacted in three areas:

1. Tubular stack elements performed below expectations, especially at higher levels of fuel utilization. Projections were based on performance of the previous smaller tubes.
2. Carbon-free operation of the CPOX reformer required higher than expected O/C ratios, lowering effective reformer efficiencies.
3. The BOP was sized to the projected stack power. Operation at the lower power levels demonstrated by the prototype stacks resulted in an effectively oversized BOP.

After some experience in control of full SOFC fuel cell systems it is apparent that proper mechanical system design allows utilization of low-cost sub-system components and reduces parts count.
V.I.2 Solid Oxide Fuel Cell Development for Auxiliary Power in Heavy Duty Vehicle Applications

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Technical Advisor:  John Kopasz  
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E-mail: Kopasz@anl.gov

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

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 Fuel Cell Technologies (FCT) Program 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-duty 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 FCT Multi-Year RD&D Plan (see Table 1). Upon completion of the project the attached technical targets verses actuals table was developed and presented to the DOE on June 22, 2010 (see Table 2).

TABLE 1. Auxiliary Power Units (3-5 kW rated, 5-10 kW peak) Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2010 / 2015 Targets*</th>
<th>Delphi 2008 SOFC APU Status*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Power</td>
<td>W/kg</td>
<td>100 / 100</td>
<td>15</td>
</tr>
<tr>
<td>Power Density</td>
<td>W/L</td>
<td>100 / 100</td>
<td>12</td>
</tr>
<tr>
<td>Efficiency @ Rated Power</td>
<td>%LHV</td>
<td>35 / 40</td>
<td>35</td>
</tr>
<tr>
<td>Cost</td>
<td>$/kW</td>
<td>400 / 400</td>
<td>665</td>
</tr>
<tr>
<td>Cycle Capability</td>
<td>number of cycles</td>
<td>150 / 250</td>
<td>125</td>
</tr>
<tr>
<td>(from cold start) over operating lifetime</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Durability</td>
<td>hours</td>
<td>20,000 / 35,000</td>
<td>4,660</td>
</tr>
<tr>
<td>Start-up Time</td>
<td>min</td>
<td>15-30 / 15-30</td>
<td>120</td>
</tr>
</tbody>
</table>

*Electrical efficiency only – does not include any efficiency aspects of the heating or cooling likely being provided.

*Cost based on high-volume manufacturing quantities (100,000 units per year).

*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.

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

Accomplishments

• Design and development of the next generation enhanced DPS3000D APU.
• Full-scale component modeling and build.
• Use of next generation stack design.
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 (see Figure 1).
Fifteen-hour continuous test and demonstration of
a diesel-fueled SOFC APU mounted on a Class 8
Peterbuilt Model 386 truck with loads.

**Introduction**

Delphi Corporation (Delphi) has teamed with
heavy-duty truck original equipment manufacturers
PACCAR Incorporated (PACCAR), and Volvo
Trucks North America (VTNA) to define system level
requirements and develop an 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
an 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-duty truck manufacturers
including VTNA and PACCAR to develop specific
technical requirements 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.

---

**TABLE 2.** Auxiliary Power Units (3-5 kW rated, 5-10 kW peak) Actual

<table>
<thead>
<tr>
<th>Units</th>
<th>2010 Targets (1)</th>
<th>2010 Actuals</th>
<th>(Production)</th>
<th>2015</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Power</td>
<td>W/kg</td>
<td>120</td>
<td>17</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>Power Density</td>
<td>W/L</td>
<td>120</td>
<td>4</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Efficiency @ Rated Power</td>
<td>%</td>
<td>35</td>
<td>25</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>Cost</td>
<td>$/kW</td>
<td>400</td>
<td>(3) See below</td>
<td>(4) See below</td>
<td>(4) See below</td>
</tr>
<tr>
<td>Cycle Capability (from cold start)</td>
<td>Number of cycles</td>
<td>500</td>
<td>(3) See below</td>
<td>416</td>
<td>416</td>
</tr>
<tr>
<td>Operating Life</td>
<td>hours</td>
<td>5,000</td>
<td>2500</td>
<td>30,000</td>
<td>30,000</td>
</tr>
<tr>
<td>Start-up time</td>
<td>minutes</td>
<td>15-30</td>
<td>180</td>
<td>90</td>
<td>60</td>
</tr>
</tbody>
</table>

1 Operating on Standard Ultra-Low Sulfur Diesel
2 Initial targets for program as defined in 2003 SOPO
3 Regulated DC Net/Lower heating value of fuel
4 Heavy duty truck market is highly price sensitive.
5 < 50 System Cycles but >200 stack Cycles

**FIGURE 1.** DPS3000A System on Shaker Table
**Status**

In the past year Delphi focused on refining and enhancing the overall APU system design and performing detailed system and subsystem testing. Specifically, work was focused on the SOFC APU hardware design and build; subsystem test fixture hardware build; and subsystem testing and development iterations.

The work this period included Tasks 2.6, 2.8, 2.10, 2.11, 3.1, 3.2, and 3.3. These tasks focus on the SOFC APU hardware design and build; subsystem testing and development iterations; system module testing and development; and bench testing of the APU. The testing was completed on time and under budget.

Tests were completed on the enclosure flow under different configurations. The original design had only one inlet, while a revised design had two inlets in various configurations. Comparative testing indicated significant flow improvement by going to the two inlet design. Figure 2 shows the flow velocity at various process air blower (PAB) rates. The dark blue line (bottom) is the flow rate for the one inlet design while the other rates are for the two inlet design under different configurations.

The development of APU hardware and test stands to validate subsystems was initiated and completed in 2010. Delphi engineers noted improvements that can be made to the stand in order to attain the most accurate data from the tests. The system vibration test stand (Figure 1) was successfully designed and fabricated with capability of the following:

- 24/7 unmanned operation
- Hot system running with diesel fuel
- Rapid thermal cycle testing
- Continues load testing
- Three-axis vibration

Positive results were gathered from the vibration testing indicating the robustness of the design for on-road application of the SOFC as an APU.

Additional full APU system development and testing was conducting including:

- Thermal cycling tests of the complete system
- Hardware development
- Software development
- Load cycling of only thermal stacks
- Usage of anode tail gas simulation to generate recycle

During this phase Delphi performed 22 full thermal cycles on ultra-low sulfur diesel (ULSD), and 160 total hours of operation. Delphi successfully demonstrated complete system “Turn-Key” starts, warm-ups, and repeated cool-downs.

Delphi also successfully performed full simulated load cycles using the DPS3000D set 3 with EC stacks, pulled power during cycle testing, monitored stack cell

![FIGURE 2. Enclosure Flow Test](image-url)
voltages, performed five ULSD starts and two additional full thermal cycles. Furthermore an initial natural frequency sweep was performed. The SOFC system was also tested for noise generation and electromagnetic compatibility at Delphi Packard Division.

Delphi has finished the final review for the completion of reports and documentation required for the final oral/visual presentation. The final presentation was completed June 22nd, 2010. The presentation was presented to DOE staff and members of the Delphi development team.

The project was completed on time and to budget.

**FY 2010 Publications/Presentations**


**Special Recognitions & Awards/Patents Issued**

US Patent Office Grant Numbers: 7562588 and 7648784:

2. 7648784 (1/19/2010) - Method and apparatus for controlling a Fuel Cell system having a variable number of parallel connected modules.
V.J.1 Novel Approach to Advanced Direct Methanol Fuel Cell (DMFC) Anode Catalysts

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Katherine Hurst, Arrelaine Dameron, Kevin
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Kathi Epping Martin
Phone: (202) 586-7425
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Subcontractors:
•	 Ryan O’Hayre, Colorado School of Mines (CSM),
  Golden, CO
•	 Charles Hays and Sri.R. Narayan, Jet Propulsion
  Laboratory (JPL), Pasadena, CA

Project Start Date:  July 20, 2009
Project End Date:  September 30, 2011

Objectives

Our objective is to improve the catalytic activity and
durability of PtRu for the methanol oxidation reaction
(MOR) via optimized catalyst-support interactions.

•
  Determine the effect of ion implantation on the catalyst activity and stability of PtRu catalyst nanoparticles deposited on highly-oriented pyrolytic graphite (HOPG) supports. Implantation will cause n- or p- doping via incorporation of various species, initially focusing on nitrogen.

•
  Determine the effect of doping level and dopants type (n or p) on the catalytic activity and durability of the PtRu/HOPG model catalyst system that improve catalyst-substrate interaction resulting in an improved catalyst material for the methanol oxidation reaction.

•
  Apply this dopant-engineering approach to high surface area carbon supports. The goal is to improve catalyst utilization, activity, and durability for membrane electrode assemblies.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan (section 3.4.4):

(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project aims to improve the catalytic activity and durability of PtRu for the MOR via optimized catalyst-support interactions. Insights gained from these studies will be applied toward the development and demonstration of DMFC anode catalyst systems that meet or exceed the following DOE 2010 Consumer Electronics targets:

•
  Cost:  $3/W
•
  Specific Power:  100 W/kg
•
  Power Density: 100 W/L
•
  Lifetime:  5,000 hours

Accomplishments

(1) Established an optimal N-implantation parameter set for HOPG, which resulted in enhanced PtRu catalytic activity for MOR.
(2) Obtained experimental results demonstrating an increase in durability on N-doped samples.
(3) Sputter deposited PtRu alloy with controlled composition, phase, and orientation from a single PtRu alloy target.
(4) Built a chamber that allows for ion-implantation and sputter deposition of powders.
(5) Established protocol for deposition of uniform PtRu catalyst particles on commercial and chemical vapor deposition synthesized B-doped and N-doped powders.

Introduction

High material cost and insufficient catalytic activity and durability are key barriers to the commercial deployment of DMFCs – the most advanced fuel cell technology for consumer electronics application. DMFCs
are attractive for portable commercial and military applications because they offer extremely high theoretical energy density (~10x better than Li-ion batteries).

To accelerate the commercialization of DMFCs for consumer electronics applications, next generation materials based on leap-frog technology are needed. In DMFCs, the MOR on the anode limits the performance and durability. Breakthroughs in DMFC anode catalysis with respect to performance, cost and durability will help enable and accelerate the commercialization of DMFCs.

**Approach**

This project focuses on improving the catalytic and durability of the anode catalyst for the MOR. Our approach is to modify and improve catalyst-support interactions in order to substantially increase activity, selectivity, and durability of PtRu catalytic systems. The team systematically investigated the effects of ion-implantation on HOPG, as a model support analogue [1-3], on PtRu catalysts. These well-defined systems allowed us to assess dopant effects and provide a test-bed for exploring new dopant/catalyst combinations. These doped and undoped carbon substrates are decorated with PtRu using both aqueous solution and physical vapor methods. The catalysts are characterized with various techniques such as microscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and electrochemistry to determine the catalyst particle size, dispersion, composition, structure, degree of alloying, MOR activity and electrochemical durability. The catalyst synthesis process and materials are down-selected based on best performance and transferred to high surface area carbon studies for further study. The highest performing materials will be used in DMFC testing.

**Results**

We demonstrated enhanced PtRu catalytic activity for methanol oxidation by achieving smaller particle size and more uniform dispersion of PtRu on N-doped HOPG. For the N-implantation conditions investigated, we determined 45 seconds as optimal for N-doping. Nitrogen was found to incorporate into the carbon network, resulting in the formation of sp3-sp2 bonding disrupting the graphitic structure of the undoped HOPG. Various oxygen groups, including C-O, C=O and N-C=O, were also observed after implantation. Ion implantation of N2 longer than 45 seconds resulted in no additional surface structural disorder. The relative amount of nitrogen (7%, determined by XPS) introduced into the carbon substrate also saturated after 30-45 seconds. Electrochemical data obtained by project partner, JPL, confirmed NREL results. (Argon implanted HOPG was used to establish benchmark performance caused by structural defects.)

Figure 1 shows examples of PtRu deposited on various HOPG samples. It is apparent from Figure 1 that the most uniform and smallest particles of PtRu catalyst were obtained using N-doped HOPG samples. Ar-doping improved the dispersion compared to undoped HOPG but resulted in a more pronounced agglomeration of catalyst particles as compared to N-doping. Similar samples to those shown in Figure 1 at higher PtRu loadings were used to measure methanol oxidation activity. Table 1 shows that nitrogen doping resulted in the highest MOR activity and highest surface roughness factor as compared to undoped and Ar-doped HOPG. Table 1 also shows that our microwave deposition of Pt and Ru onto N-HOPG gave comparable activity to commercial PtRu catalysts on a per metal surface area basis.
We developed a novel method to deposit Pt\(_{1-x}\)Ru\(_x\) alloy or amorphous films/particles by sputtering from a single, alloyed PtRu target. We were able to control the PtRu composition with sputtering power and chamber oxygen concentration. We can also demonstrate a dependence of the orientation and phases (hexagonal close packed/face centered cubic) of Pt\(_{1-x}\)Ru\(_x\) with overall chamber pressure. Finally, we designed and built a new chamber for ion implantation and sputter deposition of catalyst on high surface area carbon materials (Figure 2). Preliminary experiments were performed and the resultant materials are being characterized.

**Conclusions and Future Direction**

- Demonstrated that nitrogen implantation on HOPG enhanced MOR activity.
- Established different PtRu deposition methodologies.
- Established optimized N-doping level on HOPG via ion implantation.
- Initiated a preliminary study of the effect of different dopants.
- Developed a processing system for ion implantation of high surface area carbon materials, and initiated study of high surface area carbon.
- We will conduct studies of other dopants on HOPG (B, S, I).
- We will investigate different methods to dope high surface area carbon (in situ and ex situ) (e.g., ion implantation, chemical vapor deposition, and pyrolysis).
- We will characterize and measure methanol oxidation performance of PtRu/doped high surface area carbon.
- We will optimize materials and measure DMFC performance and durability of optimized catalysts.

**FY 2010 Publications/Presentations**


References


Objectives

- Develop ultra-thin membranes having extremely low methanol crossover, high conductivity, durability, and low cost.
- Develop cathode catalysts that can operate with considerably reduced platinum loading and improved methanol tolerance.
- Produce a membrane electrode assembly (MEA) combining these two innovations that has a performance of at least 150 mW/cm² at 0.4 V and a cost of less than $0.80/W for the membrane and cathode catalyst.

Technical Barriers

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

(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project is conducting focused research on next generation membrane and cathode catalyst materials for direct methanol fuel cells. Insights gained from these studies will be applied toward the design of a MEA for portable power applications that meet the DOE 2010 targets:

- **Performance**:
  - Specific Power (100 W/kg),
  - Power Density (100 W/L), and Energy Density (1,000 Wh/L)
- **Cost**: $3/W
- **Lifetime**: 5,000 hours

In translating DOE-published targets, we have defined the following goals for the membrane, cathode catalyst, and MEA performance based on our modeling efforts in Table 1.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>Industry Benchmark</th>
<th>Project Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol Permeability</td>
<td>cm²/s</td>
<td>1-3·10⁻⁶</td>
<td>5-3·10⁻⁷</td>
</tr>
<tr>
<td>Areal Resistance 70°C</td>
<td>Ωcm²</td>
<td>0.120 (Nafion® 117)</td>
<td>0.80 (2 mil thick)</td>
</tr>
<tr>
<td>Catalyst Mass Activity (RDE, 70°C and 0.40V)</td>
<td>mW/mg Pt</td>
<td>22.5</td>
<td>&gt;100</td>
</tr>
<tr>
<td>MEA Cathode Catalyst Loading</td>
<td>mg/cm²</td>
<td>4</td>
<td>1.5</td>
</tr>
<tr>
<td>MEA I-V Cell Performance (0.4 V)</td>
<td>mW/cm²</td>
<td>90</td>
<td>150</td>
</tr>
<tr>
<td>MEA Lifetime</td>
<td>hours</td>
<td>&gt;3,000</td>
<td>5,000</td>
</tr>
</tbody>
</table>

RDE = rotating disk electrode; I-V = current-voltage

V.J.2 Novel Materials for High Efficiency Direct Methanol Fuel Cells

Arkema and IIT are developing a new generation of thin membranes with very low methanol cross-over and high conductivity. The membranes are formed from blends of polyvinylidene fluoride with a variety of highly sulfonated polyelectrolytes, technology that was developed in two previous projects. A number of variables can be easily adjusted in the blending process to tailor the membrane properties. The key to obtaining the desired properties resides in control of composition, architecture, and morphology of the membrane components. These are controlled on a practical level through polyelectrolyte chemistry, membrane composition, processing, and additives, which
will be systematically investigated and correlated with properties.

QSI will develop a new series of cathode catalysts with improved mass activity obtained by suppressing methanol oxidation. These cathode materials will be palladium-based nanocatalysts mixed with platinum carbon with considerably reduced platinum loadings. These catalysts are prepared using gas phase condensation, which allows for control of particle size, alloy ratio, and core-shell structure.

**Accomplishments**

The award contract for this project was signed on June 30th. Work is in progress on the preparation of initial membrane and catalyst compositions for property screening. Methods are also being established for MEA preparation, conditioning, and testing. While new membrane and catalyst materials are being prepared, tests are being run on MEAs constructed from currently available Arkema and QSI materials as a baseline for the project. Without any modifications to the cathode catalyst and membrane, significant improvement in 10 M methanol is already observed over a 7 mil perfluorosulfonic acid membrane-based MEA (Figure 1).

**Future Directions FY 2010-2011**

- Prepare and screen a library of membrane samples to identify compositions that produce the lowest methanol crossover, while maintaining adequate conductivity.
- Synthesize and screen the properties of a series of Pd-based catalysts, including palladium and palladium-metal alloys. Reactor operating parameters (pre-alloy conditions, gas flow, voltage) will be optimized for the preparation of 3-10 nm particles.
- Continue efforts to establish procedures for MEA conditioning and testing.

**FY 2010 Publications/Presentations**


**FIGURE 1.** Preliminary performance of an MEA constructed with Arkema’s M43 membrane and QSI-Nano® cathode.
V.J.3 New MEA Materials for Improved DMFC Performance, Durability, and Cost

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Contract Number: DE-EE0000475

Subcontractors:
• University of Florida, Gainesville, FL
• Northeastern University, Boston, MA
• Johnson Matthey Fuel Cells, Swindon, UK

Project Start Date: January 1, 2010
Project End Date: June 30, 2012

Objectives

Optimize the functionality and internal water recovery features of the UNF passive water recovery membrane electrode assembly (MEA) to facilitate overall system simplicity, thereby increasing power and energy density and lowering the cost at the system level to address DOE's fuel cell target goals for consumer electronics applications.

• Optimize the UNF MEA design:
  – Improve durability and reliability.
  – Increase power and energy density.
  – Lower the cost.

• Develop commercial production capabilities:
  – Scale up the process to commercial batch operation level.
  - Improve performance and lower reproducibility.
  - Lower cost.

• Increase catalyst stability and lower loading:
  – Increase the anode catalyst stability.
  – Lower MEA cost.

Technical Barriers

This project addresses the following technical barriers for consumer based electronic applications of less than 50 W from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>UNF 15 WDP3 2008 Status</th>
<th>DOE 2010 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Power</td>
<td>W/kg</td>
<td>35</td>
<td>100</td>
</tr>
<tr>
<td>Power Density</td>
<td>W/L</td>
<td>48</td>
<td>100</td>
</tr>
<tr>
<td>Energy Density</td>
<td>W-hr/L</td>
<td>250 (1 x 100 ml)</td>
<td>1,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>396 (1 x 200 ml)</td>
<td></td>
</tr>
<tr>
<td>Lifetime</td>
<td>Operating Hours</td>
<td>1,000 hrs in single cell</td>
<td>5,000</td>
</tr>
<tr>
<td>Cost</td>
<td>$/Watt</td>
<td>11 (est. in volume)</td>
<td>&lt;3</td>
</tr>
</tbody>
</table>

- Beginning of life, 30°C, sea level, 50% relative humidity, excluding hybrid battery, power module alone
- Normalized from DP3 data from 150 ml cartridge to either 100 ml or 200 ml for comparison purposes
- Lifetime measured to 80% of rated power

Approach

The passive water recovery MEA (Figures 1 and 2) has been specifically designed for operation in the UNF system. This design incorporates the novel passive water recycling features of the MEA. The water recycling features enable significant simplification and miniaturization of the fuel cell at the system level, thus optimizing the resulting power and energy density. This approach optimizes the key attributes of the MEA and improves the system performance and durability. The scaling up of the manufacturing process for the MEA layers enhances both performance and reliability and reduces the overall cost. Our approach to improve
the anode catalyst structure to enhance the stability of the ruthenium improves the overall durability in direct methanol fuel cell (DMFC) applications. With our partners we will optimize the manufacturing process for preparing the passive water MEAs. We will move beyond the prototype operation by developing a batch manufacturing process which will improve the MEA-to-MEA reproducibility, increase the durability, and reduce the cost of the overall MEA. Our approach includes an evaluation of the MEA produced at both the single cell and the system level against system operating conditions required for a small compact DMFC system developed

in a related project at UNF. This process will include controlled warm-up and shut-down, standard operation and storage, and some anticipated out-of-operating specification conditions.

**Accomplishments**

The project was initiated in January 2010. Major accomplishments to date:

- Designed baseline MEA to produce passive water recovery under system operating conditions designed to optimize the overall system performance.
- Developed a Pt₈Ru₈Au on carbon catalyst that looks promising for improved ruthenium stability, with 99% of the surface area retention after long-term chronoamperometry compared to 88% retention of the surface area for a commercially available reference sample.

**Future Directions**

- Continue catalyst development and characterization:
  - Optimize and scale up of the anode catalyst with improved ruthenium stability.
  - Integrate improved catalyst into the passive water recovery MEA design.
  - Increase testing of high stability anode catalysts under system operating conditions, including long-term catalyst durability testing under operating and storage conditions.

- Improve manufacturing techniques for the liquid barrier layer:
  - Optimize steps to improve manufacturing process and lower sample to sample variation.
  - Test process variability and the effects on the MEA reproducibility and durability.

- Optimize MEA structure:
  - Develop optimized MEA coating and fabrication to produce lower sample to sample variability and improve performance.
  - Incorporate improved catalyst and liquid barrier layers to optimize performance and durability.

- Single cell and stack testing:
  - Measure performance and durability under system type operating conditions including start up, shut down, and storage conditions.
V.K.1 Development of Thermal and Water Management System for PEM Fuel Cell

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.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Multi-year Research, Development and Demonstration Plan:

(E) System Thermal and Water Management

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>Target</th>
<th>Honeywell Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity of PEM cell stack inlet air</td>
<td>% at 80°C</td>
<td>&gt;60</td>
<td>50</td>
</tr>
<tr>
<td>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</td>
<td>kW</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Radiator cost (by TIAX LLC) without markup</td>
<td>$</td>
<td>57</td>
<td>60</td>
</tr>
<tr>
<td>Reliability of radiator</td>
<td>hrs</td>
<td>5,000</td>
<td>&gt;5,000</td>
</tr>
<tr>
<td>Total parasitic power (air fan + cooling pump)</td>
<td>kW</td>
<td>&lt;2.4</td>
<td>TBD</td>
</tr>
</tbody>
</table>
Develop an advanced cooling system to meet the fuel cell cooling requirements. The heat generated by the fuel cell stack is a low-quality (lower temperature) heat 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 is based on the cooling system weight, performance, parasitic power, and initial cost. Two fin geometries -- 18 fpi louver and 40 fpi microchannel -- were down-selected. The full-scale radiators were built and tested. The results were presented in last year’s annual progress report as well as final test report submitted last year.

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 fuel cell stack operating conditions are simulated. The test results at ambient conditions are summarized here. The testing of the planer membrane module is scheduled for the third quarter of 2010. The select humidifier with optimum performance will be tested at sub-ambient conditions to simulate winter operating conditions.

**Results**

The testing of the full-scale and sub-scale Nafion® membrane module was successfully completed.

The humidity of the inlet stream (secondary flow) and outlet stream (primary in) for the full-scale module is plotted against average flow rates to humidifier inlet and outlet flow streams in Figure 1. Due to instrumentation and test stand limitations, the humidity of the humidifier inlet stream was limited to about 80 percent. The data scatter cannot be explained; each test point was taken when the system reached the steady-state condition.

The secondary inlet stream humidity data are adjusted higher (close to 100 percent), which resulted in higher humidity for the primary flow. Even after the adjustment, the primary flow is still lower than the 60 percent required for the PEM fuel cell, particularly at higher flow rates.

The sub-scale humidifier was also tested and the results are shown in Figure 2. The water transfer efficiency of the subscale humidifier was lower than full-scale by more than 10 percentage points.

**Conclusions and Future Directions**

The testing of full- and sub-scale membrane modules was successfully completed. The humidity of the fuel cell inlet air stream will be short of required 60% based on membrane module test results.

The testing of the enthalpy wheel is also completed the test data is being analysed. A full-scale planer-based
membrane module has been acquired and the testing is planned for the 3rd quarter of this year. The rectangular configuration of the planer module and the use of membrane sheets rather than fibers will result in ease of installation as well lower cost. This full-scale unit will be tested in the existing test stand.

The humidification device down-selected from the three under consideration will be tested at sub-ambient conditions. The completion of this testing will conclude the water management portion of this project at the end of Fiscal Year (FY) 2010 and the final report will be submitted in first quarter of 2011.

This testing project is conducted with close cooperation with Argonne National Laboratory, and the test data is provided to them for their PEM fuel cell system model.

**FY 2010 Publications/Presentations**

Objectives

- Demonstrate a durable, high-performance water transport membrane.
- Build and test a compact, low-cost, membrane-based module utilizing that membrane for use in an automotive stationary and/or portable fuel cell water transport exchangers.
- Model and show high volume costs associated with membrane and module.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan in Task 7, “Develop balance of plant components”:

(B) Cost
(E) System Thermal and Water Management
(A) Durability
(C) Performance

Accomplishments

- Contacts with various original equipment manufacturers (OEMs) have been initiated, and some preliminary feedback on humidifier operating conditions has been obtained for automotive and stationary conditions.
- Initial investigation of a number of membranes and processes has begun.
- A permeance testing system has been redesigned, and initial testing between 60° and 95°C, 70% relative humidity (RH) for several GORE™ humidification membranes has commenced.
- An alternate room temperature water vapor transport test protocol has been developed for rapid screening of new materials.

Introduction

Today it is essential to humidify the gases supplied to the fuel cell inlets for automotive and many stationary fuel cell stack designs. In this work, we propose to provide a new, inexpensive, composite membrane capable of very high water vapor transport and low air cross-over. The composite structure has been designed to allow lower total cost while still meeting automotive and stationary humidifier water transport and durability targets.

Because the transport rates of these new materials are so high, current planar membrane humidifier designs are not capable of fully utilizing the high rates. Therefore, the project will use an innovative, low-cost humidifier module with customized channel geometries that can take advantage of the high water transport rates. By having a materials development effort integrated with a humidifier module-system design and build program, we will be able to effectively exploit the improved material properties in an actual device.

Approach

Perfluorosulfonic acid (PFSA) membranes fulfill most of the requirements for the water transport media at the heart of the planar membrane water exchanger. They fall short primarily on cost, and secondarily on durability, especially when they are made thin to increase performance and lower cost. W. L. Gore and Associates, Inc. (Gore) has developed a composite water vapor transport membrane that has overcome both of these limitations. The basic composite structure
consists of a very thin ionomer layer sandwiched between two microporous polymer layers. The ionomer layer provides the active water transport and provides an impermeable layer to prevent gas cross-over. The water transport rate can be engineered to be very high either through the use of a material that has very high inherent water transport rates (e.g., PFSA), or by making it extremely thin (e.g., <5 µm). Of course, both can be used for the highest possible rate. The ionomer composition can be either a PFSA, or any other ionomer, for example a hydrocarbon. The microporous layer provides three critical features: first it protects the thin ionomer layer from mechanical damage during handling; second, it confers strength to the thin layer allowing it to be more durable during use. Third, it offers a strong, protective support layer for placement of a macroporous gas diffusion layer. The composition of the microporous layer is not restricted, although we believe that the high strength offered by expanded polytetrafluoroethylene is desirable. The initial tasks of the project are preparation and optimization of the various high performance water transport membrane, and characterization of the permeance and durability of the membranes. This will lead to a down selection to appropriate materials based on the performance criteria, coupled with cost modeling.

Although the basic structure described above has already been developed by Gore [1], the material has not yet been optimized for automotive or stationary humidifier applications. In particular, there is a trade-off between using a relatively expensive ionomer (e.g., PFSA) in a thicker ionomer layer, versus using a less expensive hydrocarbon ionomer in a thinner layer. Depending on thickness, each of these could have the same water vapor transport rate, yet may have very different durability at temperature, not to mention different costs. Furthermore, the microporous layer is expected to impact the durability and performance. A more open, weaker (and presumably less expensive) microporous layer would offer less resistance to water transport, but also offer less strength so could adversely impact durability. Finally, the effect of the macroporous gas diffusion layer has not been examined. Its composition, properties and attachment (loose-laid or laminated) have yet to be explored.

Our subcontractor, dPoint, has developed an innovative pleated planar membrane humidifier that is able to achieve automotive OEM water transport and pressure drop requirements. It has the advantages of low-cost materials and manufacturability, compact size, high pressure tolerance, a replaceable membrane cartridge and the flexibility to design for specific membrane characteristics. The pleated design utilizes existing low-cost, high-volume pleating equipment that is used to manufacture air filters for automotive and heating, ventilation and air conditioning applications. A flat sheet permeable membrane is folded and separated with a plastic injection molded flow field insert. The flow field inserts have an open channel design that allows excellent flow distribution, maximum membrane active area and very low pressure drop. The membrane cartridge has a potted elastomeric seal around the perimeter to prevent leakage at high-pressure conditions. The membrane cartridge is placed in a clamshell housing that has been designed to withstand automotive pressures and temperatures. The pleated humidifier is a proven technology that dPoint has been developing in cooperation with several major automotive OEMs. Further improvement in humidifier size, cost and performance is possible through the use of the Gore membrane and optimizing the flow field channel design to take full advantage of this new membrane.

### Results

At the time of writing of this report, results are very limited because we have just completed the first quarter of a two-year project. To date, a high-temperature permeance measurement system has been designed, built and tested. The design is similar to those used previously for similar measurements [2,3]. Based upon input from automotive and stationary OEMs, appropriate test conditions for measurements have been chosen as 70% RH air on the membrane wet-side, dry air on the membrane dry-side, with test temperatures between 60 and 95°C. Initial testing has commenced on various controls, as well as several variations of newly prepared materials. These initial results of various materials that have been prepared (Table 1) indicate very high permeance rates for some variants of the developed materials. One exciting material is shown in Figure 1, where the ionomer layer in the composite is ~1 micron.

### TABLE 1. Preliminary Water Permeance Results

<table>
<thead>
<tr>
<th>Material</th>
<th>∆C (kg/m³) by ln mean</th>
<th>Equivalent RH at 80°C</th>
<th>Permeance (GPU)†</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 um GORE-SELECT™ Membrane*</td>
<td>0.176</td>
<td>60.7%</td>
<td>23,100 ± 1,000</td>
</tr>
<tr>
<td>18 um GORE-SELECT® Membrane* (REPEAT)</td>
<td>0.177</td>
<td>61.5%</td>
<td>28,400 ± 1,400</td>
</tr>
<tr>
<td>Cast 1100 Equivalent Weight PFSA</td>
<td>0.180</td>
<td>64.1%</td>
<td>22,600 ± 1,200</td>
</tr>
<tr>
<td>GORE™ Hydrocarbon Ionomer Composite Structure</td>
<td>0.182</td>
<td>62.6%</td>
<td>14,600 ± 800</td>
</tr>
<tr>
<td>Perfluorocarbon Ionomer Composite Structure (GORE™ M311)</td>
<td>0.164</td>
<td>56.8%</td>
<td>47,500 ± 4,000</td>
</tr>
</tbody>
</table>

† Test conditions: 80°C; Dry inlet = 0 kg/m³ (0% RH); Wet inlet = 0.263 kg/m³ (70% RH); Ambient pressure both sides.  
‡ Listed error bars are 99% confidence interval;  
GPU = cm³/s-cm of Hg) x 10⁴  
* GORE-SELECT and Gore and design are trademarks of W. L. Gore & Associates, Inc.
thick. This composite is air-impermeable, and should have high permeance because of the very thin ionomer layer. The permeance testing of this material is underway.

One issue related to testing is the time required to measure permeance, upwards of 4 days per sample. Therefore, an alternate room temperature water vapor transport test protocol is under development for rapid screening. This new test protocol is based upon a modified version of the International Organization for Standardization Standard 15496, Measurement of Water Vapor Permeability of Textiles for Purpose of Quality Control. The initial testing indicates reasonable correlation with higher temperature permeance test results. Further analysis and testing is required to establish whether this approach is truly viable, either as a quality control tool, or for new material screening.

Conclusions and Future Directions

- Water transport rates through GORE™ humidification membranes can be very high, especially for the fluorinated ionomer-based materials.
- Transport measurements of these high-rate materials are a challenge.
- A range of alternate materials have been prepared and water permeance and air-impermeability will be measured shortly.
- Cost modeling of potential membranes, coupled with air-impermeability and water permeance data, will be used as inputs to a Go/No-Go decision to occur within the next nine months.
- A new test protocol for quick room screening water permeance has been developed. Future work will establish whether this is a correlation with results this new test and higher temperature permeance measurements that more closely model actual use conditions.

References

V.L.1 Nitrided Metallic Bipolar Plates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2010/2015 Targets</th>
<th>904L Foil (ORNL Benchmark)</th>
<th>Nitrided Foil Fe-20Cr-4V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate Cost ($/kW)a</td>
<td>5/3</td>
<td>Estimated 6-10</td>
<td>Estimated 6-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1-2 h nitriding cycle)</td>
<td></td>
</tr>
<tr>
<td>Current Density Anode (µA/cm²)b</td>
<td>&lt;1e</td>
<td>~8-9 at -0.15 V</td>
<td>~3 at -0.15 to +0.3 V (SHE)active peak at +0.4V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~5 at 0 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;1 at +0.25 to +0.6 V, no active peak</td>
<td></td>
</tr>
<tr>
<td>Current Density Cathode (µA/cm²)c</td>
<td>&lt;1e</td>
<td>1.5 at 7.5 h hold</td>
<td>~8 to 9 at 7.5 h hold</td>
</tr>
<tr>
<td>Areal Specific Resistanced (mΩ·cm²) at 150 N/cm²</td>
<td>&lt;20</td>
<td>As received:300</td>
<td>As received: 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polarized: 700</td>
<td>Polarized: 29</td>
</tr>
<tr>
<td>Forming Elongation (%)e</td>
<td>40</td>
<td>Estimated ≥ -40</td>
<td>Estimated 20-25</td>
</tr>
</tbody>
</table>

a Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).
b pH 3, 0.1 ppm hydrofluorhydric acid (HF), 80°C, peak active current < 1 X 10⁻⁶ A/cm² (potentiodynamic test at 0.1 mV/s, ~ -0.15 V to +0.84 V (standard hydrogen electrode, SHE) de-aerated with Ar purge.
c pH 3, 0.1 ppm HE, 80°C, passive current < 5 X 10⁻⁸ A/cm² (potentiostatic test at +0.84 V (SHE) for at least 24 hours, aerated solution.
d Includes contact resistance (on as-received and after potentiostatic cathode experiment) measured per Wang, et al, J Power Sources 115 (2003) 243-251. Value shown includes top and bottom face contributions.
e May have to be as low as 1 nA/cm² if all corrosion product ions remain in ionomer.

TABLE 1. Status of key technical targets relevant for metallic bipolar plates (DOE tentative revised targets). Data shown for archival nitrided Fe-20Cr-4V foil coupons from the successful 1,000 h cyclic single-cell fuel cell stamped foil test set [1-3]. Results for a benchmark untreated stainless steel, 904L, are also shown as measured corrosion current density values are sensitive to test cell setup in the pH3 sulfuric acid solutions specified by the DOE targets.

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 and contact resistance increase attributable to the bipolar plates).
- Demonstrate potential for adoption in automotive fuel cell stacks.

Technical Barriers

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

(A) Durability
(B) Cost
(C) Performance
Accomplishments

- Promising preliminary results with quartz lamp technology to reduce nitriding cycle time from 1-2 hours to <10 minutes to reduce processing costs.
- Promising preliminary automotive flow field stamping assessment of ORNL Fe-20Cr-4V alloy.

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 leads to high electrical resistance due to the formation of surface oxides and/or contamination of the 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 nitride-based protective surface layer. Proof-of-principle was established via nitridation of model Ni-Cr base alloys to form thermally grown Cr-nitride base surfaces that exhibited excellent corrosion resistance and maintained low interfacial contact resistance (ICR) in PEMFC environments [4]. Unfortunately, Ni-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 and poor corrosion resistance on nitriding instead of the desired continuous, protective Cr-nitride surface layer.

Efforts led by ORNL and NREL [4-6] have identified an approach to bypass the high nitrogen permeability of Fe-Cr base stainless steels to permit protective nitride surface layer formation. It is based on pre-oxidation to form a Cr-V-rich oxide surface, followed by nitridation of the oxide layer to form a mixed nitride/oxide surface structure [1-4]. The developed alloys contain small additions of V, up to 4 wt%, to aid in conversion of the initially formed surface oxide to nitride. For the low-cost Fe-20Cr-4V wt% alloy developed by ORNL, using short nitriding cycle times (1-2 h) to reduce nitriding cost, a mixed nitride/oxide surface consisting of “through oxide-thickness” V-rich nitride particles dispersed in Cr-rich oxide, is formed [1-3]. The Cr-base oxide and the V-nitride surface provide for corrosion resistance and the V-nitride particles provide low ICR with electrical connectivity from the surface through the oxide to the underlying metal.

Results

Single-cell fuel cell testing of pre-oxidized/ nitrided Fe-20Cr-4V foil stampings (referred to as “nitrided” in the remainder of the paper for simplicity), 904L (Fe-22Cr-24Ni-4Mo wt% base) stampings (no surface treatment), and machined graphite plates were completed in Fiscal Year (FY) 2009 [1-3]. 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 was used, with 1,000 hours (h) of durability testing evaluated for each material. All three materials showed good durability with no significant degradation in cell power output. Post-test analysis indicated no metal ion contamination of the MEAs occurred with the nitrided Fe-20Cr-4V or graphite plates, and only a minor amount of contamination was detected with the 904L plates (1.1 µg/cm² Fe and 0.18 µg/cm² Cr). The 904L was used as a benchmark material in addition to graphite because its high Cr, Mo, and Ni content result in excellent corrosion resistance in PEMFC environments. However, as shown in Table 1, the ICR value of 904L, similar to other untreated stainless steels, exceeds DOE targets by over an order of magnitude. In FY 2010, untreated stampings of type 321 stainless steel (type 316 Fe-18Cr-12 Ni stainless with 0.3-0.7 wt% Ti) were also evaluated in order to assess the aggressiveness of the aforementioned single-cell test cycle for a lower alloy content, conventional grade austenitic stainless steel. Extensive corrosion of the 321 test plates was observed after only 120 h of operation, indicating that the cyclic test conditions employed were aggressive.

Efforts in FY 2010 were directed to three primary tasks: 1) single-cell fuel cell evaluation of repeat nitrided Fe-20Cr-4V stampings treated over a range of conditions to assess robustness to variable nitridation reaction conditions, 2) assessment of the potential for reduced nitriding cost and improved performance using rapid nitriding cycles with quartz/plasma lamps, and 3) amenability assessment of the developed ferritic Fe-Cr V
alloys for stamping of state-of-the-art automotive bipolar plate flow-fields.

Figure 1 shows initial single-cell fuel cell polarization curves (<150-200 h total cycle testing) for a series of ~15 cm² active area stamped and nitrided Fe-20Cr-4V foils using a Nafion® 212 MEA. Nitridation peak temperature hold times were performed at 1, 1.5, and 2 h at 1,000°C to intentionally yield a wide range of nitrogen/oxygen mass uptakes and surface structures to simulate the degree of variability that may be encountered in mass production. For comparative purposes, results obtained with the Nafion® 212 MEA for the nitrided (1 h at 1,000°C) Fe-20Cr-4V stampings that previously accumulated ~1,500 h of total fuel cell operation (marked aged 1,500 h in Figure 1) as part of the FY 2009 durability assessment are included in Figure 1 [1-3]. The voltage-current (V-I) curves for these materials were remarkably similar, with the 1- and 1.5-h nitrided plates essentially the same as the 1,500 h aged stampings. The 2-h nitrided stampings, which were intentionally overnitrided, showed slightly higher performance V-I curves, possibly due to a higher volume fraction of conductive nitride phase.

One-thousand h durability evaluation is underway for the 1.5- and 2-h nitrided plates. After ~600 h of evaluation, the V-I curves for the 2-h nitrided material show excellent behavior with no evidence of performance degradation. However, performance degradation was observed after ~600 h for the 1.5-h nitrided material, which, based on N and O mass uptake on nitridation, was expected to exhibit good performance. Visual examination of the 1.5-h nitrided plates confirmed signs of corrosion attack. Surface chemistry and cross-section analysis are planned to identify the reasons for the unexpected susceptibility to corrosion of this material. Although preliminary, the apparent degradation of the 1.5-h nitrided stamping during the durability assessment repeat tests is a concern for scale up of the current Fe-20Cr-4V alloy and nitriding cycle to commercial production. It is possible that the steps taken to reduce bipolar plate cost, relatively low alloy Cr and V content and use of short, 1-2 h conventional furnace peak temperature holds for nitriding may result in excessive variability in corrosion resistance of the nitrided surface. Longer nitriding cycles may solve this issue, but would also result in increased production cost. Two routes to addressing this potential issue without cost increase are being pursued: 1) use of rapid thermal cycle quartz lamp technology for nitriding of Fe-20Cr-4V and 2) evaluation of a more Cr-rich alloy foil (Fe-23Cr-4V), which is expected to exhibit a more robust nitrided surface structure, but must first demonstrate sufficient amenability to stamping. The increase in Cr level from 20 wt% to 23 wt% is not expected to significantly increase alloy cost, but may decrease alloy ductility and amenability to stamping.

Initial single-cell fuel cell polarization curves for stamped Fe-20Cr-4V foil nitrided at 1,000°C for 10 minutes using quartz lamp technology for heating are also shown in Figure 1. Despite the very short nitriding cycle, V-I performance behavior superior to the conventional furnace nitrided Fe-20Cr-4V foils was observed. Figure 2 shows X-ray photoelectron spectroscopy (XPS) of the as-nitrided surface. Strong enrichment of V and N are evident, suggesting a high volume fraction of V,N phase particles in the (Cr,V)2O3 surface, consistent with the excellent single-cell V-I polarization curves obtained with this material (Figure 1). Of particular importance with regards to potential durability performance, no Fe was detected in the surface regions of the quartz lamp nitrided material. Nitridation of Fe-20Cr-4V foil using conventional furnaces typically results in a small amount of Fe retained in the surface (a few atomic percent), which may result in a lower degree of corrosion resistance. The rapid thermal cycle of the quartz lamp, which involves heating to peak temperatures in minutes rather than the hours for the conventional furnace, is speculated to minimize transient formation of Fe-rich oxidation.
and/or nitridation products compared to conventional heating technology. Further exploration of quartz lamp nitriding is underway, with cyclic single cell fuel cell durability assessment of quartz furnace treated stampings planned.

As a prelude to automotive bipolar plate evaluation of nitrided Fe-20Cr-4V foil, a preliminary stamping assessment of the Fe-20Cr-4V foil for suitability to automotive fuel cell bipolar plate flow field designs was conducted in conjunction with General Motors (GM). Figure 3 shows results of the automotive stamping screening of the Fe-20Cr-4V alloy foil relative to austenitic 316L stainless steel foil. Comparable flow-field structures were obtained, which suggests that the mechanical properties of the Fe-Cr-V alloys may be sufficient for manufacture of stamped automotive flow-field designs.

**Conclusions and Future Directions**

Although some concerns still exist regarding repeatability and robustness of the nitrided surface formed on stamped Fe-Cr-V alloy foils using short, low-cost cycle times, results obtained to date have indicated sufficient promise to warrant evaluation for scale up by industrial end users. A cost-shared subcontract was placed with GM in summer 2010 to perform an in-depth manufacturing evaluation of Fe-Cr-V alloys, including stamping and laser joining of bipolar plate cooling channels. GM will also pursue single-cell fuel cell evaluation of bipolar plates made by GM from Fe-Cr-V alloy foils after nitridation at ORNL. Both conventional furnace nitriding and quartz lamp nitriding will be evaluated. The project will conclude with completion of the GM evaluation effort.

**Special Recognitions & Awards/Patents Issued**

1. Claims for the patent disclosure “Iron-Based Alloy and Nitridation Treatment for PEM Fuel Cell Bipolar Plates” were allowed by the United State Patent Office in July 2010 (patent number not yet issued at the time of this report). Two previous patents were issued for the nitrided bipolar plate technology, #7,247,403 “Surface modified stainless steels for PEM fuel cell bipolar plates” and # 7,211,346 “Corrosion resistant metallic bipolar plate”

**FY 2010 Publications/Presentations**


**FIGURE 3.** Macrographs (a,c) of a small stamped segment and light microscopy cross-sections (b,d) of Fe-20Cr-4V and 316L foils after stamping to an automotive bipolar plate flow-field configuration.


References


V.L.2 Low-Cost PEM Fuel Cell Metal Bipolar Plates

Objectives

- Reduce or eliminate the small amount of gold used in TreadStone’s current corrosion-resistant metal plate technology for proton exchange membrane (PEM) fuel cell applications.
- Develop the low-cost metal bipolar plates using commercially available low-cost carbon steel or aluminum as the substrate materials.
- Optimize the fabrication process for large-scale manufacture.
- Demonstrate TreadStone’s low-cost metal plate technology in the applications of portable, stationary and automobile fuel cell systems.

Technical Barriers

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

(A) Durability

(b) Cost

(c) Performance

Technical Targets

The focus of this project is to further develop TreadStone’s proprietary corrosion-resistant metal plate technology reducing the metal plate cost to <$3/kW, while still meeting the performance requirements. There are a number of performance requirements to PEM fuel cell bipolar plates. The most challenging requirements for metal bipolar plates are summarized in Table 1. TreadStone’s existing (2009) technology can meet DOE’s 2010 target. This project is aimed to meet DOE’s 2015 target.

Table 1. TreadStone’s Metal Plate Status and DOE’s Targets

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>TreadStone 2009 Status</th>
<th>DOE Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate Cost a</td>
<td>$/kW</td>
<td>$4.91</td>
<td>5 3</td>
</tr>
<tr>
<td>Plate Weight</td>
<td>kg/kW</td>
<td>&lt;0.4</td>
<td>&lt;0.4 &lt;0.4</td>
</tr>
<tr>
<td>Corrosion Anode b</td>
<td>µA/cm²</td>
<td>n/a</td>
<td>&lt;1 &lt;1</td>
</tr>
<tr>
<td>Corrosion Cathode c</td>
<td>µA/cm²</td>
<td>&lt;0.01</td>
<td>&lt;1 &lt;1</td>
</tr>
<tr>
<td>Resistance d</td>
<td>Ohm cm²</td>
<td>&lt;0.01</td>
<td>&lt;0.02 &lt;0.02</td>
</tr>
</tbody>
</table>

a Based on 2002 dollars, 1 W/cm² power density and projected 500,000 stacks per year production.
b pH 3, 0.1 ppm hydrofluorhydric acid, 80°C, peak active current <1x10⁻⁸ A/cm² (potentiodynamic test at 0.1 mV/s, -0.4 V to +0.6 V (Ag/AgCl) de-aerated with Ar purge.
c pH 3, 0.1 ppm hydrofluorhydric acid, 80°C, passive current <5x10⁻⁸ A/cm² (potentiostatic test at +0.6 V (Ag/AgCl) for at least 24 hours, aerated solution.
d Includes contact resistance (on as-received and after potentiostatic experiment) measured.

Accomplishments

- Completed the low-cost conductive vias development. Demonstrated the processing technologies for Pd/Au composite vias, carbon nanotubes and conductive carbides as the conductive vias. The corrosion current of metal plates with these vias are below 1 µA/cm² in pH 3 H₂SO₄ + 0.1 ppm hydrofluorhydric acid (HF) solution under 0.8V normal hydrogen electrode (NHE) at 80°C.
- Developed the processing technology and the identified the coating materials for low-cost carbon steel substrate for PEM fuel cell applications.
Demonstrate our current metal plates in portable, stationary applications, operating at ambient pressure conditions, with short stack having 30 cm$^2$ and 267 cm$^2$ active area, respectively.

Demonstrated a 300 cm$^2$ active area, 10-cell, 2.5 kW short stack under utilizing durability testing cycle (including the Federal Test Procedure [FTP] cycle along with others) to mimic the automobile real world driving conditions. The stack has finished 800 hours stable operation, and continues to operate at Ford Motor Company.

Introduction

It has been reported that using metal bipolar separate plates can reduce the PEM fuel cell stack weight and volume by 40-50%, comparing with current graphite-based bipolar plates [1]. The major barrier to use metal bipolar plates in PEM fuel cells is the severe corrosion condition during stack operation. Most metals do not have the adequate corrosion resistance in the PEM fuel cell environment, which results in rapid performance degradation due to the formation of electrically resistive surface oxide scale, and potential contamination of the membrane electrode assembly (MEA) by the dissolved ions from the metal plates. Various corrosion protection techniques have been investigated to prevent metal plate corrosion in PEM fuel cell environments [2-7]. Some of these technologies have developed corrosion-resistant metal plates that can meet performance requirements. However, it is still a challenge to have a metal bipolar plate that can meet both the performance and cost requirements. The focus of TreadStone’s project is to develop the corrosion-resistant metal bipolar plates at the low cost to meet DOE’s 2015 targets.

Approach

Most people working on metal bipolar plates have been tried to cover the whole plate surface with an electronically conductive and corrosion-resistant material to protect the metal from corrosion and maintain the electrical conductance of the metal. The challenge of this approach is that there is only limited low-cost materials that could meet electrically conductive and corrosion-resistive requirements for PEM fuel cell applications, and the processing to apply these materials on metal substrate is either difficult or at high cost.

TreadStone takes a different approach to develop the metal bipolar plates for PEM fuel cell applications. It was found that it is unnecessary to have the whole surface electrically conductive to ensure the low contact resistance (interfacial contact resistance <10 mΩ.cm$^2$) between bipolar plates and the gas diffusion layer (GDL). TreadStone’s approach is based on this principle, as shown in Figure 1.

The majority of the metal surface area is covered with the low-cost corrosion-resistant but non- (or poor) conductive material (green layer in Figure 1). A corrosion-resistant and highly electrically conductive material (such as Au) forms the paths for electron transport, in the form of small conductive vias (yellow bars) penetrating through the non-conductive layer. Electrons generated from the anode reaction will flow through the GDL to the conductive vias (not the whole land area) pass the metal plate to the other side for the cathode reaction on the cathode of the adjacent cell. The conductive vias have a dimension as small as several micrometers, are distributed on the metal surface. The average distance between the conductive vias is 20-70 µm. The dense distribution of conductive vias ensures a uniform current distribution between the GDL and metal bipolar plates.

TreadStone’s approach is unique by using a small portion (<1-2%) of the plate surface for electrical contact. It was found that it could have more than 500,000 via/in$^2$ on the metal plate surface as the electrical contact point of metal plate with GDL, when small (<5 µm) conductive vias are used. It is because of the high amount of the contact points that ensure the low contact resistance of metal plates.

Results

TreadStone’s current metal bipolar plate uses small amount of gold as the electrical contacting material in the form of conductive vias, and stainless steel as the substrate material. In this project, we plan to develop the lower cost material to reduce the gold usage, or replace gold as the contact material. We have finished the process development to use palladium/gold composite as the contact materials. We also developed
the process to use carbon nanotubes and conductive carbides as the conduct material.

The palladium/gold composite uses the palladium particle as the base material, and the very small amount of gold plated on the palladium surface to ensure low contact resistance of the metal plate with GDL. The gold is in the form of 10-20 nm thick on the palladium particle surface. The corrosion experiments and the electrical contact resistance measurements indicate that stainless steel with the palladium/gold composite conductive vias can meet the PEM fuel cell application. Because palladium is about 30% cheaper than gold, this approach could reduce the gold via cost.

Using carbon nanotube and carbides as the conductive via materials can eliminate the gold on the metal bipolar plates. We have developed the processing technology to deposit carbon nanotube and carbide particles on metal plates. Figure 2 shows the microscopic pictures of carbon nanotube and chromium carbide on 304 stainless steel surface. Figure 3 shows the potentiostatic corrosion test of 304 stainless steel with carbon nanotubes on the surface in pH3 H2SO4 + 0.1 ppm HF solution under 0.8 V NHE at 80°C. The contact resistance of the stainless steel plates with carbon nanotube before and after 100 hours corrosion tests is below 10 mΩ.cm². The corrosion test of stainless steel with chromium carbides on the surface shows the similar performance that indicates these metal plates have the potential to be used in PEM fuel cells.

Stainless steel substrate cost is the major cost item (accounting for 50-60%) in the metal bipolar plate, even using the commercially available lower cost 304 stainless steel foil. We plan to develop lower cost carbon steel or aluminum-based substrate material for PEM fuel cell applications. In the first year of the project, we have developed the processing technology to apply a corrosion-resistant, non-conductive coating material and gold or palladium conductive vias to prevent the substrate material corrosion while maintain the desired electrical conductance requirement.

Short stacks using TreadStone’s metal plates have been designed, and assembled for portable, stationary and automobile applications. The portable power stack has 30 cm² active area on each cell. The designated power is 200 W with open cathode for air cooling. The stationary stack has 263 cm² active area on each cell. The designated power is 1 kW with liquid cooling. The initial short stacks have been assembled, and their performance has been evaluated. The experiments are continuing to demonstrate the long-term stability of the stack using Treadstone’s metal bipolar plates.

A 10-cell, 2.5 kW short stack for automobile application has also been assembled and tested at Ford Motor Company. Figure 4 shows the picture of the stack in the testing station. The stack has 300 cm² active area on each cell, and operates under high pressure. The stack is being tested for durability (which includes the FTP cycle along with others) mimicking real-world
driving conditions. It has finished 800 hours of stable operation, and continues to operate.

Conclusions and Future Directions

Treadstone’s unique corrosion-resistant metal bipolar plates have demonstrated stable operation for PEM fuel cells in portable, stationary and automobile applications. The processes to use lower cost materials have been demonstrated to further reduce the metal plate cost to meet DOE 2015 targets. Further development will be focused on:

- Scale up the lower cost conductive vias processing technique for the large scale production.
- Demonstrate the low-cost carbon steel and aluminum plates based bipolar plates.
- Demonstrate the long-term operation stability of the TreadStone’s low-cost metal plates in PEM fuel cell applications.

References

V.L.3 Metallic Bipolar Plates with Composite Coatings

Objectives

Develop a fluoropolymer-inorganic filler composite coating that is electrically conductive and provides a physical barrier to corrosive species within the fuel cell.

- Apply the composite coating to aluminum alloy substrates using an established high-volume manufacturing process.
- Synthesize titanium diboride (TiB$_2$) and calcium hexaboride (CaB$_6$) powders using a low-cost process.
- Measure the H$_2$ permeation flux, corrosion resistance, and area specific resistance of the composite coated aluminum plates.
- Demonstrate the ability to make the surface of the coatings hydrophilic.
- Create a flow field design for a plate with an active area $>$50 cm$^2$, make stamping dies for the design, and demonstrate the ability to stamp aluminum sheets.

Technical Barriers

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

(A) Durability

(B) Cost

(D) Water Transport within the Stack

Technical Targets

The goal of this work is to develop an aluminum-based bipolar plate that meets all of the DOE technical targets for bipolar plates shown in Table 1 [1]. This goal will be met by applying a composite coating that is both electrically conductive and corrosion-resistant to the aluminum plate using an established high-volume manufacturing process.

TABLE 1. Project Progress toward Meeting DOE Technical Targets for Bipolar Plates [1]

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2015 Target</th>
<th>Project 2010 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>$/kW</td>
<td>3</td>
<td>TBD</td>
</tr>
<tr>
<td>Weight</td>
<td>kg/kW</td>
<td>&lt;0.4</td>
<td>TBD</td>
</tr>
<tr>
<td>H$_2$ Permeation Flux</td>
<td>cm$^3$ sec$^{-1}$ cm$^{-2}$ @ 80°C, 3 atm</td>
<td>$&lt;2 \times 10^6$</td>
<td>$&lt;2 \times 10^6$</td>
</tr>
<tr>
<td>Corrosion</td>
<td>µA/cm$^2$</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>S/cm</td>
<td>&gt;100</td>
<td>33</td>
</tr>
<tr>
<td>Resistivity</td>
<td>Ohm-cm</td>
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<td>0.03</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>MPa</td>
<td>&gt;25</td>
<td>TBD</td>
</tr>
<tr>
<td>Flexibility</td>
<td>% deflection at midspan</td>
<td>3 to 5</td>
<td>TBD</td>
</tr>
</tbody>
</table>

TBD: To be determined

Accomplishments

- TiB$_2$ and CaB$_6$ powders have been synthesized using a low-cost process that is scalable. An invention disclosure is being filed for the CaB$_6$ synthesis procedure.
- High aspect ratio metal boride powder synthesis has been demonstrated.
- The stability of TiB$_2$ and CaB$_6$ has been tested at 80°C in sulfuric acid solutions.
- Composite coatings have been applied to aluminum substrates using electrostatic spraying and wet spraying; both are high volume manufacturing processes.
- Corrosion resistance that exceeds the DOE targets has been measured for composite-coated aluminum plates under both anodic and cathodic conditions for 24 hours.
- Hydrophilic coating surface properties were achieved using a simple two-step process.
• A flow field design and the corresponding stamping dies were created and used to stamp 75 pieces of aluminum alloy.
• The H₂ permeation flux of the stamped aluminum plates was measured under the conditions specified in the DOE target and no hydrogen permeation was detected.
• Baseline single cell tests were performed on the uncoated, stamped aluminum bipolar plates for 300 hours.

Introduction

Aluminum bipolar plates offer a potential weight reduction of up to 65% over stainless steel, while still having the desired mechanical properties that a metal offers. Furthermore, untreated aluminum can meet all of the DOE bipolar plate targets except for corrosion resistance. To overcome this one weakness, we have been applying a composite coating consisting of a matrix of an acid-resistant fluoropolymer and a filler material that is electrically conductive and acid-resistant. Metal borides and carbon-based materials, such as graphite, carbon black, and carbon fibers, were identified as candidate filler materials. Composite-coated aluminum bipolar plates can be fabricated using techniques, such as stamping, welding, and spraying, that are currently used for high-volume manufacturing of many consumer goods. In the first year of the project, we have focused on the H₂ permeation, corrosion, and electrical properties targets.

Approach

In order to meet the cost target using metal boride filler materials, it was necessary to develop a low-cost metal boride synthesis process. Furthermore, the use of high aspect ratio filler powders would allow for a reduction in the volume fraction of the filler (for lower costs), so synthesis procedures to obtain such filler powders were also developed. We have worked on identifying the combination of fluoropolymer and filler that will provide the desired electrical conductivity in a composite coating. We have made free-standing composite films and sprayed fluoropolymer (ethylene-tetrafluoroethylene, ETFE or polychlorotrifluoroethylene, PCTFE) mixed with either graphite or carbon fibers onto non-conductive substrates, and we have measured the surface conductivity/resistivity of these samples. We have varied the type of graphite, the type of fluoropolymer, and the ratio of filler to fluoropolymer in an effort to increase the electrical conductivity of the coatings. Other subtasks include corrosion testing of coated aluminum panels, flow field design and stamping of aluminum plates, and hydrogen permeation measurements. We have also developed a treatment procedure for making the coating surface hydrophilic to ease water transport within the stack.

Results

Of the metal borides, TiB₂ and CaB₆ were chosen because they have the desired combination of reported electrical conductivity [2], density, and corrosion resistance [3]. Low-cost processes were developed and used to synthesize TiB₂ [4] and CaB₆. Inexpensive Ti, Ca, and B precursors were used in the 3-step synthesis procedures, which used processing temperatures of up to 1,600°C. Powder X-ray diffraction (XRD) results showed only the desired metal boride product and, in the case of TiB₂, a small amount of excess carbon. Analysis by transmission electron microscopy (TEM) showed that particle sizes were, on average, sub-micrometer in diameter, Figure 1a. By adding a small amount of a seed element, elongated grains could be grown, Figure 1b.

It is reported that the environment inside a proton exchange membrane (PEM) fuel cell is acidic due to the presence of the Nafion® membrane and Nafion® ionomer in the electrodes combined with the humidity [5]. Acid stability tests were conducted on commercially purchased and SIUC-synthesized TiB₂ and CaB₆ at 80°C under 3.5% H₂ in helium with reflux. Two sulfuric acid solutions were used in the tests: 1) 0.5 M H₂SO₄ (pH=1) with 2 ppm NaF and 2) 0.001 M H₂SO₄ (pH=5) with 0.1 ppm NaF. The results of the tests are shown in Table 2. The values shown in the “% Sample Remaining” column were calculated from the measured change in weight of the samples. Neither of the borides was found to be completely resistant to the acid, but CaB₆ performed better than TiB₂.

Electrochemical corrosion experiments were also conducted on the CaB₆ and TiB₂ powders to corroborate the findings of the acid stability tests. Powders of TiB₂ (Cerac, -200 mesh) and CaB₆ (Alfa Aesar, -325 mesh) were ball-milled in ethanol and then mixed with Nafion®. A thin film of the mixture was applied to a rotating disk electrode and electrochemically tested in both O₂-saturated and O₂-free (i.e., Ar purged) 0.1 M H₂SO₄. Potential holds at several potentials and potential scans that are relevant to the bipolar plate application were run. The measured corrosion currents were higher than the DOE target of 1 x 10⁻⁶ A/cm², indicating that both CaB₆ and TiB₂ would not be stable in the PEM fuel cell environment.

Surface electrical conductivity/resistivity measurements of free-standing composite samples were measured using a four-point probe (Jandel) driven by a potentiostat. The free-standing samples were made by mixing the appropriate amounts of PCTFE and the
desired filler powders, and then uniaxially pressing them at 235°C to sinter the fluoropolymer and form a solid disk. Selected conductivity results are shown in Table 3 for samples that had 60 vol% electrically conductive filler with 40 vol% PCTFE. The measured electrical conductivities of the composites were significantly lower than the published bulk conductivities of the fillers. This is likely due to contact resistance between the filler particles. Furthermore, the PCFTE may act to separate the filler particles as it flows between the particles during sintering. Also, in the case of CaB₆, it is suspected that the published bulk value is erroneously high [6,7].

Based on the results in Table 3 and the acid stability tests showing that the borides are unstable, we proceeded to investigate composite coatings that had graphite-based fillers. Slurries were made by ball milling the desired amounts of graphite and fluoropolymer with solvents. They were then sprayed onto a non-conductive ceramic substrates and the resistivity/conductivity was measured using the 4-point probe. A composition that was 40% flake graphite, 20% spheroidized graphite, and 40% EFTE was found to have the best resistivity of 0.03 Ω·cm.

Having a hydrophilic surface on the bipolar plate aids with water management in the electrodes, so we have invented a method for changing the PCFTE surface from hydrophobic to hydrophilic by applying two solutions, sequentially, and heating the film up to 135-150°C for 5 minutes after each application. This method was demonstrated on a 60% graphite-filled PCTFE film, as shown in Figure 2, and on similar coatings that were sprayed onto aluminum. Contact angle measurements made using a First Ten Ångstroms system yielded contact angles of 108° for the untreated sample (Figure 2, left) and 65° for the treated sample (Figure 2, right).

---

**TABLE 2. Results of the Sulfuric Acid Stability Experiments at 80°C in 3.5% Hydrogen**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Time (days)</th>
<th>% Sample Remaining</th>
<th>Extra Phases in XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB₂ (Cerac, -200 mesh)</td>
<td>1</td>
<td>8</td>
<td>&lt;1</td>
<td>n.a.</td>
</tr>
<tr>
<td>TiB₂ (Cerac, -200 mesh)</td>
<td>3</td>
<td>20</td>
<td>77</td>
<td>TiO₂</td>
</tr>
<tr>
<td>TiB₂ (SIU)</td>
<td>3</td>
<td>27</td>
<td>95</td>
<td>TiO₂, H₂BO₃, TiOSO₄</td>
</tr>
<tr>
<td>CaB₆ (Alfa Aesar, -325 mesh)</td>
<td>1</td>
<td>8</td>
<td>131</td>
<td>H₂BO₃</td>
</tr>
<tr>
<td>CaB₆ (Aldrich, -200 mesh)</td>
<td>3</td>
<td>15</td>
<td>67</td>
<td>none</td>
</tr>
<tr>
<td>CaB₆ (SIU)</td>
<td>3</td>
<td>31</td>
<td>92</td>
<td>none</td>
</tr>
</tbody>
</table>

n.a. = not analyzed

**TABLE 3. Selected Results of 4-Point Electrical Conductivity Measurements on Free-Standing Composite Samples (60 vol% filler/40 vol% PCTFE)**

<table>
<thead>
<tr>
<th>Filler</th>
<th>Published Bulk Conductivity (S/cm)</th>
<th>Measured Conductivity of Composite (S/cm)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Black</td>
<td>0.1-100 [8]</td>
<td>5.0 (± 0.2)</td>
<td>Cabot</td>
</tr>
<tr>
<td>Graphite (spheroidized)</td>
<td>333-2,000 [9]</td>
<td>4.4 (± 1.0)</td>
<td>Superior Graphite</td>
</tr>
<tr>
<td>Graphite (flake)</td>
<td>333-2,000 [9]</td>
<td>26.3 (± 1.9)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>CaB₆</td>
<td>4,500 [2]</td>
<td>0.57 (± 0.15)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>TiB₂</td>
<td>111,000 [2]</td>
<td>11.2 (± 1.6)</td>
<td>Cerac</td>
</tr>
</tbody>
</table>
Corrosion resistance measurements of coated aluminum samples using electrochemical methods [10] were conducted to evaluate the ability of the coatings to provide a physical barrier between the aluminum substrate and the corrosive media in a fuel cell. In these experiments, the electrolyte was 0.001 M sulfuric acid (pH=3) with 0.1 ppm NaF. For cathodic corrosion tests, air was bubbled continuously through the acid solution and 0.6 V vs. Ag/AgCl (or 0.8 V vs. normal hydrogen electrode, NHE) was applied for 24 hours. For anodic corrosion tests, argon was continuously bubbled through the acid solution and -0.4 V vs. Ag/AgCl (or -0.2 V vs. NHE) was applied for 24 hours. The results for aluminum plates with a coating of 20 vol% carbon fiber/80 vol% EFTE applied by electrostatic spraying at Orion Industries are shown in Figure 3. The current densities fall below the DOE corrosion target, showing that the coatings provide a stable barrier.

A total of 75 uncoated aluminum bipolar plates with flow fields have been stamped with a 60 cm² active area. The design is based on a GTI patented trapezoid flow field structure for PEM fuel cells with very low pressure drop. The hydrogen permeability of the formed plates was tested and there was no hydrogen pass-through detected at 50 psig (3.4 atm), meeting the DOE target. In addition, the bipolar plate design was proven during fuel cell testing which demonstrated that the stacks can be well sealed against fuel, oxidant, and cooling water leaks. During fuel cell lifetime testing using the bare, uncoated aluminum bipolar plates, it was found that the use of aluminum leads to high electrical resistance, which increases with time. These baseline data will be used for comparison against the coated aluminum plates.

Conclusions and Future Directions

- TiB₂ and CaB₆ are not sufficiently acid resistant for use in PEM fuel cell stacks.
- Composites made with flake graphite as the filler have the highest electrical conductivities.

Special Recognitions & Awards/Patents Issued


References


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

(A) Durability

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>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2010 Status</th>
<th>2010 / 2011*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durability</td>
<td>hours</td>
<td>&gt;10,000 hours achieved\superscript a</td>
<td>5,000/40,000</td>
</tr>
<tr>
<td>Sealability at Low Temperature</td>
<td>°C</td>
<td>Meets DOE Targets</td>
<td>-40/-35</td>
</tr>
<tr>
<td>Cost\superscript c</td>
<td>$/kW\text{net}</td>
<td>To be evaluated</td>
<td>(2.00–3.77)\superscript d</td>
</tr>
</tbody>
</table>

\* DOE Transportation/Stationary targets.
\*\* Real-time out-of-cell testing at 90°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 Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan. See footnote (d) below for an explanation of how this target was derived.

\*\*\* Suggested cost target range for transportation applications derived from Reference 1 ($3.77/kW), Reference 2 ($2.10/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 $5.87/kW.

Accomplishments

- Completed more than 10,000 hours of compressive stress relaxation (CSR) testing at 90°C.
- Completed more than 4,500 hours of CSR testing at 120°C.
- Completed more than 10,000 hours of aging in air at 120°C.
- Developed materials that meet all minimum beginning of life (BOL) targets and most desired project goals.
- Developed additional candidate with greater measured BOL tear and tensile strength.
- Developed materials shown to be more stable than one tested silicone and a few tested ethylene propylene diene monomers (EPDMs).
- Accumulated 1,700 hours of in-cell testing.

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 (rubbers that are solid or semi-solid prior to curing) 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**

The work over the last year has been focused on four tasks:
- Material Development
- The Completion of Out-Of-Cell Testing
- Molding of Prototype Components for In-Cell Testing
- In-Cell Validation Testing

Additional experimental material development was carried out over the last year. The work has yielded FCS3, the final material candidate to be developed as a part of the project. It is a one-part material with the same cure characteristics and thermal stability as FCS2, but with increased strength, modulus, and elongation.

This brings the total of material candidates introduced to four. In Table 2, some key properties of the four are compared to each other and to the materials specification. All four meet the minimum requirements in the material specification with one exception. The viscosity of FCS3 is higher than originally desired. However, initial molding trials indicate that the higher viscosity should be acceptable. While seal components suitable for use in PEMFC applications could be produced from any of the four, the higher strength and elongation of FCS3 broadens the range of design options available.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Project Requirements</th>
<th>FCS0</th>
<th>FCS1</th>
<th>FCS2</th>
<th>FCS3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIM processable</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Viscosity @ room temperature (cPs)</td>
<td>&lt;= 700,000</td>
<td>&lt;= 600,000</td>
<td>~ 500,000</td>
<td>~ 543,000</td>
<td>~ 543,000</td>
</tr>
<tr>
<td>Mold temperature (°C)</td>
<td>&lt; 135</td>
<td>&lt;= 110</td>
<td>120 to 130</td>
<td>120 to 130</td>
<td>120 to 130</td>
</tr>
<tr>
<td>Mold time (second)</td>
<td>&lt;= 40</td>
<td>&lt;= 60</td>
<td>60 to 120*</td>
<td>60 to 120*</td>
<td>60 to 120*</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>15 to 68</td>
<td>30 to 55</td>
<td>31</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>100% Modulus (Mpa)</td>
<td>0.25 to 3.5</td>
<td>1 to 2.5</td>
<td>0.75</td>
<td>0.68</td>
<td>0.69</td>
</tr>
<tr>
<td>Tensile strength (Mpa)</td>
<td>&gt;&gt; 0.5</td>
<td>&gt;&gt; 0.8</td>
<td>1.3</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>&gt; 125</td>
<td>&gt; 150</td>
<td>15%</td>
<td>11%</td>
<td>150</td>
</tr>
<tr>
<td>Tear strength Die C (kJ/m)</td>
<td>&gt;&gt; 2.7</td>
<td>&gt;&gt; 5.0</td>
<td>3.7</td>
<td>3.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Temperature resistance (°C)</td>
<td>-40 to 85</td>
<td>-40 to 90</td>
<td>-40 to 90</td>
<td>-40 to 90</td>
<td>-40 to 120</td>
</tr>
</tbody>
</table>

Notes:
- *cure schedule: 120 second in the mold @ 120°C and then 1 hour post cure @ 130°C
- Green: Meets minimum & ultimate goal
- Lt Green: Meets minimum goal
- Yellow: Does not meet project goal, but may be acceptable
- Red: Does not meet project goal
A variety of out-of-cell tests were used in the evaluation of the materials developed for this project such as mass uptake, environmental aging and stress relaxation. The aim was to evaluate the beginning of life properties and to evaluate how those properties changed with time when subjected to combinations of temperatures and chemical environments typical of PEMFC operation.

One of the most important measures for determining the durability of seals is CSR. This is a measure of decay in sealing force with time. During the past year, over 9,000 hours of CSR testing at 90°C in air was completed on FCS2 using a sub-scale molded O-ring seal (SMORS) – a seal over-molded around the perimeter of a porous substrate. The result is summarized in Figure 1. The result agrees with results achieved previously when testing FCS0 CSR plugs in 90°C air, dionized water, and a 50/50 etylene glycol/water solution for 10,000 hours. The key result is that after 9,000 hours, less than 20% load decay was measured. This result is important. Significantly greater values are typically seen in silicones and even some EPDM materials after less than half this time. While these higher values can typically be accounted for in the design of sealing systems, lower values translate directly into increased durability and greater design flexibility.

As mentioned above, CSR testing had previously been conducted on the FCS0 material. This testing used the test specimen configuration specified in ASTM D 6147 Section 7.1.1. Because this geometry is very different than that used to produce a functional fuel cell seal, the CSR testing was repeated with SMORS in all the environments tested previously and also in a 0.1 M H₂SO₄ solution. Testing was completed this year and results are shown in Figure 2. In this case, after more than 4,000 hours, load decay for three aqueous test environments was approximately 20%. It should also be noted that the behavior in the three environments is substantially the same. This indicates, for instance, that the material is resistant to a sulfuric acid solution having a pH of approximately 1.0. This in turn suggests that the material could be directly over-molded onto poly(fluorosulfonic acid) membranes.

It is important to recall that the materials developed on this project are hydrocarbon-based elastomers. Given this fact, it is expected that one of the most significant threats to the stability of the candidate materials is oxidation. To evaluate this threat, a comparison of the oxidative stability to some other materials which have been considered for PEMFC applications was carried out. A key result of this work is provided in Figure 3. In this figure, relative change in mass with time is tracked for testing at 120°C. The inlaid figure provides results for 150°C testing completed previously. In this figure, the candidate material is being compared to three EPDM-based materials. Significant changes in the 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.

In addition to out-of-cell testing, two types of prototype seals were molded this year. The first was a seal over-molded onto a plastic sub-gasket. This seal was used for in-cell validation testing, and 1,700 operating hours were accumulated. Post-test evaluation remains to be completed. The second full-size prototype seal produced was of an integrated molded seal configuration. The purpose of this molding activity was to test the effect of different parameters and materials, such as gas diffusion media type, on mold-flow when producing parts with the integrated molded seal configuration. Learning from this activity was used to form the development of a final full-size prototype component.
Conclusions and Future Directions

Based on the work performed to date for the project, the following can be concluded:

- The material development strategy (synthesis and compounding) is sound.
- Based on all testing completed, the materials developed have a high probability of success for meeting the 2010 DOE goals for use in automotive PEMFC applications and are likely to meet the needs of longer lifetime applications as well.
- Activities for the remainder of the project will include the following:
  - Evaluation of a high volume capable injection molding technique for over-molding seals around the perimeter of full-size MEAs.
  - Additional full-size in-cell testing to further validate out-of-cell test results.
  - Complete evaluation of material and processing costs to assess likelihood of meeting suggested cost target at high volume.

References

Objectives

- Advance the state-of-the-art in technology for air-cooled proton exchange membrane (PEM) fuel cell stacks and related GenDrive™ material handling application fuel cell systems.
- Demonstrate FCvelocity™ 1020ACS stack durability of 5,000 hours (2.5x nominal durability) through enhanced system operational strategies or utilization of advanced fuel cell stack materials.
- Determine a stack/system concept that is suitable for sub-zero operation down to -30°C.
- Determine a stack/system concept that achieves a total cost that is competitive with incumbent materials handling fuel cell technology solutions.
- Develop, evaluate and trade-off the stack and system to meet materials handling requirements for freeze and cost.
- Develop an understanding around integrating air-cooled stack technology into a dynamic materials handling system.
- Perform life-cycle cost analyses for freeze tolerance strategies.

Technical Barriers

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

(A) Durability (with respect to start-up, freezing and low relative humidity operation)
(B) Cost (with respect to stack and balance-of-plant [BOP] trade-off)
(C) Performance (with respect to voltage degradation, low relative humidity and sub-zero performance)

Technical Targets

- Stack/system concept that is suitable for sub-zero operation down to -30°C.
- Durability for an air-cooled fuel cell stack ≥5,000 hours operating under material handling conditions including start-stop cycles.
- GenDrive™ product cost reduction of 25% or greater using air-cooled stack design over baseline liquid-cooled GenDrive™ product.

Accomplishments

- Through detailed stack failure analysis the key stack failure modes were identified to be platinum loss and platinum crystal growth during start-stop and membrane leak induced cathode carbon corrosion. In extreme freeze events cathode catalyst fragmentation was also seen. Materials and operating strategies were selected to mitigate these failures.
- Advanced system operating strategies for the Mk1020 air-cooled stack have demonstrated 5,000 hours of operation to date (2.5 times initial durability), testing is still ongoing. These operating strategies focus on reducing cathode catalyst dissolution and corrosion and chemical and mechanical stress on the membrane.
- Advanced Mk1020 air-cooled stack membrane electrode assembly (MEA) concepts have demonstrated an improvement in both operating hours and start-stop cycles; 2,500 start-stops have been achieved and testing is on going. Advanced MEAs contain a membrane of lower ionic resistance and higher chemical stability as well as a better dissolution-resistant cathode catalyst.
- Stack-system modeling has been used to guide balance-of-plant design to achieve freeze targets. Validation of model output is ongoing.
Although over 100 freeze-starts were demonstrated on the FCvelocity™ 1020ACS stack the variability in performance start-to-start was high and would still contribute to the dominant degradation mode of platinum dissolutions and agglomeration. To achieve the performance and durability targets for materials handling the system will be designed to provide the stack with optimal conditions where possible (within realistic BOP cost restrictions).

Introduction

To be competitive with incumbent materials handling technologies there is a need to reduce the overall cost of the materials handling stack/system. The fuel cell stack incumbent technology is the liquid-cooled GenDrive™ system. The air-cooled stack offers a chance to reduce the cost of the system by eliminating the need for a humidifier and coolant loop. In order to be a viable option for materials handling applications the air-cooled stack must also demonstrate increased durability and freeze function.

Plug Power’s objective is to advance the state of the art in technology for air-cooled fuel cell stacks and related GenDrive™ material handling application fuel cell systems. This will be accomplished through a collaborative work plan to improve freeze tolerance and mitigate freeze-thaw effect failure modes within innovative material handling equipment fuel cell systems designed for use in freezer forklift applications.

The fuel cell system, derived from Plug Power’s commercially available GenDrive™ platforms, is providing battery replacement for equipment in the material handling industry. The fuel cell stacks are Ballard’s commercially available FCvelocity™ 9SSL (9SSL) liquid-cooled PEM fuel cell stack and FCvelocity™ 1020ACS air-cooled PEM fuel cell stack. Stack modifications to the FCvelocity™ 1020ACS will be explored. Plug Power will lead design-build-test and design-of-experiment efforts for GenDrive™ systems with support from Ballard Power Systems for the fuel cell stack and stack integration.

Approach

In this project the fuel cell stack, system and fuel cell stack operation will be designed together in order to trade off stack durability and freeze function with overall stack/system cost. Both stack and system level mitigation of freeze failure modes will be explored.

The project will develop an understanding of market needs, system requirements, stack-system limitations, historical data, models and small-scale testing to define stack/system operating strategies that achieve required freeze function and durability.

Multiple design, build, test cycles will be employed to increase learning through each iteration. Stacks and systems will be operated to failure under material handling freezer conditions, failure analysis will be performed to understand the root cause, stacks and systems will be designed to mitigate the failure modes, then built and tested, and trade-off analysis will be used to determine the design solutions that are built and tested.

Results

The Mk1020 air-cooled stack must first demonstrate performance and durability targets to be considered a viable GenDrive™ product solution. Specifically, the Mk1020 must demonstrate 5,000 hours running a representative load profile including start-stop cycles. The Mk1020 stack offers system simplicity by eliminating the liquid cooling system; this is achieved through an “open cathode” design where cooling and reactants are supplied by a single fan. As a result the MEA operates very dry, all start-ups are air-air start-ups and, under freeze conditions, the cooling power of the air stream is high making low current density operation difficult. All of these conditions increase the stack degradation and make freeze function a challenge.

The failure modes of the baseline Mk1020 stack were identified by running a stack through the standard Mk1020 ACS duty cycle and removing MEAs every 250 cycles for degradation analysis. The dominant voltage degradation modes were identified as catalyst dissolution, followed by membrane transfers (internal leaks). Results show that at the onset of internal membrane leaks the catalyst failure mechanism begins to include corrosion as well as dissolution as seen by a catalyst layer thickness reduction once the stacks begins to leak; this is thought to be due to air leaking to the anode during operation and on shutdown. Wet-dry cycling as well as operating at high potentials accelerate the membrane degradation, see Figure 1. To improve the durability by way of design changes, a more dissolution resistant cathode catalyst and leak-resistant membrane were explored.

In this report advanced stack concepts are represented by the following code: Ax Mx Cx, where A represents the anode, M represents the membrane and C represents the cathode. The baseline MEA is A1 M1 C1.

Advanced MEA concept durability is shown in Figure 2. The durability of the membrane, as seen by leak rate, has been significantly improved from the baseline (M1), both M2 and M3 have longer times to leak initiation. The voltage degradation rate is improved with the advanced catalyst design C3. The stack concept that provides a low degradation rate will be considered as the primary candidate.
Failure analysis of advanced concepts shows improvements can be made to the failure propagation of the catalyst and membrane. Results indicate lower crystallite growth, lower cathode catalyst thickness loss, and lower platinum dissolution. It was also noted that more durable membranes (M2 and M3) can lower...
the impact of cathode catalyst corrosion compared to the baseline. This further supports the link between localized transfers in the membrane and catalyst corrosion.

Based on the baseline stack durability testing and failure analysis the system can impact stack durability by controlling stack-critical parameters for performance and durability, including: stack temperature, relative humidity cycles, time at open circuit voltage, cathode potential, cathode potential cycles and mixed anode potentials.

System strategies designed to mitigate the known stressors and improve stack life were evaluated via screening tests and the best strategies were downselected for long-term durability testing. Each system strategy was designed to control one or more of the above critical parameters. Figure 3 illustrates cell voltage degradation as a function of hours for the baseline system and two advanced operating strategies.

Air-cooled stack durability and start-stop cycles have been improved over the original design air-cooled stack when operating under material handling conditions via successful implementation of operating system architecture strategies. Stack life has been demonstrated at 2.5 times the original design; going from 2,500 hours to 6,300 hours. Air-Air starts have been improved by 1.6 times the original design; going from 1,000 to 1,600.

Performance test results for the baseline Mk1020 stack indicate a lower performing polarization curve at the extreme temperatures, 40°C and -10°C. This was a result of fan turn-down limitations resulting in non-optimal stack temperatures during the polarization. Stacks that run above the optimum temperature tend to experience drier conditions, while stacks that run below optimum temperature tend to run wetter; both situations can lead to performance loss. Although the freeze-start capability of the baseline ACS stack was variable from test to test, over 100 freeze-start cycles were completed. The end cells of the stack were particularly sensitive, failure analysis of the most sensitive cells showed typical freeze failure damage; i.e. catalyst cracking and fragmentation.

Based on previous Ballard design work, a MEA/stack solution for freeze and durability can significantly increase the cost of the stack. Therefore, the primary approach is to explore system options and operating strategies in order to manage a sub-zero environment with extended durability.

A stack thermal computational fluid dynamics model that combines fluid flow and heat transfer in a single air channel was developed to explore several stack-system related freeze function strategies related to increasing the rate of stack heating. The baseline operating strategy, heater use, fan turn-down and cathode recirculation were explored to determine the
Failure analysis will be performed on stacks and systems to understand the freeze failure modes.

Freeze prevention and mitigation design step following failure analysis and the best solution(s) will be down-selected using trade-off analysis.

A product life cycle cost analysis will be used to evaluate the commercial viability of using an air-cooled fuel cell stack versus a liquid-cooled stack. The key parameters for the product life cycle cost analysis are the capital, maintenance, and operational costs. A GenDrive product with an air-cooled fuel cell stack must demonstrate a 25% lower capital cost and life cycle cost when compared to the 2009 end-of-year GenDrive with a liquid-cooled fuel cell stack.

A Go/No-Go project decision review will be held with the DOE to evaluate the metric of a 25% GenDrive™ product cost reduction using an air-cooled fuel cell stack versus a liquid-cooled fuel cell stack.

Air-cooled fuel cell stacks and systems will be built with freeze mitigation design strategies and re-tested to evaluate the improvements under material handling freezer conditions.

**Conclusions and Future Directions**

- Both stack and system test data are tracking to show advanced MEA concepts and/or advanced system strategies can achieve the requisite stack-system durability.
- The baseline freeze function of the stack is not sufficient to meet the materials handling requirements. Stack-system solutions are being explored.
- Stack/system testing under material handling freezer application conditions has not been completed and is needed to understand the commercial viability of the air-cooled stack.
- Models have been developed for stack and system operation in freezer conditions and used as input for the concept air-cooled fuel cell system architecture.
- Concept air-cooled fuel cell systems will be built and tested under material handling freezer conditions.

**TABLE 1.** Results of Thermal Modeling of Stack with Inlet Air of 20°C, -10°C and -30°C

<table>
<thead>
<tr>
<th>Units</th>
<th>Nominal Conditions</th>
<th>-30°C Ambient Conditions + Heater</th>
<th>Target Ambient Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode/Air Inlet Temperature</td>
<td>C</td>
<td>20</td>
<td>-10</td>
</tr>
<tr>
<td>Cooling Flow Rate Required for Optimum Temp at 7.8 A</td>
<td>slpm</td>
<td>319</td>
<td>129</td>
</tr>
<tr>
<td>Cooling Flow Rate Required for Optimum Temp at 51.7 A</td>
<td>slpm</td>
<td>1,968</td>
<td>1,007</td>
</tr>
<tr>
<td>Fan Turn Down Ratio[1]</td>
<td>-</td>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>Heat Required to Heat Air from -30°C to Required Inlet Temp</td>
<td>W</td>
<td>345</td>
<td>52</td>
</tr>
</tbody>
</table>

[1] Calculated from 51.7 A flow at 20°C to 7.8 A flow at required inlet temperature

In all cases explored the goal was to reach optimum temperature, to minimize the performance de-rate, as quickly as possible. Table 1 summarizes some of the results, validation of these results will happen at the system level.
V.M.2 Fuel Cell Fundamentals at Low and Subzero Temperatures

**Objectives**

- Fundamentally understand transport phenomena and water and thermal management at low and subzero temperatures.
- Examine water (liquid and ice) management with nano-structured thin-film (NSTF) catalyst layers.
- Enable operational and material optimization strategies to be developed to overcome observed performance bottlenecks.
- Characterize and measure critical transport properties for operation with liquid water.
- Elucidate the associated degradation mechanisms due to subzero operation and enable mitigation strategies to be developed.

**Technical Barriers**

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

- (C) Performance
- (A) Durability
- (D) Water Transport within the Stack
- (E) System Thermal and Water Management
- (G) Start-up and Shut-down Time and Energy/Transient Operation

**Technical Targets**

This project is conducting fundamental investigations into fuel cell operation at low and subzero temperatures. The knowledge gained will enable various metrics to be met or exceeded. These include those related to durability, performance, and cost. Specially,

- **Durability**
  - 5,000 hr (automotive) and 40,000 hr (stationary)
  - Thermal cycling ability with liquid water

- **Performance**
  - Unassisted start from -40°C
  - Cold-start to 50% power in 30 seconds and with 5 MJ or less energy
  - Efficiency of 65 and 55% for 25% and 100% rated power, respectively
  - Stack power density of 2 kW/kg
  - Precious group metal (PGM) loading of 0.2 g/kW
  - Cost: $15/kWₑ

**Accomplishments**

- Project initiated.
- Completed the water movement during shutdown mathematical model including cell-position effects.
- Developed capabilities and experimental protocols for measuring capillary-pressure – saturation relationships for both gas diffusion layers (GDLs) and microporous layers (MPLs). Demonstrated that this relationship is critical and can be used to explain water transport throughout the material. Also designed a test fixture for measuring water distributions using X-ray tomography.
- Used dynamic scanning calorimetry to measure freeze kinetics and thermodynamics inside GDLs.
- Preliminary baseline cell studies finished including isothermal starts.

**Introduction**

Polymer electrolyte fuel cells experience a range of different operating conditions. As part of that range, they are expected to be able to survive and start at low and subzero temperatures. Under these conditions, there is a large amount of liquid and perhaps frozen water due to the low vapor pressure of water. Thus, water and thermal management become critical to...
understanding and eventually optimizing operation at these conditions. Similarly, durability aspects due to freeze and low temperatures are somewhat unknown and need further study in order to identify mechanisms and mitigation strategies. In addition, it is known that thin-film catalyst layers such as NSTF developed by 3M have issues with large amounts of liquid water due to their thinness. These layers provide routes towards meeting the DOE cost targets due to their high catalytic activities. This project directly focuses on the above aspects with the goal that improved understanding will allow for the DOE targets to be met with regard to cold-start, survivability, performance and cost.

**Approach**

The overall approach is to use a synergistic combination of cell, stack, and component diagnostic studies with advanced mathematical modeling at various locations (national laboratories, industry, and academia). Figure 1 shows the approach of the project. As can be seen, ex situ diagnostics will be used to quantify transport properties and to delineate phenomena that are used in the modeling. The multiscale modeling will account for stack position through boundary conditions that are fed to a pseudo three-dimensional or one- plus two-dimensional cell model. This model will be used during shutdown to predict the water profile during the subsequent cold-start. The model will be validated by comparison of measured in situ cell performance in both stacks and single cells. Durability will be probed by doing cycling and other stress tests as well as taking failed cells from the in situ testing and duplicating their failure ex situ. To understand controlling phenomena and the impact of various layers, a systematic investigation at the component scale will be accomplished. After initial baseline cell assemblies have been tested and explored, various components will be switched to understand the impact of each one on both performance and durability.

**Results**

As fuel cells operate at low and subzero conditions, liquid water and water management become more important. Thus, there is a need to study properties of the porous fuel cell layers in the presence of liquid water. This year, the focus was on the development of such diagnostic measurements. It is believed that one the key measurements for diffusion media is the capillary pressure – saturation relationship. We have developed an experimental methodology to measure such curves [1]. The results are shown in Figure 2 for both a standard SGL Group (SGL) GDL and a MPL. The MPL curve was obtained using a special layer provided by SGL in which a GDL was fully impregnated with an MP (as shown in the micrograph). The relationships clearly show that the MPL has a more hydrophobic signature, due both to its smaller pores and higher poly-tetrafluoroethylene (PTFE) weight fraction. What is interesting is that the MPL still exhibits the same intermediate wettability, where water is neither spontaneously imbibed or drained. These curves are now being used in modeling studies and going forward we aim to use this methodology to understand water distributions and the functioning of the MPL during operation [2].

Other diagnostics are aimed at determining what happens when water freezes in the various fuel cell layers. Figure 3 demonstrates measurements done with various GDLs using dynamic scanning calorimetry. For all GDLs, the crystallization temperature decreases as the PTFE content increases. Note that the SGL 24 and Toray (SGL) series GDLs follow a similar line, whereas water in the Toray (Fuel Cell Energy, FCE) GDL freezes at a higher temperature. One possible explanation is that the SGL 24 and Toray (SGL deposition) series GDLs have the same method of PTFE deposition, whereas the Toray (FCE) has a different method of PTFE deposition. This observation suggests that the method of PTFE deposition influences the crystallization...
temperature. We hypothesize that addition of PTFE to the porous network changes the average internal ice/substrate wettability (i.e., contact angle), as well as the attainable level of water saturation, causing the decrease in crystallization temperature.

A plot of crystallization temperature and saturation versus PTFE content is shown for the Toray (FCE) series in Figure 3(b). For PTFE contents between 0 and 40 wt%, crystallization temperature decreases slightly with the addition of PTFE. Above 40 wt% PTFE, the crystallization temperature decreases more steeply. Between 0 and 40 wt% PTFE, water saturation remains relatively constant (within experimental error). However, those GDLs containing 50 and 60 wt% PTFE become increasingly difficult to saturate with water due to the need for increased capillary pressure. Consequently, saturation decreases abruptly. This suggests that at low enough fractions of PTFE, the saturation is constant and the average internal ice/substrate surface energy changes, while at larger fractions of PTFE, the attainable level of saturation also contributes to the decrease in crystallization temperature.

Ice formation in traditional catalyst layers was probed using a technique in which cyclic voltammetry is done under subzero conditions after isothermal starts reach zero volts. At very low temperature and current densities, the produced ice freezes immediately upon production, and this can be used to obtain a relationship
as shown in the line in Figure 4. Then, the charge passed during isothermal starts can be plotted as shown in Figure 4. The figure shows the amount of the water produced that is in the ice phase versus liquid water. Thus, as the temperature is increased or the current density lowered, more product water can move away from the reaction site and does not freeze between the ionomer and catalyst particle. Knowing the amount of water in each phase will enable operation of the NSTF while meeting the DOE targets for survivability and cold start.

Conclusions and Future Directions

This project was initiated this year. Initial results are promising in guiding future directions and most of the year was spent on doing necessary diagnostic measurements and model development. The shutdown model clearly shows the redistribution of the water that occurs during long times and this can affect cell startup. Several novel experimental diagnostics for catalyst-layer ice, GDL freeze, and GDL liquid-related properties were developed and allow for better understanding of operation at low and subzero temperatures. In terms of future work, this can be summarized as:

- Cell performance:
  - Further testing of baseline and non-baseline assemblies.
  - Isothermal and adiabatic starts including cycling studies for tracking durability.

- Component characterization:
  - Consolidate/measure membrane properties at subzero conditions.
  - Diffusion media:
    - Neutron imaging of shutdown and water redistribution.
    - Capillary pressure – saturation relationships:
      - Impact of flowrate, temperature, injection sites (MPL analogs), materials
      - X-ray tomography for the water distribution
    - Measure effective gas diffusion coefficient and relative permeability versus saturation.
    - Measure and model freeze rate and ice-front propagation as a function of saturation.

- Modeling of shutdown, cold start, and isothermal start
- Stack studies for temperature distribution and performance characterization
- Understand and increase the operating window with thin-film catalyst layers

FY 2010 Publications/Presentations


References

Objectives

- Develop and validate a two-phase, three-dimensional transport model for simulating proton exchange membrane (PEM) fuel cell performance under a wide range of operating conditions.
- Apply the validated PEM fuel cell model to improve fundamental understanding of key phenomena involved and to identify performance-limiting processes and develop recommendations for improvements.

Technical Barriers

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

(C) Performance
(D) Water transport within the Stack

Technical Targets

Since the validated PEM fuel cell model developed in this project can be employed to improve and optimize the design and operation of PEM fuel cells, insights gained from applying the model will help meet the following technical targets:

- Performance: 650 W/L or 50% energy efficiency for automotive applications; 40% electrical energy efficiency for stationary applications.
- Cost: $30/kW for automotive applications and $750/kW for stationary applications.
- Durability: 5,000 hours for automotive and 40,000 hours for stationary applications.

Accomplishments

- Developed a single-phase, three-dimensional (3-D), single-cell model and made significant progress toward meeting the milestone of developing a 3-D, partially two-phase, single-cell PEM fuel cell model.
- Coupled the present PEM fuel cell model with DAKOTA (which is a toolkit for design, optimization, and uncertainty quantification developed by Sandia National Labs).
- Demonstrated the capabilities of the present PEM fuel cell model in case studies.
- Demonstrated utilities of the coupled PEM fuel cell model/DAKOTA capability in case studies.
- Implemented a sub-model for simulating cathode microporous layer (MPL) effect.
- Simulated performance of a PEM fuel cell with zigzag flowfield using the present model.
- Investigated water transport through cathode MPL-gas diffusion layer (GDL) using a pore-network model.
- Developed and demonstrated a sub-model for predicting membrane interfacial resistance.
- Measured pore size distributions of various GDLs with and without MPL.
- Obtained experimental polarization curves for different temperatures, relative humidity (RH), and cell segments.
- Measured axial and radial thermal conductivities of GDLs with various poly-tetrafluoroethylene contents.
- Measured liquid water profiles across GDL-MEA regions using neutron imaging for four different GDLs and two different relative humidities.
- Measured along-channel current and temperature profiles in a 12 kW PEM fuel cell stack.

Introduction

As PEM fuel cell technology matures and enters the stage of commercialization such that the industry strives
to achieve desired performance and durability and reduce costs, process design and optimization become increasingly important and indeed critical. Modeling and simulation can provide guidance in PEM fuel cell design and optimization and thus help accelerate the commercialization of PEM fuel cell technology. Despite tremendous research efforts and a large number of models published in the literature (see Chen et al. [1] and references therein), a comprehensive, multi-physics computer model suitable for practical use by PEM fuel cell engineers and designers, particularly in transportation and stationary applications, remains absent. This mainly is due to the many challenges involved in modeling the PEM fuel cell operation: multiple components and phases, multi-dimensionality, and complex physics with highly coupled transport phenomena and electrochemical reactions. The significantly disparate length scales in transport and the presence of liquid water within the PEM fuel cell when operating under practical current loads, relatively high inlet RH or moderate cell temperature, further add to the modeling challenges.

The objectives of this project are twofold: 1) to develop and validate a two-phase, three-dimensional transport model for simulating PEM fuel cell performance under a wide range of operating conditions; and 2) to apply the validated PEM fuel cell model to identify performance-limiting phenomena or processes and develop recommendations for improvements so as to accelerate the commercialization of fuel cell technology. To achieve these two objectives, a multi-institutional and interdisciplinary team with significant experience in modeling PEM fuel cells and in measuring model-input parameters and model-validation data has been assembled. This team is led by Sandia National Laboratories; and it includes two other national laboratories (Los Alamos National Laboratory and Lawrence Berkeley National Laboratory), a university (The Pennsylvania State University), and two PEM fuel cell manufacturers (Ford Motor Company and Ballard Power Systems). In addition to developing and validating a two-phase, 3-D PEM fuel cell model, we are also coupling the PEM fuel cell model with DAKOTA [2] (which is a toolkit for design, optimization, and uncertainty quantification developed by Sandia National Labs) in order to create a computational capability that can be employed for PEM fuel cell design and optimization. This report documents technical progress made in this project during the first nine months of Fiscal Year (FY) 2010.

Approach

Our approach is both computational and experimental. We first develop a two-phase, 3-D, transport model for simulating PEM fuel cell performance under a wide range of operating conditions by integrating the detailed component sub-models; FLUENT (a commercial computational fluid dynamics code) is employed as the basic computational platform. We then validate our PEM fuel cell model in a staged approach using experimental data available from the literature and those generated by team members. Lastly, we plan to apply the validated PEM fuel cell model to identify performance-limiting phenomena or processes and develop recommendations for improvements. As mentioned previously, we have assembled a team of leading experts in PEM fuel cell modeling as well as in physical, electrochemical and transport property characterization, and cell diagnostics via segmented cell measurements and neutron imaging — this means that our project team is highly qualified and in an excellent position to carry out the project.

Results

To illustrate the utility of the present PEM fuel cell model, polarization curves for three cell temperatures, RHs at the cathode inlet, cathode back-pressures, and cathode stoichiometric flow ratios, were computed in case studies. Due to space limitation, only the effect of cell temperature on cell voltage is shown here in Figure 1. A schematic of the PEM fuel cell used in these case studies and the geometrical parameters, material properties, and operating conditions are available elsewhere (see Chen et al. [1], Chen [3]). As shown in Figure 1, cell voltage increases with cell temperature. Figures 2a, 2b, and 2c display, respectively, computed 3-D contours of temperature, H2 concentration in anode flow channel, GDL and catalyst layer, and O2 concentration in cathode flow channel, GDL and catalyst layer, and O2.

![FIGURE 1. Effect of Cell Operating Temperature on Cell Voltage (RH\textsubscript{anode}=RH\textsubscript{cathode}=80%)](image)
concentration in cathode flow channel, GDL and catalyst layer. It should be noted that H₂ and air flow in a counter-flow fashion: H₂ flows from right to left whereas air from left to right in Figure 2.

To further illustrate its capability, the present PEM fuel cell model was employed to simulate the performance of a PEM fuel cell having a zigzag and trapezoid-cross-sectional flow field. Similar flow field design has already been adopted in practice [4]. Figure 3a shows the computed temperature contours. Figures 3b and 3c display the contours of H₂ and O₂ concentrations at the mid-plane of the anode and cathode catalyst layer, respectively. Though not shown due to space limitation, water content and current density distribution at the mid-plane of the membrane were also computed. In computed results shown in Figure 3, the cell was taken to operate at 200 kPa, 80°C, 1.0A/cm², 81% RH, 1.4 anode stoichiometry and 1.8 cathode stoichiometry. The simulated unit cell has an active area of 1.573 cm². The gas channels have a trapezoid cross-sectional area of 0.285 mm². The zigzag unit length and amplitude are 50 mm and 1.0 mm, respectively.

In addition to developing a baseline PEM fuel cell model, we've also implemented a sub-model of the MPL in order to investigate its effect on cell performance, particularly on water transport. It is known in industrial practices that MPL results in effective water management and improved cell performance. The present MPL sub-model is formulated based on the continuity of capillary pressure and water flux at the catalyst-layer (CL)/MPL and MPL/GDL interfaces. This allows the use of different realistic material parameters for different layers, thus automatically enabling the PEM fuel cell model to handle water transport across different porous layers. Figure 4 shows computed liquid-water saturation profile across the CL-MPL-GDL regions from a case study. Also plotted is liquid saturation for the case when MPL is absent. Clearly from Figure 4, MPL effectively reduces water saturation in the cathode MPL-GDL regions. It should be noted that in the present work, the MPL submodel was implemented in the cathode side only.

**Summary and Conclusions**

- A single-phase, 3-D, single-cell model for simulating PEM fuel cell performance was developed and the milestone of developing a 3-D, partially two-phase, single-cell PEM fuel cell model is expected to be met by the end of this FY.
- The present PEM fuel cell model was coupled with DAKOTA and this coupled computational

![FIGURE 2. Computed 3-D contours: a) temperature; b) H₂ concentration contours in anode channel, GDL and catalyst layer; and c) O₂ concentration contours in cathode channel, GDL and catalyst layer.](image)

![FIGURE 3. Computed contours of a PEM fuel cell with zigzag flowfield: a) temperature; b) H₂ concentration contours in anode catalyst layer; and c) O₂ concentration contours in cathode catalyst layer.](image)
capability will be useful in PEM fuel cell design and optimization.

- A MPL sub-model was implemented for the cathode side and results computed from a case study indicates that MPL effectively reduces water saturation in the cathode MPL-GDL regions.
- The present model was capable of simulating performance of a PEM fuel cell with complex zigzag flowfield having trapezoid cross-section.

**Future Directions**

- Complete development of a 3-D, partially two-phase, single-cell PEM fuel cell model.
- Complete measurements of model-input parameters and model-validation data in the single-phase operating regime; perform measurements in the partially two-phase operating regime.
- Perform validation of the 3-D, partially two-phase, single-cell PEM fuel cell model.
- Develop a 3-D, fully two-phase, single-cell PEM fuel cell model.
- Develop a sub-model for specifying boundary conditions at the GDL/channel interface.
- Couple PEM fuel cell model with DAKOTA for parameter estimation and uncertainty quantification.

**FY 2010 Publications/Presentations**


**References**

DOE Hydrogen Program

V.M.4 Transport Studies Enabling Efficiency Optimization of Cost-Competitive Fuel Cell Stacks

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Contract Number: DE-EE0000472

Subcontractors:
• Johnson Matthey Fuel Cell Ltd. (JM), Swindon, UK
• Lawrence Berkeley National Laboratory (LBNL), Berkeley, California
• Pennsylvania State University (PSU), State College, Pennsylvania

Project Start Date: July 1, 2009
Project End Date: September 30, 2012

Objectives

The objective of this project is to optimize the efficiency (electric potential at rated current) of a stack technology that meets DOE cost targets – the specific technical goal is to demonstrate stable and repeatable high performance on a full-format fuel cell stack, namely 7.5 W/mg-Pt. As cost reduction is of central importance in commercialization, the objective of this project addresses all applications.

Technical Barriers

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

(B) Cost

(C) Performance

(E) System Thermal and Water Management

Technical Targets

The key deliverable of this project is a performance model validated over a range of stack architectures operating at high power. Validation will be performed using a new, gradient-preserving test fixture that will enable high power density operation. The test campaign will consider: loadings from 0.5 mg/cm² to less than 0.2 mg/cm², current densities from 1.0 to 3.0 A/cm², and two flowfield architectures (land-channel and open). Results from these parametric studies will be used to inform and calibrate an electrode sub-model and a thermo-fluidic transport model. The integrated models will be used to investigate design and process aspects limiting performance. Throughout this project cell element designs will be refined and operating protocols will be adjusted accordingly. The operating map of the most promising architecture will be optimized in full-format testing. As mentioned earlier the experimental target consists of running a fuel cell stack at 7.5 W/mgPt and achieving a performance greater than 0.6 V at a power density greater than 1 W/cm².

Accomplishments

• System and cost analyses were conducted in collaboration with external partners. Data collected confirmed the value of studying high power density operation and increasing efficiency.

• Results collected on existing single cell hardware confirmed the need for an optimized fixture for this project.

• Initial tests on full active area hardware (Andromeda™) demonstrated 2.2 W/mgPt using a membrane electrode assembly (MEA) with 0.3 mgPt/cm² loading.

• A roadmap was defined by JM to describe the necessary steps of material development that are needed to achieve the goal of the project.

• A fuel cell performance model was built by PSU to represent both the channel/land and the open flowfield architectures.

Introduction

Hydrogen fuel cells are recognized as one of the most viable solutions for mobility in the 21st century, however there are technical challenges that must be addressed before the technology can become available for mass production. One of the most demanding aspects is the cost of present-day fuel cells which are prohibitively high for the majority of envisioned markets. The fuel cell community recognizes two major drivers to effective cost reduction: (1) decreasing the noble metal content, and (2) increasing the power density in order to reduce the number of cells needed to achieve a specified power level. Nuvera’s technology exhibits great promise for increasing power density on account of its proven ability to operate stably at high current densities (>1.5 A/cm²). However doing so compromises efficiency because it entails an increase of heat rejection duty and is thus more demanding on the cooling system. These competing aspects are being assessed in order to identify the proper trade-off, and ensure the modeling and experimental activities of the AURORA Program with respect to system-level constraints for automotive applications.

Approach

Nuvera structured the activities in the scope of the project to orbit around a focal point consisting of the fuel cell predictive model. Cost and system analyses are being performed in order to define the boundaries of the design space that the model should represent. This analytical work will inform the experimental tests on a new single-cell fixture to illuminate the physics and the parameters composing the backbone of the fuel cell model. The predictions generated by the model will drive both the process of optimization of the fuel cell operating conditions and the material development. The combined results of these two activities will be verified on single-cell fixtures as well as on full active area hardware, and the experimental data obtained will be used to validate and calibrate the model through multiple iterations.

Results

In Fiscal Year (FY) 2010 Nuvera worked with Directed Technologies, Inc. (DTI) to understand the impact of high power density on stack cost. The analysis was performed while minimizing the discrepancies between the most promising technical solutions identified respectively by DTI and Nuvera. This allowed for full leverage of DTI assumptions and experience in the cost analysis field. The results of this activity are shown in Figure 1 where the stack efficiency is benchmarked against the stack cost for different fuel cells characterized by increased level of performances. The advantage of high power density is clear. Depending on the achievable performance and the acceptable efficiency, this advantage translates into saving between $300 and $840/vehicle (with respect to DTI case). On the other hand Nuvera used a detailed vehicle model to predict heat rejection and radiator size for a spectrum of driving conditions and car types. This analysis showed the heat management is particularly challenging for large-size fuel cells vehicles (like sport utility vehicles) at any power density while it becomes a milder issue for small to medium-size cars.

PSU ran preliminary tests on existing single-cell fixtures consisting of a parallel channel/land flowfield with an active area of 14.6 cm² and 25 cm². In both cases, the polarization curves collected show the inability of the hardware to reach very high current densities. As shown in Figure 2, the mass transfer limitation for the 14.6 cm² cell becomes evident beyond 1 A/cm². In order to explore a broader range of current densities, Nuvera will provide PSU with a new fixture, that is equipped with Nuvera’s open flowfield and enables such characterization. A prototype of the fixture is represented in Figure 2.

Nuvera and JM performed a first test on a full active area, and 8-cell Andromeda stack with low loading MEAs (0.3 mgPt/cm²). This test represented the first attempt at running with Pt content below 0.5 mgPt/cm² and neither the stack architecture nor the materials used were optimized for the purpose. The performance recorded was quite low (0.33 V @ 2 A/cm²) but it was stable at all the current densities and the stack was capable of reaching 2.2 W/mgPt that is far from meeting the target but confirmed the feasibility of operating low loading materials at high current densities.

Based on the targets for this project JM crafted a roadmap to delineate the actions needed to achieve the project performance goals. This roadmap will be refined as more information becomes available through the model predictions, but for the time being it is
articulated into two major areas of research: (1) JM will develop a membrane optimized in terms of thickness and equivalent weight (to help lower the resistivity of the membrane and accordingly boost the performance in the ohmic region), and (2) JM will tune the catalyst layer to perform with a Pt loading approaching 0.2 mgPt/cm². Tuning will involve several steps including reducing Pt content of the existing catalyst structures, developing new catalyst structure that will enable lower loading, and using a gradient of Pt over the layer surface to optimize the local use.

PSU and Nuvera selected a model approach suitable to represent both channel/land and open flowfield stack architectures. In order to minimize the computational effort a two-dimensional (2-D)+1 geometry was preferred to a three-dimensional (3-D) one. The fuel cell is ideally divided in N control volumes in the Y direction (see Figure 3). The Y direction parameters (such as temperature, pressure, etc.) do not vary inside the control volume therefore each volume can be treated as a surface that can be represented by a 2-D model. This model is built with a fine mesh that is capable of properly capturing the phenomena in the XZ plane for the specific control volume. However, species concentrations and temperature are allowed to vary in Y direction along different control volumes (based on the equations describing mass conservation and heat transfer). Therefore each 2-D model simulating the corresponding control volume (or better surface) is inferred by the respective discrete variations along Y and is then solved for in the XZ plane.

PSU started the construction of the model (“Aurora model”) developing the convergence algorithm, implementing the equations that describe the variations.
in the Y direction, and using their pre-existing 2-D model (“PSU model”) as a first representation of the XZ plane. The Aurora model was adjusted to simulate Nuvera’s open flowfield and the predictions generated were compared to those corresponding with the Nuvera internal model. This benchmark offered a first level of confidence in the approach and it will also be pursued in the next phase of development when PSU integrates the LBNL membrane and catalyst sub-models into the Aurora model.

Conclusions and Future Directions

Nuvera will deliver the new single-cell fixture to PSU in order to start exploring the design space and to provide feedback to the model predictions. At the same time Nuvera will use the fixture internally to test new components with specific focus to high current density operation.

JM will pursue their material development roadmap and in 2010 the first generation of low-resistivity, low-Pt loading MEAs (0.2 mgPt/cm²) will be available for testing in both single-cell fixtures and full active area hardware.

LBNL will build the first version of the membrane and electrode sub-model while incorporating parameters to be provided by JM. The sub-model will then be embedded into the Aurora model and the predictions will be verified and tuned through the comparison of the Nuvera internal model and the experimental results collected.

FY 2010 Publications/Presentations

1. May 2010 - Detroit, MI - FreedomCar Review.
2. June 2010 - Crystal City, VA - 2010 DOE Hydrogen Program Merit Review (FC028).
V.M.5 Transport Studies and Modeling in PEM Fuel Cells

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Contract Number:  DE-EE0000471

Subcontractors:
• Tech-Etch, Plymouth, MA
• Ballard Material Products, Inc., Lowell, MA
• Virginia Polytechnic and State University, Blacksburg, VA
• University of South Carolina, Columbia, SC

Project Start Date:  October 5, 2009
Project End Date:  October 4, 2012

Objectives

- Design of fuel cell components targeting specific transport properties:
  - Synthesis of block copolymers.
  - Design of flow fields and gas diffusion layers (GDLs).
- Determination of bulk membrane properties:
  - Water uptake and diffusivity.
  - Gas permeability.
  - Electro-osmotic drag.
- Transient, 3-dimensional modeling of fuel cell operation

Technical Barriers

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

Objectives

- (C) Performance
- (D) Water Transport within the Stack
- (E) System Thermal and Water Management
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

The goals of this project are not to reach specific technical targets put forth by the DOE (i.e., target catalyst loading, target cost per kilowatt). Instead, this project aims to develop fuel cell components (i.e., membranes, GDLs, bipolar plates and flow fields) that possess specific properties (i.e., water transport and conductivity). A computational fluid dynamics model will then be developed to elucidate the effect of certain parameters on these specific properties (i.e., the effect of membrane type and thickness on membrane water transport). Ultimately, the model will be used to determine sensitivity of fuel cell performance to component properties to determine limiting components and guide research.

Accomplishments

- Specified first iteration of GDL:
  - 150-190 μm thick.
  - One with no wet-proofing, one with 10 wt% Teflon® – poly-tetrafluoroethylene.
  - Target 77–80% porosity.
- Developed test station to measure diffusion coefficient of water through membrane. Test station measures diffusivity by contacting membrane with water vapor at different percent relative humidity (RH) on each side at nearly identical total pressures (i.e., by controlling ~10% RH difference between both sides of the membrane).
- Developed first iteration of fuel cell flow fields to achieve specific water transport and thermal management targets.
- Designed segmented cell to quantify fuel cell voltage vs. current at different points along the active area. Segmented cell will be used to identify regions of varying water transport and thermal management properties.
- Preliminary development of proton exchange membrane.

Diamonds:
**Introduction**

Many fuel cell component properties that influence water transport and thermal management are not well-understood [1,2]. A better understanding of how water transport and thermal management can be controlled would represent a significant step forward in meeting the DOE's stated 2015 targets. This project aims for a better understanding of water transport and thermal management by tailoring fuel cell components to exhibit specific transport properties. These transport properties will then be modeled, which will enable the prediction of the effect of changing component parameters on transport properties.

**Approach**

This project seeks to develop fuel cell components possessing specific transport properties. Membranes will be developed to achieve certain water transport and conductivity. Bulk membrane properties (i.e., diffusivity, water uptake, conductivity) will be evaluated and modeled. GDLs and bipolar plates and flow fields will be developed, also tailored to achieve specific water transport and thermal management targets. The fuel cell performance will be evaluated using these components. The model will be used to predict the effect of changing component parameters (i.e., changing membrane type and thickness, changing flow field configuration) on component transport properties and fuel cell performance.

**Results**

The first iteration of GDLs has been developed by the University of South Carolina and Engineered Fibers Technology, a subcontractor that has recently been replaced by Ballard Material Products. The GDLs are carbon-paper based and tailored to specific water transport properties. Engineered Fibers Technology is no longer able to supply customer-designed GDL materials; the subcontract has recently been moved to Ballard Material Products who can supply GDL materials possessing properties that are specified.

A test station designed to measure water diffusion in membranes has been developed, the schematic of which is shown in Figure 1. The test station consists of two sets of fuel cell hardware. One set serves as a membrane saturator, while the second set is the diffusion cell. Liquid water is kept on one side of the membrane saturator while the water vapor RH on the other side is controlled by a proportional valve. This is the water vapor in contact with one side of the membrane in the diffusion cell. The other side of the diffusion cell is in contact with water vapor at a lower RH, also controlled by a proportional valve. The flow rate of water through

![Diffusivity Test Station](image1)

**Figure 1. Diffusivity Test Station**

![Preliminary Diffusion Coefficient Data for Nafion® 212 at 80°C](image2)

**Figure 2. Preliminary Diffusion Coefficient Data for Nafion® 212 at 80°C**
the system is measured by a micro-flow meter. The diffusion coefficient is calculated by Fick’s law assuming steady state. Figure 2 presents preliminary data measured.

The first flow field has been designed by the University of South Carolina and will be manufactured by Tech-Etch. A schematic of the design is shown in Figure 3. Virginia Tech has been exploring options to design proton exchange membranes for this project. GES has designed a segmented cell to measure voltage and current density in separate regions of the active area, along with water transport and thermal management properties.

Conclusions and Future Directions

Continued determination of bulk membrane properties will be a main focus of this ongoing project. These properties will be included in future modeling activities.

• Continue to measure diffusivity.
• Develop water uptake/conductivity test station.
• Work with new subcontractor (Ballard Material Products) to design GDLs.
• Develop bipolar plates and flow fields for system design.
• Implement rigorous fuel cell testing protocol.
• Develop computational fluid dynamics model to predict water transport and thermal management.
• Extend model develop components possessing optimal transport properties.

FY 2010 Publications/Presentations


References

Objectives

The objective of project is to advance reversible solid oxide fuel cell (RSOFC) technology in the areas of endurance and performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells and Production sections of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

Fuel Cells

(A) Durability
(B) Cost
(C) Performance

Production

(G) Capital cost
(H) System efficiency
(I) Grid Electricity Emissions (for distributed)
(J) Renewable Electricity Generation Integration (for central)

Technical Targets

The project objectives are to meet the following performance and endurance targets in a kW-class RSOFC stack demonstration:

- RSOFC dual mode operation of 1,500 hours with more than 10 solid oxide fuel cell (SOFC)/solid oxide electrolysis cell (SOEC) transitions.
- Operating current density of more than 300 mA/cm² in both SOFC and SOEC modes.
- Overall decay rate of less than 4% per 1,000 hours of operation.

Meeting these performance and endurance technical targets will be key RSOFC technology development steps towards meeting DOE’s Technical Targets for Distributed Water Electrolysis Hydrogen Production by an RSOFC system.

Accomplishments

- Developed several candidate cell material systems meeting both performance (area specific resistance [ASR] less than 0.3 Ω-cm²) and endurance (degradation rate less than 4% per 1,000 hours) targets in both fuel cell and electrolysis modes.
- Validated cell material systems through long-term (1,000+ hours) tests, with two tests exceeding 8,400 and 6,400 hours exhibiting degradation rates under 3% per 1,000 hours.
- Conducted several RSOFC stack development tests in both SOFC and SOEC modes with SOEC/SOFC transients.

Introduction

RSOFCs are energy conversion devices. They are capable of operating in both power generation mode (SOFC) and electrolysis modes (SOEC). RSOFCs can integrate renewable production of electricity and hydrogen when power generation and steam electrolysis are coupled in a system, which can turn intermittent solar and wind energy into “firm power”. In order to address the technical and cost barriers, DOE funded a number of research projects over the past 10 years [2]. Although significant progress was made in those projects, further development is required especially in the areas of RSOFC performance and endurance. In this project, Versa Power Systems (VPS) is addressing performance and endurance issues for RSOFC cells and stacks.
Approach

VPS has identified four task areas in an effort to improve the performance and endurance of RSOFC systems: degradation mechanism study, cell material development, interconnect material development, and stack design and demonstration. In order to mitigate project risk, a stage-gate project management process is employed with a quantitative Go/No-Go decision point. The scope of the work has been carried out by:

- Building on VPS’ strong SOFC cell and stack baseline and leveraging cell and stack advancements from the DOE Solid State Energy Conversion Alliance (SECA) project.
- Carrying out parallel materials development activities and integrating them with cell production technology development.
- Conducting RSOFC stack and process designs to address durability, performance, and cost in both fuel cell and electrolysis operating modes.

Results

The development path for RSOFC cell material systems thus far can be summarized in Figure 1. Prior to the current project, three cell types—EC-1, EC-2, and EC-3—were developed based on VPS’ baseline TSC-2 cell. In the project, four RSOFC cell types were developed from the base of EC-1 and EC-2 cells. Most recently, two additional cell types—MAC-RSOFC-1 and MAC-RSOFC-5—were developed and tested. In total, 10 materials systems have now been evaluated for performance in SOFC and SOEC modes, some of which have already run for significant time periods under steady-state electrolysis conditions. Table 1 summarizes cell material systems’ ASR under both electrolysis and fuel cell conditions. It shows that several of these materials systems are now capable of meeting the ASR targets at 750°C.

Another key target is to achieve degradation rates under 4% per 1,000 hours of operation at more than 300 mA/cm² current density. Table 2 shows degradation rates in electrolysis mode at fixed operating conditions (750°C, 0.5 A/cm² and 50% steam utilization) in both mV and percent per 1,000 hours (percentages were calculated using a fixed voltage of 1.25 V). Figure 2 shows the steady-state operation of RSOFC-1 cell system in SOEC mode at 750°C and 0.5 A/cm². The degradation rate is about 2.7% per 1,000 hours for over 6,400 hours.

Interconnect material development has focused on testing in high steam and pure oxygen environments. Six different steel alloys (450, 434LN2, Sanergy, ZMG252, ZMG232L, and Haynes 230) have been tested in a high steam environment while three (434LN2, Sanergy, and Haynes 230) have undergone pure oxygen testing (one still in progress). 434LN2 had the best oxidation

### Table 1. Summary of Cell ASR under SOFC and SOEC Operation

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Electrolysis (SOEC) ASR (mΩ·cm²) at 50% humidity</th>
<th>Fuel Cell (SOFC) ASR (mΩ·cm²) at 3% humidity</th>
<th>Test No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>650°C 700°C 750°C 800°C</td>
<td>650°C 700°C 750°C 800°C</td>
<td></td>
</tr>
<tr>
<td>Target</td>
<td>&lt;300</td>
<td>&lt;300</td>
<td></td>
</tr>
<tr>
<td>TSC-2</td>
<td>547 372 275 241</td>
<td>501 359 269 182</td>
<td>101670</td>
</tr>
<tr>
<td>EC-1</td>
<td>954 587 366 266</td>
<td>474 350 281 241</td>
<td>101695</td>
</tr>
<tr>
<td>EC-2</td>
<td>-- 526 362 284</td>
<td>-- 521 393 374</td>
<td>101706</td>
</tr>
<tr>
<td>EC-3</td>
<td>726 422 278 221</td>
<td>425 311 251 218</td>
<td>101728</td>
</tr>
<tr>
<td>RSOFC-1</td>
<td>784 466 308 245</td>
<td>405 298 245 214</td>
<td>101737</td>
</tr>
<tr>
<td>MAC-RSOFC-1</td>
<td>671 383 251 189</td>
<td>392 290 229 204</td>
<td>101750</td>
</tr>
<tr>
<td>RSOFC-2</td>
<td>754 422 285 229</td>
<td>502 365 295 254</td>
<td>101738</td>
</tr>
<tr>
<td>RSOFC-3</td>
<td>1,003 623 386 279</td>
<td>495 359 283 238</td>
<td>101741</td>
</tr>
<tr>
<td>RSOFC-4</td>
<td>711 413 268 203</td>
<td>397 293 238 207</td>
<td>101744</td>
</tr>
<tr>
<td>MAC-RSOFC-5</td>
<td>957 530 341 254</td>
<td>404 304 253 218</td>
<td>101758</td>
</tr>
</tbody>
</table>
behavior (least amount of weight gain) in a high steam environment. The pure oxygen testing was performed in a thermo-gravimetric analyzer at 800°C for over 800 hours while monitoring each test coupon’s weight gain. Thorough analyses of the surface oxide and oxide thickness in cross section were carried out by scanning electron microscope. The chemical compositions of the oxides were determined by energy dispersive spectroscopy and X-ray diffraction. The final alloy selection will be made for stack development once all tests and analyses are complete.

VPS has developed electrochemical modeling code that integrates with Fluent to allow fully coupled electrochemical, thermal, and flow modeling of an operating solid oxide stack. This tool is used extensively in stack design and operating condition selection. Figure 3 shows the temperature distribution across the cells in a 28-cell stack with 121 cm² active area cells (1.4 kW SOEC stack). Modeling results indicate that the total temperature range across all cells is 9°C, representing an almost ideal thermal environment for the operating stack in SOEC mode.

A preliminary stack test protocol was proposed and evaluated in a short stack test. A six-cell stack was built and tested to the protocol. As shown in Figure 4, it had completed 10 fuel cell-to-electrolysis cycles and a steady-state hold in SOEC mode. The electrochemical performance and degradation of the cells in stack are comparable to that of single cell test. Some degradation was observed over the 10 reversible cycles. In addition,
RSOFC-1 cells have been incorporated into two stack tests. Both tests focus on steady-state electrolysis at the six-cell (250 W) and 28-cell (1.4 kW) levels. These tests incorporated advances in contact design that had been developed by VPS under the DOE SECA program 550 cm² active area cells [3]. Some adjustment was made to fit the smaller 121 cm² cells used in this testing, and the results are promising. These advances will be rolled into future stack tests.

Conclusions and Future Directions

In the coming year, the project team will continue on the current development path. This includes:

- Testing of different conditions (temperature, current density, and utilization) for the chosen cell materials and reversible cyclic testing of cells in short stacks.
- Concluding the degradation mechanism study.
- Selecting final alloys following the completion of all tests.
- Continuing RSOFC stack development and testing.

FY 2010 Publications/Presentations

1. An oral presentation for this effort was made at the 2010 DOE Hydrogen and Vehicle Technologies Programs Annual Merit Review and Peer Evaluation Meeting.

References

**Objectives**

- Develop new anion exchange polymer electrolytes that have high hydroxyl conductivity and stability under alkaline conditions.
- Demonstrate an improved single-cell performance of solid-state alkaline fuel cells using the polymer electrolytes and non-precious metal catalysts.

**Technical Barriers**

(A) Durability: stability of fuel cells under highly basic conditions is not well understood. Strategies for mitigating performance loss over time are needed.

(B) Cost: material costs for platinum-based catalysts and membranes are the major barriers for fuel cell commercialization.

(C) Performance: anode and cathode performance depends on electrode structure and interactions between electrode materials.

**Technical Targets**

This project is conducting fundamental aspects of solid state alkaline fuel cells for practical use in transport applications. Insights gained from these studies will be applied toward next stage of development of alkaline fuel cell systems. Since there were no technical targets for solid state alkaline fuel cells provided by the current U.S. DOE Fuel Cell Technologies Program, we propose technical targets based on state-of-the-art alkaline fuel cells/materials in the original proposal. Key technical targets and current status are shown in Table 1.

**TABLE 1. Technical Targets and Current Status for Solid State Alkaline Fuel Cells**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>State-of-the-art</th>
<th>2011 Target</th>
<th>LANL 2010 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion conductivity (mS/cm)</td>
<td>27 (20°C)</td>
<td>50 (80°C)</td>
<td>80 (80°C)</td>
</tr>
<tr>
<td>Stability (hour at 10% conductivity loss at 80°C in 1M KOH)</td>
<td>&gt;48 h 1 M KOH at (60°C)</td>
<td>500 h 1 M KOH at (80°C)</td>
<td>380 h 0.5 M NaOH at 80°C (42% loss)</td>
</tr>
<tr>
<td>Fuel Cell Performance</td>
<td>196 mW/cm² H₂/O₂ (80°C)</td>
<td>200 mW/cm² H₂/air at (80°C)</td>
<td>NA</td>
</tr>
</tbody>
</table>

Accomplishments

- Discovered that traditional aqueous quaternization produces incomplete amination due to undesirable alcohol formation while non-aqueous quaternization provides precise control of amination without forming alcohol.
- Prepared hydrocarbon-based guanidine base (HCGB) homopolymer which has extremely low water uptake (9%) with reasonable anion conductivity (35 mS/cm at 80°C) and stability (ca. 380 h in 0.5 M NaOH at 80°C).
- Prepared perfluorinated guanidine base (PFGB) polymer electrolyte. The anion conductivity of this material met the 2011 conductivity target (80 mS/cm at 80°C) but showed limited stability.
- Identified the degradation mechanism for PFGB polymer electrolytes and discovered that the electrolyte stability can be significantly improved by having an electron donating group next to the cation functional group.
- Prepared nano-structured whiskers for electrode supporting materials. This material will be used as a high surface area support for alkaline fuel cell electrodes.

**Introduction**

Recently, renewed interest has grown in the development of solid-state alkaline fuel cells, since the efficiency of oxygen reduction reaction of electro-catalysts in an alkaline environment is likely greater than...
in acidic conditions and therefore, expensive platinum-based catalysts can be replaced with inexpensive ones such as nickel, silver and carbon [1,2]. However, current quaternary ammonium-tethered anion exchange polymer electrolytes do not show enough stability under alkaline conditions due to the nucleophilic substitution reaction under highly basic conditions [3]. Furthermore, ionomer used in electrode layers have limited gas permeability that significantly reduces cell performance.

**Approach**

Our approach to achieve stable anion exchange polymer electrolytes is to use highly basic cation functional groups instead of traditional tetra-methyl ammonium group. Tetramethyl guanidine (TMG) has high basicity (i.e. pKa=13.6) and formed resonance structure which contributes further stabilization of cation through uniform electron distribution. In order to maximize the fuel cell performance, anion exchange membranes and ionomeric binders should be designed in a separate manner, as the requirements for each role are somewhat different. Another key approach is to prepare perfluorinated ionomer for electrode binding material that has significantly higher gas permeability. An alternative approach is to prepare nano-structured thin film electrodes which do not need an ionomeric binder which minimizes the limited gas permeability problem.

**Results**

One of the technical barriers for anion exchange polymer electrolytes is poor synthetic control of cationic functional groups [4]. We found that when quaternization was accomplished by soaking halogenated polymer electrolytes in aqueous trialkylamine, hydroxide ions can act as nucleophiles and compete with alkyl amines to produce primary alcohols in addition to alkylammonium salts. Once alcohols are formed in polymer chains, the ion exchange capacity of the polymer is reduced, and water sorption is increased which dilutes the concentration of cation functional groups and gives a significant impact on ion conductivity and water uptake. Figure 1 compares the water uptake and ion conductivity of aqueous quaternized and non-aqueous quaternized anion exchange polymer electrolytes. It is noted that much higher water uptake and lower proton conductivity was achieved with aqueous quaternized anion exchange polymer electrolytes. Non-aqueous quaternization improves hydroxyl conductivity significantly which is an encouraging result and the non-aqueous quaternization technique was used for our research.

Typically quaternary ammonium-tethered polymers are prepared from chloromethylated (or alkyl brominated) polymers and subsequent reaction with a tertiary amine to form the quaternary ammonium groups [5]. The amination step is typically performed by soaking a film of the halomethylated polymer in a solution of trimethylamine (TMA) such that the polymer remains in the solid state throughout the reaction (the heterogeneous method). Alternatively the amination can be done with the halomethylated polymer dissolved in a polar aprotic solvent such as N,N-dimethylacetamide (the homogeneous method). The heterogeneous method is somewhat simpler to perform in practice although it was our hypothesis that membranes prepared this way should have lower conductivities than their homogeneously-formed analogs due to lack of phase separation. Since the heterogeneous method involves casting films before the polymer has any attached ionic groups, the placement of those ionic groups should be random throughout the polymer matrix. By contrast,
in the homogeneous method the polymer is cast in its ionomeric form and the highly polar ammonium groups would have a chance to form highly-conductive microdomains within the membrane. We prepared anion exchange membranes from a halomethylated poly(phenylene) using both methods and were surprised to find that the membrane properties (particularly conductivity) were nearly independent from the amination method used. The presence or absence of water with the TMA (as discussed above) had a much greater impact on the membrane properties than the amination method did.

When tetramethyl guanidine is used instead of TMA, two vicinal chloromethyl groups can react to form hexamethylated guanidinium-containing polymers. Since two chloromethyl groups are involved in the reaction, the reaction ends up with gelation. In order to prevent the possible gelation, we synthesized guanidine functionalized polymers with TMG-fluorine reaction without the chloromethylation process. HCGB polymers were synthesized by reacting tetramethyl guanidine with polyarylene ether sulfone containing pendant 4-fluorophenyl sulfide groups and followed by methylation (Figure 2). PFGB polymers were prepared from perfluorosulfonic acid precursor using similar fluorine-TMG reaction. Fourier transform infrared (FTIR) analysis showed that after the methylation reaction, the C=N form of tetramethyl guanidine was changed to a resonance hybridization structure CN$_3$ form.

Anionic conductivity of OH$^-$ and CO$_3^{2-}$ form of HCGB and PFGB polymers was measured by an impedance analyzer. CO$_3^{2-}$ conductivity of both polymer electrolytes is about half of OH$^-$ conductivity. HCGB and PFGB anion exchange polymer electrolytes exhibited excellent hydroxyl conductivity in the range of 0.01-0.08 S/cm, depending on molecular structure and temperature. The conductivity of PFGB (0.08 S/cm) exceeded our target conductivity (0.05 S/cm) at 80°C. Figure 3 compares conductivity of various anion exchange polymer electrolytes as a function of water uptake. Water uptake of guanidine base polymers is extremely small compared to previously developed anion exchange membranes so effective anion conduction can be achieved at relatively low water uptake [6,7]. The stability was evaluated by immersion of the membrane into 0.5 M NaOH solution at 80°C. While HCGB showed reasonably high stability (~40% conductivity decrease for over 380 h), PFGB showed rapid degradation. Based on FTIR and solid state nuclear magnetic resonance data, nucleophilic attack to the center carbon molecule of the guanidine base was proposed as a main degradation mechanism as shown in Figure 4. The degradation via nucleophilic substitution produced two neutral species to lower ion exchange capacity and conductivity. Significantly different degradation rates between HCGB and PFGB suggested that electron-withdrawing and donating characteristics

![FIGURE 2. Synthesis of HCGB Base Polymer.](image-url)

![FIGURE 3. Hydroxyl conductivity of anion exchange polymer electrolytes as a function of water uptake.](image-url)
of the cation adjacent group is critically important and affects the nucleophilicity of the central carbon. We have therefore proposed to modify the polymer structure in order to mitigate cation degradation to achieve our stability target, which is our ongoing study.

Conclusions and Future Directions

- New highly conductive guanidine-based anion exchange polymer electrolytes were prepared using non-aqueous quaternization.
- Conductivity of anion exchange polymer electrolytes met or exceeded our internal target.
- Stability of anion exchange polymer electrolytes is strongly influenced by electron density of the adjacent cation group. Currently we are changing polymer structures to improve cation stability.
- We are planning to synthesize binary and ternary late-transition-metal (LTM) alloys based on Ni, Co, and Fe; and these LTM elements alloyed with the valve metals (Ti, Zr), in order to determine their performance for use as electrode materials in alkaline electrolytes.
- We are planning to fabricate a membrane electrode assembly for fuel cell performance evaluation as component materials are prepared.

Special Recognitions & Awards/ Patents Issued


FY 2010 Publications/Presentations


References

V.N.3 Engineered Nano-Scale Ceramic Supports for PEM Fuel Cells

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Start Date:  September 2009
Project End Date:  2012

Objectives

- Develop a ceramic alternative to carbon material supports for a polymer electrolyte fuel cell cathode.
- Ceramic support replacement for carbon must:
  - Have enhanced resistance to corrosion and Pt coalescence.
  - Preserve positive attributes of carbon such as cost, surface area, and conductivity.
  - Be compatible with present membrane electrode assembly (MEA) architecture and preparation methods.
- Ceramic properties goals:
  - High surface area
  - High Pt utilization
  - Enhanced Pt-support interaction
  - Adequate electronic conductivity
  - Corrosion resistance
  - Synthetic methods amenable to scale-up
  - Reasonable synthesis costs

Technical Barriers

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

(A) Durability: Pt sintering, corrosion loss, effects from load-cycling and high potential.
(B) Cost: Better Pt utilization balanced by cost difference of new support vs. carbon.
(C) Performance: Pt sintering, corrosion loss, and loss of electroactive surface area.

Technical Targets

- Precious metal loading (0.2 mg/cm²)
- Cost (<$3/kW)
- Activity (0.44 A/mg Pt @ 0.9 V_{th,voc})
- Electrocatalysis support loss (<30 mV after 100 hrs @ 1.2 V)
- Electrochemical surface area loss (<40%)

Accomplishments

Synthesis of Non-Carbon Support Materials

- Ceramic materials with critical physical/chemical requirements for polymer electrolyte membrane fuel cell (PEMFC) catalyst support applications have been prepared.
- Utilized polymer-assisted deposition process to prepare conductive, cubic phase Mo₂N with surface area ca. 500 m²/g.
- Transmission electron microscope (TEM) analysis confirms highly crystalline structures less than 2 nm with carbonaceous material forming agglomerates.
- Prepared Pt/Mo₂N catalysts with Pt dispersed with an average Pt crystallite size as small as 36 Å.
- Synthesized black, conductive sub-stoichiometric titanium oxides (TiO₂-x, TiO) with surface areas up to 250 m²/g.
  - Oxygen deficient titanium oxide phases (TiO) exhibit average crystallite sizes as small as 40 Å.
- Accelerate Go/No-Go decision point for rare earth hexaboride materials.

Testing, Characterization and Evaluation

- Mo-N ceramics are electronically conductive and are stable in acid media (0.5M H₂SO₄).
- Performed initial cyclic voltammetry (CV) characterization using glassy carbon disk electrode showing Pt/C-like activity for both hydrogen redox and oxygen reduction reaction (ORR).
- ORNL TEM analysis of first samples of Mo₂N confirming small particle sizes.
Theory and Computation

- Completed density functional theory (DFT) calculations to optimize the structures of bulk molybdenum nitride polymorphs (α-MoN, β-MoN, γ-MoN). Experimental crystal structures are reproduced to within 3% confirming validity of approach.
- Started studies of platinum adhesion on selected molybdenum oxides surfaces. Platinum shown to be most stable in three-fold site of (001) surface of α-MoN.

Introduction

Catalyst support durability is currently a technical barrier for commercialization of PEMFCs, especially for transportation applications. Degradation and corrosion of the conventional carbon supports leads to losses in active catalyst surface area and, consequently, reduced performance. As a result, the major aim of this work is to develop support materials that interact strongly with Pt, yet sustain bulk-like catalytic activities with very highly dispersed particles. This latter aspect is key to attaining the 2015 DOE technical targets for platinum group metal (PGM) loadings (0.20 mg/cm²).

The benefits of the use of carbon-supported catalysts to drastically reduce Pt loadings from the early, conventional Pt-black technology [1–4] are well known. The supported platinum catalyzed membrane approach widely used today for fabrication of MEAs was developed shortly thereafter these early reports [5–7]. Of direct relevance to this present work, are the investigations into Pt particle growth in PEMFCs [8], and subsequent follow-on work showing evidence of Pt particles suspended free of the support within the catalyst layer [9]. Further, durability work has demonstrated the detrimental effects of potential cycling on carbon corrosion [10–14] and the link between electrochemical surface area and particle growth [15].

To avoid the issues with carbon degradation altogether, it has been proposed by numerous fuel cell research groups to replace carbon supports with conductive materials that are ceramic in nature [16, 17, and references therein]. Intrinsically, these many conductive oxides, carbides, and nitrides possess the prerequisite electronic conductivity required, and offer corrosion resistance in PEMFC environments; however, most reports indicate that obtaining sufficient surface area remains a significant barrier to obtaining desirable fuel cell performance. Ceramic materials that exhibit high electrical conductivity and necessary stability under fuel cell conditions must also exhibit high surface area as a necessary adjunct to obtaining high Pt dispersions and Pt utilization targets. Our goal in this work is to identify new synthesis approaches together with materials that will lead to ceramic supports with high surface areas and high Pt dispersions. Several strong candidates for use as PEMFC catalyst supports include: transition metal nitrides and sub-stoichiometric titanium oxides, which hitherto now have been prepared by other researcher groups with relatively low surface areas (ca. 1–50 m²/g typical [16–19]).

To achieve our goals of engineering high surface area, conductive ceramic support for utilization in PEMFCs, a multi-institutional and multi-disciplinary team with experience synthesizing and investigating these materials has been assembled. This team is headed by LANL and includes ORNL and the UNM. This report describes our Fiscal Year (FY) 2010 technical progress related to applying advanced synthetic methods towards the development of new ceramic supports for Pt catalysts for PEMFCs.

Approach

Our approach to preparing ceramic powders with prerequisite properties for use as a PEMFC Pt catalyst support is centered on the application of several novel materials synthesis methods. Initially, in this first year of work, the methods were conducted in parallel to insure the best possible results that ceramic support materials would be available with desirable physical characteristics for platinum disposition and subsequent electrochemical characterization for oxygen reduction activity. The first synthesis method used in this work is the aerosol through plasma (A-T-P) process. In this method, largely developed at LANL, a gas or liquid aerosol containing precursor species is passed through the hot zone (T >3,500 K) of plasma (virtually any gas including Ar, oxygen, nitrogen, air) with a residence time on the order of 0.1 second. The particles, modified by the plasma, then enter a zone of rapid cooling (10⁵ K/s or more) where nucleation and growth of new structures generally takes place. A particularly relevant example of the capability of the process was the production of supported metal particles. We are also employing a new materials synthesis process called polymer assisted deposition (PAD) that was developed at LANL. This is a solution method for the formation of materials ranging from oxides to nitrides and oxynitrides. In general we have employed this methodology to prepare conformal epitaxial films of metal oxides and nitrides. However, high surface area powder materials can also be obtained using an accelerated heating rate to generate low density, foam-like structures. The UNM component of the collaborative research project will focus on developing synthesis methods for high surface area, oxygen-reduction catalysts supported on conductive metal oxides. Their goal will be develop a new approach...
for Pt/NbO$_x$ electrocatalysts synthesis based on sol-gel synthesis of mesoporous niobia.

Computational methods will be used to complement the experimental effort. Although these techniques provide insight into fundamental processes occurring at the atomic level, our work will focus primarily in two areas, that of aiding the characterization and understanding of experimental data and providing additional direction to the experimental team in the preparation of new support materials with optimized properties. The theory and modeling work will focus on several areas of importance to the development and optimization of new electrode support materials. Initially, computational studies have been carried out to understand the structure and stability of the support materials in the absence of platinum particles. Following this, the parameters may then be used to study the nature of the platinum binding sites on the support and the platinum adhesion energy, the mobility of platinum on the support and the interplay between the electronic structure of the support and the platinum particle, which is reflected in the calculated density of states. Comparison of these values with bulk platinum can be used as a predictive tool for the optimization of the material.

Results

Alternative Support Materials

The use of the PAD process has immediately been successful at producing conductive ceramic materials with high surface areas. A milestone for this task has been accelerated such that the Go/No-Go decision in Q8 may be brought forward to early FY 2011. High surface area, conductive foams were successfully synthesized for molybdenum as Mo$_2$N. The materials have been accelerated such that the Go/No-Go decision in Q8 may be brought forward to early FY 2011. High surface area, conductive foams were successfully synthesized for molybdenum as Mo$_2$N. The materials have been accelerated such that the Go/No-Go decision in Q8 may be brought forward to early FY 2011.

A special insulated fixture of fixed volume has been fabricated and will be used in the near future to quantify the two-point resistance of ceramic supports in powder form under uniform compaction.

Figure 1 shows the X-ray diffraction (XRD) pattern obtained for Mo$_2$N sample final anneal temperature of 950°C in 6%H$_2$/Ar. The data have been fit to a cubic crystal structure (indices indicated) with a lattice parameter calculated to be 4.268 Å. Full profile fitting of the diffraction data indicates an average crystallite size of 1.6 nm. The Brunauer-Emmett-Teller (BET) surface area for this sample was approximately 500 m$^2$/g. This is an exceptionally high surface area for a transition metal nitride powder. TEM analysis performed by ORNL also indicate highly crystalline structures on the order of 2 nm with 0.2 to 2 μm agglomerates comprised of carbonaceous material holding together the smaller crystallites. Samples prepared using the PAD process typically show broad, amorphous diffraction characteristics ca. 26° two-theta and this would be explained by the presence of carbon. The exact weight percentage of carbon in these samples is presently being determined. Also to be determined is whether the residual carbon is only present in between Mo$_2$N particles or whether it is in solution with the moly-nitride. Mo$_2$N samples have also been prepared at 700°C with slightly higher surface area and a smaller average crystallite size on the order of 1 nm. A glassy carbon electrode (0.5 cm dia.) was prepared using a 1 mg/ml suspension of the as-synthesized Mo$_2$N (both 700 and 950°C preparation temperatures) after grinding the sample in an alumina mortar with isopropyl alcohol. Initial CV characterization (in 0.5 M H$_2$SO$_4$) showed no Faradic activity when the voltage was swept at a sweep rate of 100 mV/s from 0 to 1.2 V using a hydrogen electrode with 6% H$_2$ forming gas. The rotating disk electrode experiment (0.5 M H$_2$SO$_4$ saturated with O$_2$) did not show any oxygen reduction activity.

Figure 2 is the XRD pattern obtained after Pt disposition (20 wt%) onto the 700°C-prepared Mo$_2$N using incipient wetness approach and hexachloroplatinic acid post reduction. The Mo$_2$N sample prepared at 950°C was treated to a similar Pt disposition with the same loading with similar XRD but with slightly larger average Pt crystallite sizes. The dried samples were placed into a tube furnace and annealed at 70°C for 12 hours to reduce the platinum salt. Full profile analysis of these data indicates an average Pt crystallite size of 36 Å. Two new suspensions were prepared using the Pt/Mo$_2$N catalysts. The catalyst samples were applied to two glassy carbon electrodes (0.5 cm dia.) at
two different Pt loadings: 30.6 μg Pt/cm² for the sample prepared with the 950°C annealed Mo₂N and 20.4 μg Pt/cm² for the sample prepared with the 700°C annealed Mo₂N sample.

Figure 3 (a-top) shows the CVs of these catalyst samples. In both experiments, the conditions were identical: 0.5 M H₂SO₄ saturated with Ar with voltage scanned at a rate of 100 mV/S for 8 cycles each. The CVs shows hydrogen activity similar to Pt/XC-72 carbon with an apparent reversible oxidation peak at 0.45 V and reduction peak at 0.4 V. It is interesting that both CVs show similar activity despite different Pt loadings. This would tend to suggest that more work must be done to better optimize and utilize the Pt. Although the nature of the redox couple at potentials beyond the features well known to hydrogen redox reactions have not been explained, integration of the area under the anodic peak (up to 0.6 V) yields an electrochemical active surface area (EASA) values of 9.8 m²/gₚt and 20.8 m²/gₚt for the platinized Mo₂N prepared at 950 and 700°C, respectively. These particular values for EASA serve as a reference mark and an upper bound only. In our near-term future work, we will probe these features and calculate a more accurate EASA for these materials. The Ar was removed from the electrolyte and it was replaced with O₂. The disk electrode was rotated between 400 and 1600 rpm and the CV characterization was performed at a scan rate of 20 mV/s. Figure 3 (b-bottom) shows the results for oxygen reduction activity for the Mo₂N sample prepared at 950°C and at a loading of 30.6 μg Pt/cm². As with the hydrogen CVs, the Mo₂N sample prepared at the lower temperature, 700°C, and at a lower Pt loading, 20.4 μg Pt/cm², again shows comparable ORR current densities.

Sub-Stoichiometric Titanium Oxides

High surface area, conductive foams were successfully synthesized for titanium as both TiO and TiO₂ using a modified PAD process. As with the molybdenum nitride materials, the titanium oxide ceramics are prepared by first creating a water-based solution of the desired metal bound to a PEI polymer and EDTA. The solution is concentrated to a thick gel before being heated in a tube furnace to 950°C under forming gas. During the heating process, the polymer depolymerizes and EDTA decomposes to give gaseous products, which aid in foam formation. In the case of titanium oxide materials, the variation of the flow rate and purge time determine the extent of oxygen reduction. This important control parameter is presently being studied in greater detail and will be greatly expanded upon in future reports. As of preparation of this report, high surface area, black titanium oxide foams have
been prepared using the PAD approach. The black color is highly indicative TiO$_{2-x}$ with 0<\(x\)\leq 1. The two-point resistance of a typical piece of foam (ca. 1 cc in approximate volume) was similar to that of the Mo$_2$N foams; e.g. on the order of 10 ohms. The initial BET surface area measurements performed on the first samples of black titania powders confirm gas accessible surface areas similar to Vulcan XC-72 (e.g. 200–250 m$^2$/g). These surface areas are significantly higher than commercial, conductive Magnéli phase Ti$_2$O$_n$ synthesized through bulk synthesis and reduction (ca. 1-2 m$^2$/g) or even through hydrogen reduction of nano-crystalline anatase or rutile TiO$_2$ powders (ca. 25-50 m$^2$/g) [16,17]. We have started structural characterization of these recently prepared titania supports.

**Rare-Earth Hexaborides**

Lanthanum hexaboride solution was prepared using the PEI polymer and EDTA as a water solution. Preliminary experiments were conducted to create a crystalline mixed phase materials; however, further investigation is required to obtain a pure sample. Initial attempts to use A-T-P process or rare earth hexaborides including cations such as europium, barium, and lanthanum have proven to be unsuccessful at this point. Elemental analysis using XRF indicate the presence of rare earth component in the amorphous powders collected from the plasma torch exhaust however XRD data show the materials are devoid of any apparent long range structure. Subsequent annealing at high temperature (given very slow kinetics at moderate temperatures) initiates crystallization and grain growth but only at temperatures sufficiently high to cause enough grain growth to the extent that original purpose for applying the A-T-P process becomes moot. The remainder of FY 2010 will be used to further adjust and optimize synthesis conditions for this process.

**Computational Studies of Molybdenum Nitride Supports**

Computational studies of ceramic support candidates commenced in FY 2010 to provide theoretical input to experimental work. Periodic density functional calculations were carried out using the VASP software on three bulk molybdenum nitride polymorphs (tetragonal $\beta$-Mo$_2$N, orthorhombic $\delta$-Mo$_2$N, and cubic $\gamma$-Mo$_2$N). These calculations provide a calibration for the quantum chemical method used via a comparison of the experimental and calculated structural parameters. The calculations reproduce the structure data to within 4%, confirming the validity of the computational approach. The simplest surface structure was then selected as a model for the catalyst substrate (001 surface of $\delta$-Mo$_2$N) and a geometry optimization calculation was performed to examine the effects of surface relaxation compared to the bulk structure. Using this structure, the effects of surface adhesion of platinum were investigated. Three platinum binding sites on the MoN surface were considered: the on-top site, a bridging site and a three-fold binding site as shown in Figure 4. The calculated binding energies for each of the sites was found to decrease in the order: three-fold $\gg$ bridging $\gg$ on-top. The binding energy for the three-fold site is calculated to be comparable to that of a single platinum atom on a Pt(111) surface (approximately 550 kJ/mol$^{-1}$). The bulk structures of three Mo-N phases (tetragonal $\beta$, orthorhombic $\delta$, and cubic $\gamma$) were calculated with excellent agreement to literature data. The simplest surface structure ($\delta$-Mo$_2$N) was then selected, a model created, and the relative binding energies for the three possible Pt sites were calculated. The results were obtained using plane wave DFT with VASP software from calculations of the same class used to obtain the parent molybdenum nitride structures.

**Conclusions**

- Synthesis of high surface area ceramic nitride and oxide materials.
  - Mo$_2$N synthesized at 700 and 950°C using polymer-assisted deposition with BET surface area of 500 m$^2$/g.
  - Mo$_2$N samples are electronically conductive.
  - PAD procedure modified to prepare sub-stoichiometric TiO$_{2-x}$ and TiO with BET surface areas exceeding 200 m$^2$/g.
- Pt disposition onto Mo$_2$N support samples produced an active catalyst.
  - Initial CV and rotating disk electrode characterization performed.
  - Pt utilization and optimization required.

*FIGURE 4. Calculated binding sites for Pt on $\delta$-Mo$_2$N (001) surface showing onto p (A), bridging (B) and three-fold (C) sites.*
• TEM analysis confirms average crystallite sizes calculated from full profile fitting of the XRD data (e.g. <2 nm crystallites) and has found evidence of residual carbon remaining from the synthesis process.
• Plane wave DFT and VASP calculations reproduce the crystal structure data to within 4%, confirming the validity of the computational approach and the calculated binding energies for Pt nucleation on the surface of \( \partial \)-phase MoN.

Future Directions

• Finish rare earth hexaboride work – proceed to Go/No-Go decision early in FY 2011.
• Understand the nature and extent of carbon residual in materials prepared via PAD approach. Understand effect on durability and performance of PEMFC catalysts prepared using this approach.
• Better optimize the incipient wetness disposition/ utilization of Pt onto high surface area Mo\(_2\)N materials.
• Continue electrochemical characterization of the Pt/Mo\(_2\)N catalysts – increase number of potential cycles, study and determine the nature of the redox couple at 0.45 V.
• Continue computational studies of platinum thin films on molybdenum nitride surface and use the developed method to investigate titanium oxide phase as supports.
• Begin Pt disposition onto high surface area, sub-stoichiometric titania and perform electrochemical characterization.
• TEM characterize next round of Mo\(_2\)N and Pt/Mo\(_2\)N supports as well as perform initial characterization of sub-stoichiometric titania materials.

FY 2010 Publications/Presentations


References

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V.O.1 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: June 30, 2010
*Congressionally directed project

Accomplishments

Area I: Heat and Water Management

- Most Conductive Material: 2.5 wt% Akzo Nobel Ketjenblack EC-600 JD carbon black/65 wt% Asbury Carbons Thermocarb TC-300 synthetic graphite particles/6 wt% Hyperion carbon nanotubes/26.5 wt% Dow homopolymer polypropylene 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/mK (DOE target is >20 W/mK) via compression molding and 18 W/mK via injection molding.

Area II: Development of New Electrode Materials

- Porous, machinable current collectors and mechanical supports.
- Pyrolysis of peroxyacetyl nitrate (PAN)-based foams in an oxygen-free environment at 1,200°C.
- Positive (cathodic) battery electrodes with a large macropore/mesopore space to hold electrochemically-active material.
- Supercapacitor battery anodes with a large accessible micropore surface area (i.e., >1,000 m²/g) for electric double layer charge storage.
- Carbon supports for fuel cell pseudomorphic overlayer anode catalyst(s) that promote dissociation of diatomic hydrogen into constituent protons and electrons.

Area III: Enabling Technologies for Membrane Synthesis

- Developed apparatus for continuous electrospinning of a single material fiber utilizing polymer solutions of a variety of types.
- Adapted the process to spin continuous fibers that are highly aligned utilizing a rotating electrode system.
- Developed a coaxial needle system to electrospin/electrospray core-shell fiber and particle of hybrid materials.
- Developed a novel pulsed direct current (DC) electrospray apparatus top allow better control over the particle size distribution and particle shell thickness.

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

<table>
<thead>
<tr>
<th>Task</th>
<th>Target</th>
<th>Progress</th>
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<tr>
<td>1 - Development of Lightweight, Thermally-Conductive Bipolar Plates for Improved Thermal Management in Fuel Cells</td>
<td>Fuel Cell Bipolar Plates: - Electrical Conductivity &gt; 100 S/cm - Thermal Conductivity &gt; 20 W/m.K</td>
<td>100% Complete</td>
</tr>
<tr>
<td>2 – Exploration of Pseudomorphic Nanoscale Overlayer Bimetallic Catalysts for Fuel Cells</td>
<td>Ability to construct pseudomorphic overlayer catalysts on carbon supports, that are designed to mimic conventional PEM anode catalysts</td>
<td>100% Complete</td>
</tr>
<tr>
<td>3 – Development of Hybrid Inorganic/Organic Polymer Nanocomposites</td>
<td>Develop enabling technologies for rapid production techniques</td>
<td>100% Complete</td>
</tr>
<tr>
<td>4 – Development of Oriented Polymeric Materials for Membrane Applications</td>
<td>Demonstrate the production of nanostructured polymeric membranes utilizing electrodynamic synthesis methods</td>
<td>100% Complete</td>
</tr>
<tr>
<td>5 – Preparation of Graphitic Carbon Foam Current Collectors</td>
<td>Ability to tailor the properties of carbon foam supports to meet PEM fuel cell electrode requirements</td>
<td>100% Complete</td>
</tr>
<tr>
<td>6 – Development of Lightweight Carbon Electrodes Using Graphitic Carbon Foams for Battery and Fuel Cell Applications</td>
<td>Design a complete battery cell in symmetric and asymmetric designs</td>
<td>100% Complete</td>
</tr>
<tr>
<td>7 – Movement of Water in Fuel Cell Electrodes</td>
<td>Improved GDL performance, durability, and resistance to flooding</td>
<td>100% Complete</td>
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</tbody>
</table>

GDL = gas diffusion layer; PEM = proton exchange membrane

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 polymer electrolyte membrane, 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:

1. Development of lightweight, thermally-conductive bipolar plates for improved thermal management in fuel cells;
2. Exploration of pseudomorphic nanoscale overlayer bimetallic catalysts for fuel cells;
3. Development of hybrid inorganic/organic polymer nanocomposites with improved ionic and electronic properties;
4. Development of oriented polymeric materials for membrane applications;
5. Preparation of a graphitic carbon foam current collectors;
6. The development of lightweight carbon electrodes using graphitic carbon foams for battery and fuel cell applications; and
7. 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)

Fundamental and applied research needs to be done to improve the potential for fuel cells to be used in stationary and transportation applications. The goal of this project is to develop lightweight composite materials to be used for bipolar plates within a fuel cell. Bipolar plates require high thermal and electrical conductivity. Dr. King’s research group extruded and molded into test specimens polypropylene (Dow H7012-35RN, a semi-crystalline thermoplastic homopolymer) based composites containing different carbon fillers (Akzo Nobel’s Ketjenblack EC-600 JD carbon black, Asbury Carbon’s Thermocarb TC-500 synthetic graphite particles, and Hyperion Catalysis International’s FIBRIL carbon nanotubes). Composites containing varying amounts of a single filler (maximum of 15 wt% carbon black, 15 wt% carbon nanotubes, and 80 wt% synthetic

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graphite particles) along with combinations of different fillers were fabricated and tested. Results 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/m² K (through-plane) and 24 W/m² K (in-plane). These values are near the DOE conductivity targets of 100 S/cm and >20 W/m² K. Figure 1 shows a photomicrograph of this material.

**Task 2 - Exploration of Pseudomorphic Nanoscale Overlayer Bimetallic Catalysts for Fuel Cells (Holles)**

The reload synthesis technique has been used to prepare a series of bimetallic overlayer catalysts. Supported Re@Pd overlayers were found to have hydrogen heats of adsorption lower than that of pure components. Adsorption isotherms also support altered hydrogen adsorption on Pd in Re@Pd catalysts. Ethylene hydrogenation reactivity results support decreased binding of hydrogen. These reactivity results also suggest initial hydrogenation barrier stronger influence for apparent activation energy. All results consistent with first principles and single crystal studies of Pdₜₚ/Re. Ethylene hydrogenation activity can be correlated with computationally predicted shifts in the center of the d-band through heat of adsorption (Figure 2). These results are a strong indication that we can make catalysts that demonstrate the properties of pseudomorphic overlayer bimetallics.

**Task 3 - Development of Hybrid Inorganic/Organic Polymer Nanocomposites (Mullins)**

We studied the effects of pulse width, pulse amplitude, and pulse frequency on the particle’s shape, size, and size distribution systematically. We varied the pulse amplitude from 5 to 15 kV, pulse width from 15% to 95% and pulse frequency from 10 ms to 100 s; other parameters were kept constant. Particles were successfully fabricated using the pulsed-DC voltage. Results from this study were presented at the 2009 Materials Research Society Fall Meeting and were published in the 2009 Materials Research Society Fall Meeting Proceedings Volume 1239 Symposium VV. Part of the results was included in the January Quarter Report. We have continued our experiments with the coaxial electrospraying needle to produce hybrid composite particles. We have been working with polymeric shell materials including poly-l-lactic acid (PLLA) with cores containing aqueous metallic solutions, aqueous polymeric solutions, and normal hydrocarbons with metal acetyl acetonates. Our preliminary results from fluorescent microscopy and field-emission scanning electron microscopy showed that the fluorescein dye was successfully encapsulated in the PLLA. We are continuing to look for the best core-shell pair which would allow us to obtain the complete engulfing. Also, we believe that with the best choice of the processing parameters, we should be able to produce core-shell particles with controllable size in just a single-step process.

**Task 4 - Development of Oriented Polymeric Materials for Membrane Applications (Gilbert)**

Highly aligned PLLA electrospun fibers were fabricated using an electrospinning technique. Before electrospinning, a layer of PLLA film was cast onto coverslips to secure fiber position and alignment following electrospinning. The working conditions for electrospinning were the following: working voltage: 14 kV; working distance: 11 cm; flow rate: 2 ml/hr; using a 22 gauge sharp-tip needle. The fiber samples were coated with 5 nm gold, and the images were taken using a field emission scanning electron microscope.

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**FIGURE 1.** Most Conductive Material: 2.5 wt% Akzo Nobel Ketjenblack EC-600 JD carbon black/65 wt% Asbury Carbons Thermocarb TC-300 synthetic graphite particles/6 wt% Hyperion carbon nanotubes/26.5 wt% Dow homopolymer polypropylene H7012-35RN.

**FIGURE 2.** Relationship between measured \( \Delta H_{\text{ads}} \) and turnover frequency (TOF) for ethylene hydrogenation. Heat of adsorption can also be predicted based on computationally predicted shifts in the d-band. Thus activity can be correlated with d-band predictions.

Under Task 5, investigators at Clemson University have synthesized PAN-based carbon foams that can function as mechanical supports for electrochemically-active material (e.g., nickel oxyhydroxide active mass) or catalytically-active metals. Because carbon foams are graphitic, they are excellent lightweight, porous current collectors for battery or fuel cell electrodes. Electrochemical deposition of nickel oxyhydroxide active mass has been used in Task 6 to demonstrate the use of carbon foams as scaffold materials in rechargeable positive (working) battery electrodes.

To test commercial foams (purchased from Poco Graphite and Koppers) and novel foams produced at Clemson University, we have examined the electrochemical performance of nickel electrodes by performing charge/discharge cycles in flooded and sealed cells. 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. We have developed a flooded-cell protocol for depositing, forming, and cycling nickel-carbon foam working electrodes under positive-limiting conditions.

Using these electrodes, long-term cycling tests are being performed in asymmetric sealed cells (Figure 3), sometimes called an ultracapacitor configuration. In these cells, the nickel electrode serves as the positive, and up to three layers of a microporous carbon as the negative. The positive electrode stores and releases charge via a Faradaic (redox) mechanism, while the negative electrode uses an electrolytic mechanism, i.e., charge is stored in the electric double layer. Our negative electrode material is fabricated at Michigan Tech using Ketchen Black (manufactured by Akzo Nobel Corporation) and a Teflon® binder, and it has a measured capacitance of about 60 F/g. In sealed asymmetric cells that are negative electrode limited, we have achieved long-term performance in excess of 13,000 cycles before losing 20% of the initial cell’s discharge capacity.

In a related electrocatalytic application, we have conducted successful hydrogen dissociation experiments 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)

Technical accomplishments for the last year include a 2nd-level thermostat fabricated for environmental chamber; improved temperature control (including improved humidity control, potential hydrogen atmosphere). We addressed dependence of contact angles on drop size and improved algorithm for contact angle determination. A new drop deposition method was developed which injects water through GDL. The experimental phase of the work is complete and the funds expended. During the next month we will continue to compile the final reports and complete the data analysis.

Conclusions and Future Directions

The Center for Nanostructured and Lightweight Materials is funded until the end of June 2010. Data collection and analysis is complete; the final technical report will be finished by September 28, 2010.

FIGURE 3. Charge-discharge curves from an asymmetric cell (SW #63 as positive and carbon-filled Teflon® negative electrode) at 1.44 mA/cm² current density. The positive electrode was deposited in 1.8 M Ni(NO₃)₂ and 0.26 M Co(NO₃)₂ solution for 48 minutes. The current profile is in pink and the voltage profile is in blue. The cell shown achieved approximate 1,500 cycles.
**FY 2010 Publications/Presentations**


V.O.2 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 Corporation, Broomfield, CO
• Reaction Systems, LLC, Boulder, CO

Project Start Date: July 1, 2008
Project End Date: June 30, 2010
*Congressionally directed project

** Objectives **

- Develop solid oxide fuel cell (SOFC) materials for robust operation on renewable and logistics fuels.
- Identify optimal reforming strategies for renewable and logistics fuels.
- 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 **

- Durability: Broaden SOFC operating windows under logistics fuel streams.
- Performance: Increase efficiency through system optimization.
- Transient operation: Develop model-predictive control algorithms for use in dynamic control.

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell 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 auxiliary power units. Insights gained from these studies will be applied toward the design and synthesis of SOFC materials and systems to meet the DOE 2015 Technical Target for durability (35,000 hours), start-up time (15-30 minutes), and cycle capability (250 cycles).

** Accomplishments **

- Demonstrated expanded trouble-free operating windows of hydrocarbon-fueled tubular SOFCs through addition of barrier-layer architectures.
- Demonstrated stability of next-generation strontium-doped lanthanum titanate (Sr$_{0.8}$La$_{0.2}$TiO$_3$ - SLT) SOFC anode materials across all ceramic-processing conditions. These nickel-free perovskite anode materials have far greater resistance to re-oxidation and deposit-formation failure mechanisms than established nickel-yttria-stabilized zirconia (YSZ) anode materials.
- Demonstrated solid-state reaction sintering of barium-cerate-zirconate proton-conducting ceramics at 1/10th the current fabrication cost. Measurements of ionic conductivity of these materials exceed the highest previously reported levels.
- Established liquid-fuel processing strategies and experimentation.
- Utilized new experimentation to demonstrate catalytic partial oxidation (CPOX) of renewable liquid fuels, including ethanol and butanol.
- Evaluated SOFC performance under CPOXed butanol-reformate streams, with comparisons made to performance under hydrogen fuel.
- Developed hybrid computational fluid dynamics (CFD)-electrochemical modeling tools to examine heat transfer within 600-Watt tubular-SOFC stacks.
Utilized hybrid models to quantify effects of design changes on thermal and chemical non-uniformities within the stack.

Developed rapid, lower-order dynamic models to map response of slower, high-order physical models for use in dynamic system control.

Demonstrated fidelity of lower-order models in mapping system response across large changes in system operating conditions.

Established outreach to national and international scientists in the field of energy through the Distinguished Lecture Series.

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 are developing new SOFC and catalyst materials to improve the robustness of system operation on hydrocarbon fuel streams. Additionally, modeling and experimentation is being conducted to examine and mitigate the formation of carbon deposits during fuel reforming and electrochemical-oxidation processes. Physically based models are being developed to examine SOFC-system operation and performance in auxiliary power unit (APU) applications, including control strategies for improving the dynamic response of such SOFC APU systems. Finally, outreach is being conducted through the Distinguished Lecturer Series, promoting collaboration between fuel cell researchers and scientists.

Approach

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, this team examines both the fundamental underpinnings and the key technical problems facing SOFC operation on renewable and logistics fuels. We 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 develop catalyst materials and reforming strategies for optimal processing of liquid hydrocarbons and biomass-derived fuels for use in fuel cells. We develop system-integration strategies to create robust SOFC systems that utilize renewable and logistic fuels. Through advanced fuel cell modeling and simulation, we 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 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. We are developing a perovskite-based nickel-free anode material for achieving sulfur tolerance and robust, deposit-free operation on renewable and logistics fuels. Today's SOFCs are widely designed around a composite nickel/YSZ anode formulation. While this anode material provides high electronic conductivity and good internal fuel-reforming characteristics, the cost of the nickel material can be high. Additionally, nickel suffers from problems during operation, including long-term sintering that decreases cell performance, intolerance to sulfur-containing fuel streams, and susceptibility to oxidation that can lead to cell fracture. Perovskite-based anodes can mitigate a number of these issues, as they have been shown to be more sulfur and redox tolerant than today's nickel anodes, while also achieving high power density in button-cell experiments.

The primary focus of our next-generation perovskite anode material is SLT. Within this project, we have fabricated SLT powders through solid-state powder-processing techniques, and confirmed the stability of the SLT with other SOFC materials (like the YSZ electrolyte material) throughout all high-temperature cell-fabrication processes. We have developed a host of experimental methods to quantify anode performance, including an electronic-conductivity test stand, and a unique separated anode experiment to compare gas transport and internal-reforming chemistry of next-generation anodes to that of traditional Ni-YSZ anodes. We have used this experimentation to confirm that the electronic conductivity of SLT is among the highest of perovskite-based ceramic materials, making it a leading material for replacing the nickel found in today's SOFCs. We are using these results to fabricate complete SLT-based tubular SOFCs, like those shown in the high-resolution micrographs of Figure 1. Note the high porosity of the SLT anode, the finer porosity of the...
SLT/YSZ anode functional layer, and the thin and dense YSZ electrolyte layer captured in these images.

We have also extended our development of a novel, inexpensive solid-state reactive-sintering (SSRS) technique from fabrication of BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ to creation of BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (BZCY), two proton-conducting ceramics. As shown in Figure 2, we have demonstrated that the ionic conductivity of our SSRS-fabricated BZCY material is higher than any previously reported proton-conducting ceramic, while be fabricated at one tenth the cost of traditional fabrication methods.

**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 and biomass-derived liquid fuels for use in SOFCs. Within this task, CSM researchers work with subcontractor Reaction Systems, LLC to synthesize thermally stable catalysts and catalyst supports, and then measure 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. Construction of a catalyst testing rig has been completed, and used to explore operating windows for catalytic partial oxidation of butanol, a high-energy-density biomass-derived liquid fuel. After establishing operating windows, the CPOX'ed butanol reformate has been fed to a conventional tubular SOFC fabricated by industrial partner CoorsTek, Inc, with cell-performance comparisons made to that under hydrogen fuel streams. As shown in Figure 3, cell performance under CPOX'ed butanol reformate fuel reached 60% of the pure-hydrogen performance level.

**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. Modeling and analysis efforts are 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.

Utilizing the commercially available Fluent CFD software, a hybrid CFD/electrochemistry model of the 600 W tubular Protonex stack has been established and utilized to examine heat transfer and oxygen usage within the stack tube bundle. Results are shown in Figure 4; imbalances in O₂ mole fraction are fairly modest. However, temperature variations from cell to cell can reach nearly 50°C, presenting significant degradation issues to tubular-stack developers. Alternative designs may enable a more-uniform temperature distribution within the stack.

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, 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 models 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.

This project has focused on control of the fuel cell stack in isolation. 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 of either desired signal trajectories (e.g. current set-point) or desired signal bounds (e.g. minimum voltage or fuel utilization). We have utilized this model to demonstrate robust dynamic control of SOFC stack performance with a broad load variation. This control was established within the constraints of cell voltage and fuel utilization, validating the performance of the reduced-order models for capturing the response of the higher-order physical models.

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, Prof. Robert Dibble of the University of California, Berkeley provided CSM Engineering Division students with a seminar entitled Recent “Developments in the Combustion Analysis Laboratory at the University of California at Berkeley”. Additionally, Dr. Marco Hartmann of the Karlsruhe Institute of Technology provided a talk entitled “Generation of Hydrogen and Synthesis Gas from Higher Hydrocarbon Fuels by Catalytic Partial Oxidation.” This talk was given as part of CSM’s Chemical Engineering Department Seminar Series.
**Future Directions**

**Task 1. Ceramic Materials and Architecture**
- Measure electrical conductivity and catalytic activity of novel anode compositions over a range of anode conditions.
- Establish fabrication protocols for perovskite-based tubular SOFCs.
- Evaluate the long-term stability of protonic conductors using thermogravimetric analysis, differential thermal analysis, and dilatometry.

**Task 2. Fuel Processing**
- Extend partial-oxidation experiments on butanol fuel.
- Develop process windows for deposit-free SOFC operation under butanol reformate.

**Task 3. System Optimization and Control**
- Extend tube-stack models to examine relationships between stack design and performance.
- Implement explicit form for model predictive control.

**FY 2010 Publications/Presentations**


V.O.3 Development of Kilowatt-Scale Coal-Based Fuel Cell Technology*

Objectives

Develop a kilowatt-scale coal-based solid oxide fuel cell (SOFC) technology. The outcome of this research effort will form the technological basis for developing megawatt-scale coal-based SOFC technology. Objectives for 2010 included the following:

- Determine the effect of CO and CO$_2$ on the performance of the coal-based fuel cell.
- Study the long-term electrochemical oxidation of coke.
- Investigate the integration of fuel cells in series and parallel for the coal-based fuel cell stack.
- Evaluate the operation conditions of a steel coal injection unit.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Multi-Year Research Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project is directed at the development of kilowatt-scale coal-based SOFC technology. This 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/cm$^2$ at 0.4 V was the initial target for demonstration of a coal-based SOFC.

Accomplishments

Year 2010 focused on the following milestones:

- Studied the effect of CO and CO$_2$ on the activity of the anode catalyst and the performance of the coal-based fuel cell. Exposure of the Ni anode to CO was found to improve the fuel cell performance and decrease the fuel cell energy efficiency.
- Investigated the integration of fuel cells in series and parallel for the coal-based fuel cell stack. Integration of fuel cells in parallel was found to produce maximum current densities 30% higher than integration in series.
- Demonstrated the long-term electrochemical oxidation of coke.

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 CO$_2$, (iii) the production of a nearly pure CO$_2$ exhaust stream for the direct CO$_2$ 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) improving the anode catalyst structure and the interface between electrodes and electrolyte, (ii) developing and refining the coal fuel cell fabrication techniques, and (iii) testing a small-scale coal fuel cell system. Successful
development of this novel coal fuel cell technology will significantly enhance the 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 the tape casting and screen printing approach, which involves: (i) generating a Ni-ytria-stabilized zirconia (YSZ) anode support layer (70 wt% Ni), a Ni-YSZ interlayer (50 wt% Ni), and a high purity YSZ electrolyte layer, (ii) cutting the layers in the shape of a 2 cm diameter disc and co-firing at 1,400°C, and (iii) screen printing and firing at 1,200°C a lanthanum strontium manganese (LSM)-YSZ cathode layer. The cells were tested in a steel reactor comprising a gas inlet port, a coke feeding mechanism, and a gas exhaust outlet port connected to a mass spectrometer (Pfeiffer Omnistar) and a gas chromatographer (SRI 8610 C). Ag paste was coated along the perimeter of the anode electrode to enhance the contact between the anode and the steel reactor serving as anode current collector; Ag mesh and Ag paste current collectors were attached to the cathode electrode. The fuel cell performance and energy efficiency was evaluated by introducing the fuel (H2, coke and coal) and monitoring the current produced at different voltage loads.

The microstructure of the fuel cell electrodes was characterized before and after the testing experiments by X-ray fluorescence, scanning electrode microscopy, and energy dispersive X-ray spectroscopy, with the purpose of monitoring the reducibility of the fuel cells fabricated in-house. The performance and energy efficiency of the fuel cell was tested in coke, a carbonaceous fuel produced by the pyrolytic reaction of coal at high temperature (800-950 °C). The effect of CO2 product on the anode catalyst activity and performance was investigated. Fuel cell efficiencies were calculated by considering the power produced by the cell and the heat of combustion of the fuel consumed during the electrochemical reaction. Once sufficient understanding was gained for (i) the reaction mechanism of electrochemical oxidation of coal-based fuel on the anode electrode, (ii) the effect of CO2 on the performance of the fuel cell, (iii) the microstructure of the anode electrode (porosity, tortuosity, and stability), and (iv) the coal feeding approach, efforts were expanded to the development of new anode catalysts, fuel cell fabrication methods, and current collection assemblies for stack fabrication.

Results

The effect of CO on the performance of the fuel cell was studied by testing of the cell in coke and different concentrations of CO, monitoring the power produced and the composition of the gases at the fuel cell exhaust. Figure 1(a) shows testing of the fuel cell in 5.0 g of coke and He (200 sccm) under open circuit voltage (OCV) conditions and at a load of 0.4 V produced a maximum current of 190 mA, and the formation of CO and CO2 product. The concentration of the CO and CO2 products were determined from the mass spectrometer profiles and gas chromatograph analysis of the exhaust stream. The thermodynamic efficiency (εT) of the fuel cell during operation in coke was determined to be 49.4% from the data of Figure 1(b), by relating the electric power produced by the fuel cell at the operating voltage, Wf, and the enthalpy change of the carbon oxidation reaction, DH. Wf was estimated from Figure 1(b) by integrating the highlighted area under the current vs time curve. The enthalpy change of reaction, DH, was estimated considering the amount of carbon consumed during the electrochemical oxidation reaction and the low heating value of coke. The amount of coke consumed was determined by combination of the increase of CO and CO2 concentration in the outlet stream when changing the operating conditions from OCV to 0.40 V, as summarized below

\[
\eta = \frac{W_f}{\Delta H} = \frac{U}{\eta} = \frac{0.4 \cdot 144.75}{355,200 \cdot 0.0915 \cdot 1 \cdot 1} = 49.4\%
\]

LHV=lower heating value of carbon (J/mol)

\( (CO+CO_2)_{\text{exhaust}} - (CO+CO_2)_{\text{inlet}} \) = increase in the concentration of CO and CO2 (mol/ml)

U=fuel utilization (%)

t=time (sec)

FIGURE 1. CO and CO2 concentration at the exhaust of the fuel cell and current produced at 800°C, OCV, and 0.4 V during testing in (a) coke (3g) and He (200 sccm), and (b) coke (3g) and He containing 6.97% CO.
Figure 1(b) shows testing of the fuel cell in coke and a He stream (200 sccm) containing 6.97% CO at OCV and 0.4 V produced a higher current than that observed with coke, reaching values close to 320 mA. The efficiency of the fuel cell during testing in coke and CO, determined from the data in Figure 1(b), was found to be lower than that of the fuel cell in coke despite producing a higher current. The efficiency of the fuel cell in coke and CO was calculated by relating the electric power produced by the fuel cell at the operating voltage, \( W_e \), and the enthalpy change of the carbon oxidation reaction, \( \Delta H \). The enthalpy change of reaction, \( \Delta H \), was estimated considering the amount of CO consumed during the electrochemical oxidation reaction and the low heating value of CO. The amount of CO consumed was determined by the difference in CO2 concentration in the outlet stream when switching the operation from 0.40 V to OCV.

\[
U = \frac{W_e}{\Delta H} = \frac{\text{increase in CO}_2 	ext{ concentration of (mol/ml)}}{16.5 \times 0.5 \times 18 \times 10^{-3} \times 1 \times 0.05} \times 100\%
\]

\( LHV \) = lower heating value of carbon (J/mol)

\( \text{increase in CO}_2 \text{ concentration of (mol/ml)} = [\text{CO}_2]_{OCV} - [\text{CO}_2]_{Inlet} \)

\( U \) = fuel utilization (%)

\( t \) = time (sec)

The reproducibility of these results was further investigated, quantifying the concentration of gas species at the exhaust, as summarized in Tables 1 and 2.

**TABLE 1. Fuel Cell Efficiency and Composition of Gases at the Fuel Cell Exhaust**

<table>
<thead>
<tr>
<th>Setting (V)</th>
<th>Inlet (%)</th>
<th>Outlet (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (V) Inlet gas</td>
<td>CO</td>
<td>He</td>
</tr>
<tr>
<td>OCV He</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.4 He</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.4 He/CO</td>
<td>6.97</td>
<td>93.03</td>
</tr>
<tr>
<td>OCV He/CO</td>
<td>6.97</td>
<td>93.03</td>
</tr>
</tbody>
</table>

**TABLE 2. Fuel Cell Efficiency in Coke and CO**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Thermodynamic Efficiency</th>
<th>Net Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>49.4%</td>
<td>52.8%</td>
</tr>
<tr>
<td>Carbon + CO</td>
<td>40.7%</td>
<td>33.1-52.8%</td>
</tr>
<tr>
<td>CO</td>
<td>N/A</td>
<td>33.1%</td>
</tr>
</tbody>
</table>

FIGURE 2 shows a schematic representation of the approach used for integrating two fuel cells in series and in parallel, and their corresponding fuel cell voltage and current characteristics (i.e., fuel cell voltage-current curves) during testing in H2 fuel. The experimental apparatus was intentionally constructed to allow measuring the individual performance of each cell. Inspection of Figure 2 shows integration of the fuel cell series produced a maximum current of 1.8 A, which corresponds to nearly 95% of the sum of each individual cell maximum current; the current expected from the two cells connected in a series arrangement. The maximum power output produced by the cells in series arrangement was found to be 0.35 W, as evidenced from the curves in Figure 2.

Testing of the cells in a parallel arrangement produced a fuel cell current close to that of the individual cells, with a maximum power output of...
0.495 W, 30% higher than observed for the cells in the series configuration.

The higher power outputs observed with parallel configuration was further investigated by testing a system composed of four small cells (1 cm diameter) in H2 fuel, as shown in Figure 3. Testing of the cells in the parallel configuration demonstrated the buildup of power output needed for the coal fuel cell stack. Future experiments will evaluate the performance characteristics of the fuel cell stack configuration during operation in coal and coke fuel. The efficiency of the coal fuel cell stack in the parallel configuration will be analyzed in future work.

Figure 4 shows the current density as function of time during testing of a fuel cell in coke fuel and He flow at 800°C and a load of 0.35 V. Exposure of the fuel cell to H2, CO and CO2 after 15 h of continuous operation resulted in rapid increases in the fuel cell current density. The increases of the fuel cell current density can be explained by the combined electrochemical oxidation of H2 and coke, and CO and coke. The increase in the fuel cell current density during exposure to CO2 evidenced the electrochemical oxidation of coke produced by the reaction of carbon and CO2 (C+CO2 →2CO). The effect of CO2 on the performance of the fuel cell will be further investigated in future experiments.

Conclusions and Future Directions

- Exposure of the Ni anode to CO was demonstrated to improve the fuel cell performance and decrease the fuel cell energy efficiency.
- Integration of fuel cells parallel configuration was found to produce maximum power outputs exceeding those of similar cells integrated in a series configuration by 30%.
- Long-term testing of the fuel cell in coke was demonstrated.

The proposed future research would be focused in the following directions:

- Identification of catalyst composition for long-term electrochemical oxidation of solid carbon fuels at 800°C
- Evaluation of the energy efficiency of fuel cell stacks in the series and parallel configuration.

**FIGURE 3.** (a) A digital image of 4-cell fuel cell stack, (b) voltage-current curve of the individual cells and the fuel cell stack.

**FIGURE 4.** Current density of a fuel cell during testing in coke at 800°C and a load of 0.35 V. Note: 1. Voltage changed from 0.35 to 0.5, 0.1, and 0.35 volt, respectively, the inlet gas changed from He to He/H2, He/CO2, He/CO respectively, while the voltage was kept at 0.35 volt.
• 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 2010 Publications/Presentations

Objectives

- Molecular-morphological tailoring and evaluation of novel, low-cost hydrocarbon fuel cell membranes with high-temperature performance and long-term chemical/mechanical durability. This effort supports the Hydrogen Program stated in the Multi-Year Program Plan by developing high-temperature, low relative humidity (RH), high proton conductive membranes for use in polymer electrolyte membrane (PEM) fuel cells – focus is on alternative materials with performance up to 120°C at low RH.

- Synthesis of aromatic hydrocarbon polymers. Organic structure tailoring includes variation of linking moieties between aromatic groups, ion exchange density/distribution, molecular weight and block vs. random copolymers. Three synthetic directions by Storey, Patton, and Savin.

- Fundamental information regarding microstructure and physical properties and correlation using advanced characterization tools (Mauritz, Savin).

- Having identified superior materials and optimized membrane electrode assembly (MEA) processing, the nature/mechanisms of coupled chemical and mechanical degradation and morphological alteration investigated during accelerated ex situ degradation and PEM fuel cell testing (Mauritz).

- Mechanical/chemical/thermal stability of the membranes will be increased over a broad temperature-humidity range. MEAs fabricated from synthesized ionomers and tested for fuel cell performance and durability.

Technical Barriers

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

(B) Cost

(C) Performance

Technical Targets

- Synthesize bisphenolic comonomers for poly(arylene-ether-sulfone) (PAES) that contain an ion-exchange moiety on a perfluoroalkyl chain tether. Polymerize new comonomers and study membrane conductivity, accelerated degradation, and fuel cell in situ properties. Reproduce known sulfonated poly(arylene-ether-sulfone) (sPAES) benchmark polymers and subject to identical testing. Compare our materials to performance standards established by the DOE.

- Investigate influence of annealing on macromolecular structure, chain dynamics and morphology.

- Knowledge of chemical and mechanical degradation mechanisms and their inter-relationship in membranes.

Accomplishments

- Synthesized/characterized new ion-containing bisphenolic monomer, N,N-diisopropylethylammonium 2,2-bis(p-hydroxyphenyl) pentafluoropropanesulfonate (HPPS).

- Synthesized PAES copolymers with various ion contents from HPPS, bisphenol (BP), and bis(4-fluorophenyl)sulfone (FPS). Molecular weight, polydispersity index, copolymer composition characterized with nuclear magnetic resonance (NMR) and gel permeation chromatography. Thermal properties characterized with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

- Developed chemistry for synthesis of triazole tethers and postmodification of PAES backbones.
Initial studies of poly(perfluoropropylene oxide)-b-poly(styrene sulfonate) (PFPO-PSS) model copolymers and extended to use novel proton conducting blocks.

- Determined equivalent weights, proton conductivities of sPAES membranes.
- Generated water vapor pressure isotherms for sPAES membranes.
- Established thermal degradative stabilities and Tgs of sPAES membranes using dynamic mechanical analysis (DMA).
- Uncovered molecular motions in, monitored kinetics of formation of sPAES membranes using broadband dielectric spectroscopy.

**Introduction**

The scope is a vertically-integrated project of synthesis-characterization-evaluation of novel hydrocarbon fuel cell membranes for high-temperature performance with excellent durability. While we continue research performed in Fiscal Year (FY) 2008 and FY 2009, the synthetic scope is broadened. The basic theme is continued which is synthesis of polymers of the PAES or poly(arylene ether ketone) type, containing ion exchange groups, e.g., sulfonic or phosphonic acid, tethered to the backbone via perfluorinated alkylene linkages. In the renewal grant, new structural variations are examined, e.g., nature of the attachment point of tether to backbone, tether length, tether branchiness, number of ion exchange sites at a comonomer. Use of N-based heterocyclics instead of acid groups for proton conduction broadens the synthetic scope. Polymer backbones will also be of the PAES and poly(arylene ether ketone) type. Use of nitrogen-based heterocyclics is proposed for high-temperature, low-RH membranes that combine high mechanical/thermal/chemical stability of aromatic hydrocarbon polymers with pendant moieties that exhibit high proton conductivities in the absence of water.

In a second new theme that broadens the synthetic scope, block copolymers will be synthesized via coupling reactions between a proton conducting block, including any of the aromatic hydrocarbon polymers discussed above and acidic polymers. Phase behavior will be mapped vs. block composition using transmission electron microscopy (TEM), atomic force microscopy (AFM), small angle X-ray scattering (SAXS). Synthesized materials will be characterized for proton conductivity and mechanical/chemical/thermal stability over broad temperature and RH ranges using a variety of spectroscopic, dielectric, microscopic and viscoelastic methods and evaluated for performance in fuel cells.

**Approach**

There are three synthetic directions in the project (Storey, Patton and Savin). Storey will synthesize bisphenolic comonomers that contain one or two ion-exchange moieties connected through perfluoroalkyl tethers and copolymerize them with biphenol and FPS to create PAES. Patton will synthesize N-heterocycle (i.e. 1H-1,2,3-triazoles) containing tethers that will be installed on PAES backbones via a post-polymerization functionalization approach. Savin will synthesize block copolymers containing proton conducting blocks (PSS) with perfluoroether blocks (PFPO) using a modular coupling approach.

Fundamental information is gathered regarding microstructure, physical properties and how they are related using advanced characterization tools by Mauritz and Savin. Having identified superior membranes and optimized MEA processing, the nature/mechanisms of coupled chemical-mechanical degradation and morphological alteration will be investigated during accelerated ex situ chemical degradation and PEM fuel cell testing by Mauritz.

**Results**

We synthesized the ion-containing bisphenolic monomer, HPPS, in three steps from hexafluoroacetone. A monomer structure was confirmed using NMR and X-ray. HPPS was copolymerized with BP and FPS to form a series of PAES with the general structure shown in Figure 1 and specific compositions as shown in Table 1.

We successfully synthesized a series of model tethers with terminal triazole moieties. Intermediate alkynyl bromides (1) were prepared by phase transfer catalyzed alkylation of propargyl alcohol with excess of appropriate dibromoalkanes (3 equivalent) to minimize bis-alkylation products. Copper-catalyzed 1,3-dipolar cycloaddition of 1 with (2-azidomethoxyethyl) trimethylsilane gave terminal N-protected triazole...
alkylbromides (2). De-protection of 2 under acidic conditions gave the terminal 1H-1,2,3-triazole alkylbromide in near-quantitative yields. These model tethers will be used for modification of PAES polymer backbones to achieve N-heterocycle containing polymers for membrane fabrication.

Optimal reaction conditions were determined for modular coupling of PFPO and polystyrene with five varying molecular weight and block ratios. Successful coupling was verified using light scattering. A sulfonation protocol was determined using acetyl sulfate under dilute conditions and successful sulfonation to afford PFPO-PSS was demonstrated using light scattering. Initial studies were performed using DSC and AFM to determine thermal transitions and thin film morphology.

EW, water vapor pressure isotherms and proton conductivities were determined for sulfonated (s) PAES and HPPS membranes and conductivities are low. Thermal degradation was studied using TGA. Glass transitions related to upper fuel cell operating temperature were identified for HPPS variants using DMA. Thermal degradation occurs immediately after the glass transition temperature (Tg). Sub-Tg relaxations can be related to physical durability in RH cycling. Evolving macromolecular motions in sPAES and HPPS were monitored in real time as kinetics of film formation was tracked using BDS. Figure 2 shows ion viscosity (IV) vs. film formation time for HPPS and sPAES samples and 2-step processes and gelation asymptotes are seen. BDS was used to study drying of these materials.

Conclusions and Future Directions

- Synthesized PAES block copolymers from HPPS, BP, and bis(4-fluorophenyl)sulfone.
- Synthesized ion containing bisphenol monomers with two tethered sulfonate moieties per bisphenol monomer unit and longer perfluorinated tethers for enhanced H⁺ conduction.
- Synthesized N-heterocycle aromatic polymer.

- Evaluated thermal properties/conductivity of 1,2,3-triazole tethered polysulfone vs. composition.
- Synthesize other compositions for model PFPO-PSS block copolymers and characterize morphology using TEM, AFM and SAXS
- Incorporate of other proton conducting blocks with PFPO using our modular approach: PBI, poly(arylene ester sulfones).
- Test membranes synthesized by Storey, Patton and Savin with BDS from -80 to 300°C; determine Tg and sub-Tg molecular motions relating to proton conductivity, high temperature stability and chemical and mechanical degradation (durability).
- Samples will be tested with 100% of either hydrophobic or hydrophilic blocks to assign broadband dielectric spectroscopy transition peaks in block copolymers.
- In situ annealing experiments will be conducted at temperatures from 80 to 140°C to obtain information on shifts in macromolecular dynamics and nature of water desorption during high temperature fuel cell operation.

### Table 1. Comonomer Charge Amounts and Copolymer Yield for Copolymerizations

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>FPS (g)</th>
<th>HPPS (mmol)</th>
<th>BP (g)</th>
<th>HPPS (mmol)</th>
<th>Copolymer Yield (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEAS-20</td>
<td>0.7943</td>
<td>3.1240</td>
<td>0.3205</td>
<td>0.6008</td>
<td>2.4675</td>
</tr>
<tr>
<td>PEAS-31</td>
<td>0.7873</td>
<td>3.0965</td>
<td>0.4818</td>
<td>0.9031</td>
<td>2.1501</td>
</tr>
<tr>
<td>PEAS-40</td>
<td>0.7777</td>
<td>3.0588</td>
<td>0.6401</td>
<td>1.2060</td>
<td>1.8006</td>
</tr>
<tr>
<td>PEAS-49</td>
<td>0.7775</td>
<td>3.0580</td>
<td>0.8003</td>
<td>1.5078</td>
<td>1.5007</td>
</tr>
<tr>
<td>PEAS-61</td>
<td>0.7797</td>
<td>3.0666</td>
<td>0.9647</td>
<td>1.8176</td>
<td>1.2023</td>
</tr>
</tbody>
</table>

Purity of monomers back-calculated from polymerization degree: a 98.9%; b 100.7%; c 99.4%; d 99.2%
• Generate water vapor pressure isotherms to correlate broadband dielectric spectroscopy results with water content.

• Perform complementary DMA-RH studies.

**FY 2010 Publications/Presentations**

**Publications**


**Presentations**


V.O.5  Extended Durability Testing of an External Fuel Processor for SOFC*

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E-mail: Jesse.Adams@go.doe.gov

Contract Number:  DE-FG36-08GO88113
Project Start Date:  August 1, 2008
Project End Date:  December 31, 2011

*Congressionally directed project

Objectives

The main goal of this project is to perform extended durability testing of the external fuel processor (EFP) for a 1-MWe solid oxide fuel cell (SOFC) power plant concept being developed by Rolls-Royce Fuel Cell Systems (US) Inc. (RRFCS). The specific objectives are to:

• Conduct long-term tests in relevant environments for the three EFP subsystems that support operation of a 1-MWe SOFC power plant. The subsystems include:
  – Synthesis-gas subsystem
  – Start-gas subsystem
  – Desulfurizer subsystem

• Determine long-term performance of key components such as catalysts, sorbents, heat exchangers, control valves, reactors, piping, and insulation.

• Evaluate the impact of ambient temperatures (hot and cold environment) on performance and component reliability.

• Determine system response for transient operation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration 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 three External Fuel Processor subsystems.

Technical Targets

This project addresses milestone 59 in the Fuel Cells section of the Fuel Cells Technologies Program Multi-Year Research, Development and Demonstration (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 of the EFP subsystems.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2005 Status</th>
<th>DOE 2011 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold start-up time to full load @ -20ºC ambient*</td>
<td>minutes</td>
<td>&lt;90</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Transient response (10 to 90% load) Load rate of change</td>
<td>Minutes % / min</td>
<td>&lt;5</td>
<td>16</td>
</tr>
<tr>
<td>Durability</td>
<td>hours</td>
<td>20,000</td>
<td>40,000</td>
</tr>
<tr>
<td>Survivability (min and max ambient temperature)</td>
<td>ºC</td>
<td>-25</td>
<td>-35</td>
</tr>
<tr>
<td></td>
<td>ºC</td>
<td>+40</td>
<td>+40</td>
</tr>
<tr>
<td>Sulfur content in product stream</td>
<td>ppbv (dry)</td>
<td>&lt;10</td>
<td>&lt;4</td>
</tr>
</tbody>
</table>

* or at values limited by weather conditions

Accomplishments

The following work has been completed since last year’s annual report (June 2009):

• Hydrogen Safety Plan was issued and approved by DOE’s Hydrogen Safety Panel.
• Completed fabrication of outdoor test facility.
• Installed desulfurizer and start-gas subsystems in outdoor test facility.
• Commissioned control software, mechanical and electrical hardware for desulfurizer subsystem.
• Commissioned control software, mechanical and electrical hardware for synthesis-gas subsystem.
• Completed 1,000-hour durability test of synthesis-gas subsystem.
Introduction

RRFCS is developing a 1-MWe SOFC power plant for stationary power application. An integral part of the SOFC power plant is the EFP. It uses pipeline natural gas and air to generate all the gas streams required by the SOFC power plant for start-up/shutdown (non-flammable reducing gas or start gas), low-load operation (synthesis gas) and normal operation (desulfurized natural gas). Thus it eliminates the need for on-site storage of high-pressure, bottled gases of nitrogen or hydrogen.

Approach

The approach for this project is to conduct durability tests in relevant environments using full-scale components for the EFP of a 1-MWe SOFC power plant. The components were designed and built as part of another project and made available for the durability testing. An outdoor test facility was constructed as part of a third project so that the EFP could be tested under hot- and cold-weather conditions that would be expected for a 1-MWe SOFC power plant operating in northeast Ohio. Figure 1 shows a photograph of the EFP in the outdoor test facility.

The durability testing includes:

- Synthesis-gas subsystem operation for multiple start-ups and 1,000 hours of operation in a heated, indoor enclosure. This subsystem is used only during low-load operation of the SOFC to balance the thermal input and is required to operate for only a few hundred hours per year. Therefore the 1,000-hour test will simulate a 5-year service life.
- Start-gas subsystem testing for multiple start-ups and 1,000 hours of steady-state operation in an outdoor (hot and cold) environment. This subsystem is used only during start-up and shutdown of the SOFC and is required to operate for only a few hundred hours per year. Therefore the 1,000-hour test will simulate a 5-year service life.
- Desulfurizer subsystem testing for 8,000 hours in an outdoor (hot and cold) environment. This subsystem operates whenever the SOFC is making power therefore it is expected to operate for much longer periods compared to the other two subsystems. The 8,000-hour test represents the time period between yearly maintenance intervals.

After completing the durability tests, post-test analyses of the hardware will be performed. Subsystem components (catalysts, sorbents, piping, reactors, insulation, valves, heaters, heat exchangers, nitrogen membrane, etc.) will be inspected for deposits, signs of wear, damage, corrosion, and erosion. Physical and chemical analyses will be performed on components as required.

The durability tests will demonstrate that the EFP subsystems are ready for a full-scale SOFC system demonstration.

Results for 2010

Synthesis-Gas Subsystem

The synthesis-gas subsystem was installed inside a room temperature test enclosure to simulate its operating environment which is inside the SOFC enclosure. The start-gas subsystem and desulfurizer subsystem were installed in the outdoor test facility since that environment would be representative of their operation outside of the SOFC enclosure in an unheated area.

The synthesis-gas subsystem was the first subsystem to be tested. It was designed to generate hydrogen from natural gas and air to support low-load operation of the SOFC. It was tested to determine its start-up characteristics and the impact of operating time on performance. The synthesis gas reactor was heated to 350°C using warm air. The heat-up required 62 minutes. Once the catalyst was at temperature the natural gas flow was initiated. Within 40 seconds the reactor began to produce hydrogen and after 120 seconds the hydrogen concentration was approaching the target level. The hydrogen production during start-up trended closely with the catalyst outlet temperature. Figure 2 shows the results from the start-up of the synthesis-gas subsystem. The total start-up time was 64 minutes. This was slightly above the 60 minute target however the start-up procedure can be modified to significantly reduce the time for heat-up and thus meet the required performance.
After start-up, the synthesis-gas subsystem was operated for 1,000 hours to characterize its durability. The reactor was cycled periodically between minimum load (15%) and maximum load (100%) conditions. The hydrogen content in the product gas slowly declined over time (see Figure 3). At the completion of the test, the hydrogen concentration had dropped to about 85% of the initial target value (15% decline per 1,000 hours). This was within the acceptable range for the synthesis-gas subsystem for the SOFC application.

The transient response for the synthesis-gas subsystem was evaluated during a load change from 17% to 50% load. The load change was performed over a 55-second period. This gave a load rate of change of about 36% per minute. This was very close to the target value of 40% per minute. A faster load rate of change is likely possible with additional tuning of the control valves. The plot in Figure 4 shows the transient response for the synthesis-gas subsystem. The hydrogen concentration in the product gas remained near the target value during the transient while the outlet temperature increased from 815 to 855°C during the same period.

The synthesis-gas subsystem was disassembled after the 1,000-hour test was completed. The reactor vessel and its internal components were found to be in good conditions with no signs of corrosion, erosion or melting. The heaters, thermocouples and control valves showed no signs of significant degradation. A light coating of carbon was observed at the outlet of the catalyst and in the outlet piping. The carbon deposition on the catalyst may have contributed to the observed reduction in hydrogen yield over time.

Samples of the catalyst were removed from the reactor and will be submitted for chemical and physical analyses. Surface area, pore volume, precious metals, carbon and sulfur contents will be determined. Small samples of the reactor components will be analyzed to quantify any metal loss due to hydrogen dusting or corrosion.
Desulfurizer Subsystem

The desulfurizer subsystem has been installed into the outdoor test facility. Natural gas and compressed air lines were connected to supply the reactant gases to the subsystem. The outlet of the subsystem was connected to a ground flare for the safe disposal of the desulfurized natural gas since a 1-MWe SOFC is not available to use the gas.

The desulfurizer subsystem’s mechanical and electrical hardware were commissioned. All hardware is operating properly. The control software also was commissioned. Its function was tested in the semi-automatic mode through all six operational states. Once the control software has been commissioned in the fully-automatic mode the desulfurizer subsystem will be ready for durability testing.

Start-Gas Subsystem

The start-gas subsystem was installed into the outdoor test facility. Natural gas and compressed air lines were connected to supply reactant gases to the subsystem. The outlet of the subsystem was connected to a ground flare for safe disposal of the start-gas since a 1-MWe SOFC was not available to use the gas. The start-gas subsystem is ready for mechanical and electrical commissioning.

Conclusions

The durability testing of the synthesis-gas subsystem was completed and test results showed that the performance was at or very near the target values. These include:

- Start-up time of 64 minutes.
- Transient response (load change rate) 36% per minute.
- Hydrogen concentration declined 15% per 1,000 hours.
- No signs of corrosion, erosion or melting of the synthesis-gas subsystem components were observed.

Future Directions

2010

- Complete post-test inspections of synthesis-gas subsystem (third quarter Fiscal Year [FY] 2010).
- Complete commissioning of start-gas and desulfurizer subsystem (third quarter FY 2010).
- Begin durability testing of start-gas and desulfurizer subsystems (fourth quarter FY 2010).

2011

- Complete durability testing of start-gas and desulfurizer subsystems (third quarter FY 2011).
- Complete inspections of start-gas and desulfurizer subsystems (fourth quarter FY 2011).
- Issue final report for project (fourth quarter FY 2011).

FY 2010 Publications/Presentations

Objectives

- Development of metal-free oxygen reduction catalysts to reduce cost, facilitate manufacturing, and enhance durability of fuel cells.
- 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.
- 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.
- Development of understandings and methodologies to establish hydrogen quality as it relates to PEM cell applications for transportation needs.
- Development of a first principles multiphysics durability models based on interpretations of electrochemical impedance spectroscopy (EIS) data that link the multiphysics processes, the microstructure, and the material states, with cell impedance responses and global performance, mechanistically, as a foundation for engineering durability during design and manufacture of fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance
(E) System Thermal and Water Management
(F) Air Management
(G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

Carbon-Based Catalysts: To develop non-precious-metal catalysts for PEM fuel cells 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 NH₃ 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., H₂O and O₂.

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
• First principles multiphysics durability models based on interpretations of EIS data have been developed that form a foundation for engineering durability during design and manufacture of BSC SOFC fuel cell designs.

Introduction

The activities of the present project are contributing to the goals and objectives of the Fuel Cell Technologies Program of the Department of Energy through five sub-projects. Three of these sub-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 sub-projects address barriers in SOFCs; an effort to create a new symmetrical and direct hydrocarbon fuel SOFC designs with greatly increased durability, efficiency, and ease of manufacturing, and an effort to create a multiphysics engineering durability model based on electrochemical impedance spectroscopy 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-FC36-05GO13108, was leveraged to create new carbon-based, metal-free catalysts for oxygen reduction.
• Develop new materials and materials designs to create a high-performance SOFC that can directly operate on hydrocarbon fuels with high power density.
• 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, and to develop a fundamental understanding how the degradation mechanisms of polymeric materials affects the performance and life of gasket/seals in PEM fuel cells.
• On-going work with the National Renewable Energy Laboratory, Argonne National Laboratory (ANL), Savannah River National Laboratory, 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. The study will provide equilibrium and rate constants suitable for use in new and existing models, and in computer codes at ANL.
• Conceptual foundations laid by research supported by the National Science Foundation, Air Force Office of Scientific Research 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 SOFC fuel cells 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 is presented in the limited space available here. Other results appear in the quarterly reports.

Sr- and Mn-doped LaGaO	extsubscript{3} (La	extsubscript{0.5}Sr	extsubscript{0.5}Ga	extsubscript{0.5}Mn	extsubscript{0.5}O	extsubscript{3}−δ, LSGM) have recently been synthesized in Dr. Chen’s group and applied as sulfur tolerant anode materials for SOFCs [1]. LSGM has demonstrated very promising catalytic activity for hydrogen oxidation. In an all perovskite-type fuel cell consisting of a La	extsubscript{0.5}Sr	extsubscript{0.5}Ga	extsubscript{0.9}Mg	extsubscript{0.1}O	extsubscript{3}−δ (LSGM) pellet with a thickness of 400 μm as the electrolyte, LSGMn as the anode, and LSCF as the cathode, an impressive power density of 400 mW/cm	extsuperscript{2} has been achieved at 800°C, as shown in Figure 1, using H	extsubscript{2} as fuel and ambient air as oxidant. Furthermore, LSGMn exhibits a mixed ionic and electronic conductivity of 10 S/cm at 800°C in air and can be potentially used as an oxygen electrode. Figure 2 shows the performance of a fuel cell pellet constructed with this combination of materials subjected to a sulfur containing fuel for a period of about 100 hours. The drop in performance quickly stabilizes and when hydrogen is re-introduced as the fuel about 80% of the original performance is recovered.

Dr. Chen’s group has also recently discovered a perovskite material with a composition of Sr	extsubscript{2}Fe	extsubscript{1+y}Mo	extsubscript{6}O	extsubscript{19} (SFM) [2], showing remarkable redox stability and high conductivity (>100 S/cm at 750°C) in either a reducing or an oxidizing environment. This new perovskite material has been applied as both hydrogen and oxygen electrode materials in a symmetrical SOFC, demonstrating very promising cell performance as shown in Figure 3 [3]. In addition, such redox stable mixed ionic and electronic conducting material will potentially simplify the electrode infiltration process since both the electrodes can be infiltrated in the same step.
FIGURE 1. Measured performance of LSGM electrolyte supported (400 µm) SOFC with LSGM as an anode and lanthanum strontium cobalt iron oxide as the cathode (left) and the cell impedance (right) for materials developed under this program.

FIGURE 2. Measured performance of LSGM-electrolyte supported (400 µm) SOFC with LSGM as an anode and LSCF as the cathode when subjected to a sulfur containing fuel.

FIGURE 3. Symmetrical fuel cell SFM|LSGM|SFM performance with wet (3 vol% H₂O) H₂ or CH₄ as fuel. a) current/potential and current/power density curves; impedance spectra of single cells in b) wet H₂ and c) wet CH₄.
Conclusions and Future Directions

Future work includes the following tasks:

- **Hydrogen Quality** - Extract rate constants from experimental data for the case of a contaminant that desorbs from the catalyst surface; establish correlations between experimental data and model that will allow predictions of the effect of contaminant concentration and electrode potential.
- **Carbon Composite Catalyst** – Confirm protocol for preparation of mesoporous carbon support; improve integrity of the carbon composite catalyst layer in the membrane electrode assembly (MEA); reduce MEA resistance by decreasing the catalyst layer thickness and by increasing the specific gravity and activity of the catalyst.
- **Hydrocarbon-Fueled SOFC** - Evaluate SOFC performance using hierarchically porous electrode and LaGaO₃₋ as well as SFM-based ceramic anode.
- **Gaskets and Seals** - design new compression set tests to include various compression strains and more realistic heating/cooling cycles to fuel cell operation; develop a life prediction model.
- **Durability SOFC Modeling** - complete button cell test system and EIS test protocols; complete conductivity model of BSC electrode configuration.

Special Recognitions & Awards/Patents Issued

1. Prof. Ken Reifsnider, PI of this effort gave an invited keynote lecture at the ACS meeting in San Francisco in May, 2010.
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 2010 Publications/Presentations

Objectives

- Double the speed of the extrusion line manufacturing process without negatively affecting cell performance.
- Transfer a new membrane production process from research and development to the manufacturing floor for increased shelf life and consistent quality control parameters.
- Complete research and development on the effects of optimizing the fuel cell module electrical connections to allow enhancement of module performance.
- Design and develop industrial-grade automated Unicell production process equipment for mass production.
- Transfer the fuel cell module production from research and development to the manufacturing floor for production level assembly.

Technical Targets

- Extrusion line speed of 2 meters/minute
- Power Output: 10-12 Watts per Unicell

Approach

The objective of this project is to continue the research and development required to take a microfiber fuel cell technology to a high-volume manufacturing level while maintaining product performance and quality. This microfiber fuel cell technology has the potential to meet the need for high volume fuel cell manufacturing processes. With the sub-recipient’s patented technology all the components of a single fuel cell, i.e., the electro-catalyst of cathode and anode, the polymer electrolyte membrane, and the current collector are extruded into a single microfiber (Figure 1). As the speed of the extrusion line is increased, it is important that no bottlenecks occur in the subsequent processes.

In support of the project objectives, additional process equipment for extrusion of microfibrous fuel cells was designed and constructed based on prior designs at the research and development level. This equipment was installed at a manufacturing facility for doubling the production line speed while maintaining cell performance. In addition, a membrane preparation system was designed, installed and tested at the manufacturing facility for increased shelf life and consistent quality of production. For the next step in the process, Unicell production, research and development was conducted on the production machinery necessary for Unicell production (Figure 2). New programs and
software were developed to enhance human interface and operability for efficiency and increased productivity. For the last step in the fuel cell assembly process, module production, design enhancements for the module electrical connections were developed and tested for increased module performance. Module production was transferred from research and development to the manufacturing floor while performance targets were maintained the same as those produced at the research and development level (Figure 3).

**Accomplishments**

- Production line equipment has been procured/constructed, installed and commissioned at the manufacturing facility. High-speed production line testing continues.
- Membrane production system has been designed, constructed and installed at the manufacturing facility. Manufacturing level volumes of membrane material are now produced and successfully extruded with the requisite rheology and properties.
- A new software program was developed for single cell wrapping to enable faster wrapping speeds and increased cell throughput.
- Standard operating procedures for Module assembly and testing have been developed (Table 1). Production equipment has been purchased, installed and commissioned. Training on Module assembly has been completed and production employees have shown successful assembly at the manufacturing level.

**TABLE 1. Fuel Cell Module Characteristics**

<table>
<thead>
<tr>
<th></th>
<th>Production</th>
<th>R&amp;D</th>
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</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>65-70°C</td>
<td>65-70°C</td>
</tr>
<tr>
<td>Module Size (inches)</td>
<td>3”OD x12”L</td>
<td>3”OD x12”L</td>
</tr>
<tr>
<td>Voltage</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Single Cell Voltage</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Current (A)</td>
<td>44.2</td>
<td>45</td>
</tr>
<tr>
<td>Power (W)</td>
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</tbody>
</table>

OD - outside diameter

**FY 2010 Publications/Presentations**

2. A poster presentation was made at the DOE Annual Merit Review (June 8, 2010).
V.O.8 Fuel Cell Balance-of-Plant Reliability Testbed*

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 Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

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:

(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. Failure or performance degradation of BOP components has been identified as a life-limiting factor in fuel cell systems [1]. 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 work force development program will result in students trained in PEM fuel cell system technology.

Accomplishments

- Two testbeds have been assembled.
- The third testbed is under development.
- Students are being trained to the Hydrogen Safety Plan.
- Students are being trained on the construction, programming and operation of the testbeds.
- Several test components have been identified.

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, the 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 of Technology 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 the Stark State College of Technology and one at Lockheed Martin. Those at the Stark State College of Technology 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 ≤80°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 recirculation loop. The humidified hydrogen would be circulated using a hydrogen blower such as the Parker Hannifin Model 55™ Univane rotary compressor [2].

As required by the 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 and 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 Fuel Cell Balance of Plant Reliability Testbed 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 been completed and complies with the safety standards.

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 the 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.

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.

Several issues with PEM fuel cell commercial off-the-shelf components have been documented as components for testing have been identified. Reliability data is incomplete for limited production components. Many components with design capabilities within the PEM fuel cell specifications have never been tested for any length of time under those conditions. Other components do not have the correct material compatibility to operate within PEM environment, especially with respect to exposure to hazardous gases and deionized water. Additionally, high development costs were necessary to modify some existing off-the-shelf components to become compatible with the PEM environment.
Testbed Design-Hydrogen Recycle

Life Cycle Test  
Long Term Testing

Dynamic Response Test  
Pre- and Post- Test Assessment

PFA vs. Stainless Steel

Coextrusion: Permeation-Resistant Cladding

PFA-Perfluoroalkoxy polymer

FIGURE 1. Fuel Cell BOP Reliability Test Bed Design

FIGURE 2. Pressure Decay Data for PFA Polymer Tubing
One component that has completed qualification testing is a limited run perfluoroalkoxy (PFA) polymer tubing with a permeation resistant cladding. This tubing is lighter weight than stainless steel and is resistant to deionized water, corrosion and chemicals. Initial pressure decay testing of the PFA tubing, shown in Figure 2, exhibits behavior similar in magnitude to stainless steel. The tubing must still be evaluated with respect to long-term exposure to the temperature, pressure and humidity of the PEM fuel cell environment. Other components designated for test include sensors and, potentially, valves which are known sources of reliability issues [3].

Student training has been ongoing for the operation of the test bed. The training has continued for participating students to have a greater depth of understanding in LabVIEW programming and exposure to a broader range of software programming techniques. The training has included embedded controller information for LabVIEW programming and compiling to make a stand-alone program for data acquisition, control and analysis of the data. The MET231 Fuel Cell System class visited Lockheed Martin and thoroughly reviewed the test stand setup, the hardware instrumentation devices, and software of the Lockheed Martin’s test stand. This opportunity greatly assisted the building process of the student’s first test stand.

Conclusions and Future Directions

Safety protocols are in place at both Stark State College of Technology and subcontractor, 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 assembled and instrumented for reliability testing. Candidate components are being pre-tested in preparation for long term 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:

• 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 2010 Publications/Presentations


References


V.O.9 Biomass Fuel Cell Systems*

Objectives

- Develop solid-oxide fuel cell (SOFC) materials for robust operation on renewable/biomass fuel streams.
- Identify optimal fuel-processing strategies for renewable fuels (i.e. biogas and butanol).
- Employ system modeling to optimize SOFC system configurations.
- Extend model-predictive control to integrate system hardware.

Technical Barriers

- Durability: Broaden SOFC operating window under hydrocarbon and bio-derived fuel streams.
- Performance: Increase efficiency through system optimization and balance-of-plant component integration.
- Transient operation: Develop model-predictive control algorithms for use in dynamic control.
- Balance-of-plant costs: Integrate fuel reforming and heat recuperation hardware into a single low-cost ceramic micro-channel reactive heat exchanger.

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell 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 systems. Fuel streams for these systems include anaerobic-digester derived biogas, and biomass-derived liquid fuels such as butanol. Insights gained from these studies will be applied toward the design and synthesis of SOFC materials and systems to meet the DOE 2015 Technical Target for durability (35,000 hours), start-up time (15-30 minutes), and cycle capability (250 cycles).

Accomplishments

- Established biogas fuel processing strategies and experimentation.
- Quantified performance of SOFCs under biogas reformate fuel streams, and established performance comparisons under hydrogen fuel streams.
- Demonstrated operation of low-cost ceramic micro-channel fuel reformer/heat exchanger for reformation of butanol fuel stream.
- Developed hybrid computational fluid dynamics (CFD)-chemical kinetics model to examine design tradeoffs in ceramic microchannel fuel reformer/heat exchanger.
- Utilized hybrid models to quantify effects of materials changes on ceramic heat-exchanger effectiveness.
- Developed rapid, lower-order dynamic models to map response of slower, high-order physical models for use in dynamic system control of fuel-reformer hardware.
- Demonstrated fidelity of lower-order models in mapping reformer response across numerous temperature changes.
Introduction

The objective of this project is to advance the current state of technology of SOFC systems to improve performance when operating on biomass-derived fuel streams. These fuel streams include biogas generated by the anaerobic digesters that are widely used in municipal waste-water treatment facilities, and biomass-derived butanol fuel, a gasoline-compatible liquid fuel that boasts an energy density that is 75% that of diesel fuel. In this project, we are developing new SOFC and catalyst materials to improve the robustness of systems operating under these biomass-derived fuel streams. Additionally, modeling and experimentation is being conducted to examine performance tradeoffs across numerous fuel-processing strategies for these fuels. Fuel-reforming processes are being integrated with exhaust-gas recuperation processes through development of a single low-cost ceramic micro-channel reactive heat exchanger, created in collaboration with industrial partner CoorsTek, Inc. Finally, model-predictive control strategies are being developed and applied to improve the dynamic response of the fuel-reformer hardware.

Approach

The Colorado School of Mines 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 examines both the fundamental underpinnings and the key technical problems facing SOFC operation under biomass-derived fuel streams. We develop new SOFC materials for use in biomass-derived fuel streams, addressing the technical challenges and operating windows associated with fuel processing of both gaseous- and liquid-phase fuels. Through development of low-cost ceramic microchannel reactive heat exchangers with industrial partner CoorsTek, Inc., we are creating system-integration strategies to combine balance-of-plant processes into single hardware units, increasing system simplicity and decreasing cost. Model-predictive control strategies are being developed and applied to fuel-reforming hardware in an effort to improve the dynamic response of SOFC systems.

Results

Biomass-Derived Fuel Processing

In this task, we examine fuel-reforming strategies to reform two model fuels into syngas for subsequent electrochemical conversion in SOFCs. These model fuel streams include biogas generated by the anaerobic digesters and biomass-derived butanol fuel. The goal is to develop flexible, efficient fuel-processing strategies for the robust use of biomass-derived fuels in SOFCs. The effort includes computational model development on biomass-derived fuel reforming, and experimental validation and electrochemical-performance measurements of biogas-reformate-fueled SOFCs.

Ideally, the anaerobic-digester-derived biogas streams could be fed directly to the SOFC anode with no upstream reforming or fuel processing beyond trace-contaminant cleanup. Unfortunately, the composition of biogas (approximately 65% CH$_4$/35% CO$_2$) can prove problematic, leading to carbon-deposit within the stack, and rapid performance degradation. To address these concerns, we are developing upstream fuel-reforming processes to efficiently convert the biogas fuel into high-H$_2$-quality reformate to be subsequently fed into the fuel channels of a SOFC. To examine the tradeoffs in reforming approaches, a fuel-reforming facility has been constructed in the CFCC. The experiment includes extensive reactive-gas manifolding and steam addition to enable creation of a broad range of biogas-reforming streams. These mixtures are then fed to a rhodium-based catalyst coated onto high-performance strontium-hexaaluminate catalyst supports on alumina-foam monoliths. Reformate composition is measured using an Agilent micro-gas chromatograph. The experiment can be integrated with an SOFC electrochemical test stand currently on hand and operational at the CFCC.

In concert with this experiment a chemical-kinetics computational model has been developed to predict reformate composition across the range of reforming approaches. Utilizing the Sandia-developed Cantera chemically reacting flow software package, this reforming model employs porous-media transport and multi-step elementary heterogeneous chemistry for reformation of methane on a rhodium-based catalyst. The computational and experimental tools developed through this project have been used to explore three types of biogas-reforming approaches: catalytic partial oxidation (CPOX) using air as the oxidizer, CPOX using pure O$_2$ as the oxidizer, and dry (CO$_2$) reforming of biogas fuels. It is important to note that waste-water treatment facilities often include cryogenic-oxygen systems for more-efficient oxidation of water-bound wastes. This oxygen could also be directed to the fuel cell system for use in biogas fuel processing, motivating our study biogas-CPOX using pure-O$_2$ oxidizer streams.

The biogas reformate generated by these three different reforming strategies was fed to a SOFC provided to the CFCC by industrial partner CoorsTek, Inc. Performance results are shown in Figure 1 at an operating temperature of 850°C under flooded-fuel conditions. Cell performance is compared across the different biogas fuel-reforming approaches, and compared to hydrogen-fueled operation. Cell performance under CPOX reforming rivals that of pure hydrogen, while performance under dry-reforming conditions is significantly lower. As these tests were conducted under “flooded-fuel” conditions, fuel dilution and concentration polarization losses were minimized,
possibly masking the effects of the high nitrogen dilution found in CPOX-air conditions. In future studies, we will expand on this biogas fuel-processing work to include steam reforming, and more-widely explore biogas fuel-processing operating windows.

We are also examining the on-board processing of biomass-derived butanol fuel by mating efficient vaporization and mixing with high-performance ceramics-based micro-channel reactive heat-exchanger/fuel-reformer devices. This effort builds on the biogas fuel reforming experiment discussed above, adding a liquid-fuel, gas-oxidizer mixing unit and micro-channel reactive heat exchanger. We are developing the ceramic micro-channel reactive heat-exchanger technology through close collaboration with industrial partner CoorsTek, Inc, with reactor images shown in Figure 2. These micro-channel reactors offer great advantages over conventional shell-and-tube reactors through improved heat transfer and thermal regulation of reforming processes. Exothermic reforming processes can cause hot spots in conventional reactors that reduce the efficiency and effectiveness of the reforming process. Similarly, supplying heat for endothermic-reforming processes can pose significant parasitic losses in SOFC systems. In micro-channel reactors, the hot and cold streams are tightly integrated, so that thermal regulation is maximized. Additionally, this micro-channel heat exchanger is fabricated using low-cost ceramic materials ($\text{Al}_2\text{O}_3$) that are joined in a single high-temperature sintering process, greatly reducing the materials and fabrication costs of the device, which greatly decreases SOFC balance-of-plant expenses.

Ceramic heat exchangers are being fabricated at CoorsTek, and provided to the CFCC for application of a catalyst onto the reactive side of the heat exchanger. Building on the biogas-reforming work described above, a rhodium catalyst with a Sr-hexaaluminate support is utilized. The reactive heat exchanger has been used for catalytic partial oxidation of butanol to syngas; reformate compositions are shown in Figure 3 as a function of total fuel flow rate. As flow rate increases, the quality of the reformate composition is found to increase dramatically. This highlights the close coupling of heat transfer and fuel-reforming effectiveness in this type of reactor. While this demonstration is highly encouraging in validating the concept of the integrated ceramic reactive heat exchanger, further work will be conducted during the course of this program to optimize the fuel-processing conditions.

Advanced hybrid computational modeling tools are being developed that mate high-order Fluent-based computational fluid dynamics with high-fidelity Cantera-based chemically reacting flow. The tools are being applied to the integrated reactive heat exchanger discussed above, and used to examine the effects of design choices on heat-exchanger and fuel-reformer effectiveness. A result for the non-reactive case is shown in Figure 4. The flowfield appears to be well

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**FIGURE 1.** Electrochemical performance of SOFC under biogas reformate. Chart includes comparison to performance under hydrogen fuel.

**FIGURE 2.** Integrated ceramic micro-channel reactive heat exchanger: a) exploded design image; and b) photograph of heat exchanger cross section, highlight micro-channels.
balanced, with near-uniform flow conditions across the micro-channels that constitute the heat exchanger. Additionally, the gradual changes found in the temperature field create confidence that thermal stress is well balanced in the device, a significant concern when utilizing ceramic components. Further modeling work will include the chemically reacting flow simulations to provide guidance for optimizing fuel-reforming operating windows in the reactive heat exchanger.

Model-Predictive Control

Model-predictive control provides a means to incorporate fundamental physical and chemical understanding into real-time, multiple-input/multiple-output, process-control strategies. The reduced-order models are derived from large high-fidelity physical models, while system identification is accomplished by driving the physical models with actuation inputs consisting of pseudo-random binary series and observing the responses. The process depends upon having time-accurate physical models. The effort here is two-fold. First is to develop and validate the physical models for SOFC systems operating on reformed biomass-derived fuels. Unlike many fuel cell models based upon steady-state assumptions, the models here must be written to represent time-accurate transient solutions. Moreover, they must be written to accept pseudo-random binary series inputs and return high-accuracy transient response signals used for the system identification.

In this task, we are applying model-predictive control strategies to operation of fuel reformers like the micro-channel devices described previously. Initial efforts are directed toward the simpler ceramic-foam reformer utilized in the biogas experiments. We are now examining the thermal capacitance of the biogas reactor to establish dynamic response to process variations. We have successfully mapped the thermal response of the reactor under non-reactive conditions, and compared this response to dynamic-model predictions; excellent agreement was obtained. In future efforts, we will expand this work to reactive conditions; as model fidelity improves, we will expand this work to examine and control the response of the micro-channel reactive heat exchanger devices.

Future Directions

Biomass-Derived Fuel Processing

- Explore steam-reforming and anode-recycle processing of biogas fuels.
- Extend partial-oxidation experiments on butanol fuel in integrated ceramic micro-channel reactive heat exchanger.
- Develop process windows for deposit-free SOFC operation under butanol reformate.
- Extend hybrid CFD/chemical-kinetics modeling to examine effects of fuel-processing strategies on heat-exchanger effectiveness and fuel-reformate composition and quality.

System Control

- Implement explicit form for model-predictive control for use in biogas-reforming system.
- Extend model-predictive control strategy to reactive heat exchanger.
Objectives

The overall objective of this project is to optimize and scale up the process to make Dynalene FC fuel cell coolant with a great deal of reproducibility. The following are some specific objectives that would help to reach the overall goal of the project:

- Demonstrate the production of one key ingredient of the coolant (a nanoparticle) in 10 L, 20 L and 100 L batches in a pilot-scale operation and study the effect of various process parameters on the size and charge density of the particles.
- Produce the nanoparticles necessary for the fuel cell coolant, Dynalene FC, in a very consistent manner (i.e., particle size, charge density and yield).
- Optimize the filtration process for the nanoparticles to minimize the cleaning time for different scales of operation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Durability
- Cost

Technical Targets

Dynalene FC is expected to help the fuel cell industry achieve their durability and cost targets to some degree. First of all, the coolant itself is being designed to have a life of 5,000 hrs. It is also expected to have excellent compatibility with the system materials and inhibit corrosion in the coolant loop. This will help in extending the durability of the fuel cell system components such as the pump, the radiator, valves, seals/gaskets and any other components coming in contact with the coolant. The coolant is also designed to work at -40°C, which will assist both transportation and stationary fuel cells to quickly warm up during cold starts.

The cost target for the coolant (in plant-scale production) is about $10/gallon, which is very close to the retail price of current automotive coolants. This coolant will also eliminate the deionizing filter and other hardware associated with it (i.e. fittings, valves). It is also being designed to work with cheaper, lighter and thermally efficient components such as aluminum radiators (instead of stainless steel) and brass heat exchangers.

Accomplishments

Dynalene FC has been demonstrated by field testing to maintain a very low electrical conductivity and stay stable over several years. This was possible due to the addition of a nanoparticle into the coolant. This project addresses the optimization and scale up of this nanoparticle ingredient. The main accomplishments in the first few months of the project are the design of the reactor systems, procurement of the reactors and the components and commissioning.

Introduction

This project addresses the goals of the Fuel Cell Technologies Program of the DOE to have a better thermal management system for fuel cells. Proper thermal management is crucial to the reliable and safe operation of fuel cells. A coolant with excellent thermophysical properties, non-toxicity, and low electrical conductivity is desired for this application.

Dynalene Inc. has developed and patented a fuel cell coolant with the help of DOE Small Business Innovation Research Phase I and Phase II funding (Project # DE-FG02-04ER83884). However, this coolant can only be produced in lab-scale (500 ml to
2 L) due to problems in optimization and scale up of a nanoparticle ingredient. This project will optimize the nanoparticle production process in 10 L, 20 L and 100 L reactors, optimize the filtration process, and develop a high throughput production method for the final coolant formulation.

**Approach**

Dynalene researchers have been producing the nanoparticles ingredients used in the fuel cell coolant in 100 ml, 500 ml and 2 L reactors. The main parameters that contribute to the quality of the nanoparticles are size and surface charge density. Another important factor needs to be optimized is the yield from the production as well as cleaning/filtration. At 100 ml scale, the nanoparticles were produced using magnetic stirring and the heating was provided by a constant temperature bath. At the 500 ml scale, the stirring mechanism was changed to a mechanical stirrer with impellers, while the heating mechanism was still through a constant temperature bath. At the 2 L scale, the stirring was through a mechanical stirrer whereas the heating was accomplished by pumping hot water through the jacket of the reactor. In this project (for 10 L and 100 L reactors), mechanical mixers with multiple impellers and heating systems using the jacket of the reactor will be used. Mixing/stirring mechanism as well as the heating method impacts the particle size, charge density and the yield of the reaction. Therefore, an understanding of the influence of these parameters is very essential to obtain the nanoparticles with reproducible properties. Dynalene and Lehigh University have partnered to develop the scale up criteria needed to go from a 2 L scale to a 10, 20 or 100 L scale.

**Results**

Three glass reactors (one 10 L, one 20 L, and one 100 L) were purchased by Dynalene (Figures 1 and 2). During the course of the last quarter all reactors have been received and assembled.

A great deal of time was spent modifying the 20 L reactor that was purchased in an auction and not pre-customized to the specifications necessary to complete the scope of this project. Those modifications are completed and mixing studies have begun to optimize impeller placement and mixing speed. Reactors of this size require two impellers on the stir shaft and proper placement is crucial. The mixing experiments were done using an oil containing dye along with water to simulate the monomer/water mixture that is the basis of the nanoparticle synthesis. The studies are progressing well but more thorough experiments are necessary.

The heating and cooling system for the three reactors has been completed and installed. Heating and cooling experiments on the 20 L reactor have been run with water as the medium to simulate the reaction conditions. Some minor modifications were necessary to correct some initial problems with the system.

The 10 L and 100 L reactors have been assembled and similar testing on these will be performed in the future.
Optimization experiments on the 500 ml and 2 L scale of the anionic and cationic nanoparticles have led to narrowing some of the independent and dependent variables of scale. These small-scale reactions on the cationic nanoparticles have produced two possible recipes for further scaling. Both of these recipes will be studied at the 10 L scale to determine the best candidate for further work. The variables that need to be considered for scaling are listed below and need to be monitored at each scale up step.

Independent Variables:
- Mixer type
- Angle
- Speed
- Reactor type
- Baffled/non-baffled
- Recipe
- Temperature
- Heat transfer mechanism

Dependent Variables:
- Size
- Surface charge density
- Yield
- Time of reaction

More than 20 batches of anionic nanoparticles were produced at the 2 L scale. All batches showed yield of greater than 20% solids. Purification of the nanoparticles will be carried out at this level. Purification by tangential flow filtration (TFF) requires that the solids concentration be a maximum of 8%. A large dilution was necessary to achieve the proper flow through the membrane. Purification of 500 ml scale reactions can typically take two to three days after dilution so this larger purification would definitely lead to a bottleneck in the process.

The TFF system was set up with two membranes instead of one to double the surface area for cleaning. A dilution of 2 L to approximately 16 L was necessary for purification. A system using a large reservoir and the vacuum caused by the filtering was set up to constantly replenish the water lost during the process. This allowed for continuous filtering at a constant volume and decreased the time needed for cleaning from two or three days down to one day.

Following is a list of parameters for optimization of filtration:
- Flow rate
- Pressure
- Concentration (solids percentage)
- Membrane pore size
- Membrane construction (polyether sulfone or ceramic)
- Additives
- Mixing in reservoir

Dynalene is also studying a new ceramic TFF filter system, which may speed up the filtering process. This system may also have another benefit of allowing purification of both anionic and cationic particles in the same filter. The current process requires two separate systems for filtering. An initial study showed proof of concept in a short-term test with a membrane manufacturer. A longer, more substantial trial is being scheduled at this time.

Conclusions and Future Directions
Dynalene has set up all the reactors for the nanoparticle production. After some preliminary testing, the 10 L and the 20 L reactors will be used for the synthesis of the nanoparticles. The scale up criteria developed in collaboration with Lehigh University will be verified.

The immediate tasks to be performed are as follows:
- Further testing of the heating and cooling components of the reactor system will be carried out to make sure that they are operating.
- Mixing parameters for the 10 L and 20 L reactors will be optimized.
- Scale up experiments for the anionic and cationic nanoparticles will be started.

FY 2010 Publications/Presentations
Objectives

• The overall objective of the research program is to provide new electrolyte membranes and electrode materials consisting of integrated catalysts and fluorinated electrolytes for use in PEMFC power sources.

• The research will be pursued in two thrusts, one focused on new proton-conducting fluoropolymer electrolyte membranes for use under high-temperature (95 - 120 °C) and low-humidity (25 - 50% RH) conditions, and another focused on electrolyte integration into fuel-cell electrodes by covalent attachment of electrolytes onto carbon supports.

• The objectives of work in the first thrust area are the discovery, synthesis, characterization, and evaluation of new polymeric proton-conducting electrolyte membranes.

• The objective of work in the second thrust area is to develop methods for accomplishing robust attachment of proton-conducting polymer electrolytes onto carbon supports, and to characterize the resulting materials with special attention to their mixed electronic and ionic conduction and electrochemical properties.

Technical Barriers

• This research seeks to overcome technical barriers to implementation of PEMFC technology associated with low protonic conductivity in polyelectrolyte membranes at high temperatures and low water activities.

• It seeks to develop polymer electrolyte membranes that will overcome this conductivity barrier while also retaining dimensional stability (little to no swelling on contact with liquid water) and durability (lifetimes up to 5000 hours are desired).

Abstract

Project work focusing on blended fluoropolymer ionomers, mesoporous carbon supports for PEM fuel cell electrode, and grafted electrolytes within pores of mesoporous carbon and nanocomposite mesoporous carbon / zirconis supports is reported. Blended ionomers have conductivity comparable to that of PFSA ionomers with less swelling and improved dimensional stability. Mesoporous carbon supports were prepared by a silica sol templating approach and were shown to have very high pore volume, which is posited to allow for rapid transport into and out of pores. Monomolecular (non-polymeric) electrolytes were grafted inside pores but so far improvements in fuel-cell performance have not been realized. Ongoing work will seek to graft polyelectrolytes inside support pores, which is believed to be necessary to realize improved performance.

Progress Report

1. Blended ionomers. Blends of PFSI and S-PFCB (see Figure 1 for structures) were prepared in various compositions between 70:30 and 50:50 mole ratios of PFSI to S-PFCB. The resulting blends have conductivity comparable to Nafion® 112 in the 0-70% RH range, and also lower swelling than the non-blended S-PFCB ionomer. Preliminary studies on blending heteropoly acids (HPAs) and
on electrospinning of ionomer blends were also undertaken.

2. **Mesoporous carbon supports.** Mesoporous carbon (MC) supports for Pt in PEMFC electrodes were prepared by making resorcinol-formaldehyde (RF) carbon aerogels with colloidal silica added, followed by silica removal using caustic. The resulting supports had high surface area and very high pore volume (over 4 cc/g). Platinum deposition was accomplished via formaldehyde reduction of hexachloroplatinate deposited by the incipient wetness method. In-situ CV of electrodes fabricated on glassy carbon supports (Figure 2) showed high Pt surface area and small particle sizes. Membrane-electrode assembly fabrication onto Nafion® membranes using conventional conditions (approx. 30 weight percent Nafion®) failed due to poor dimensional stability of the composite electrodes. This fact is thought to be due to Nafion® being taken up into the support pores, which left none to accomplish electrode binding. Ongoing work will focus on electrode formulations having more Nafion®, and on covalently grafted ionomers in the pores.

3. **Mesoporous carbon supports with grafted electrolytes.** Work on grafting small-molecule aryl fluorosulfonimide electrolytes onto mesoporous carbon continued and was completed this year. Grafting of monolayers of acid electrolyte onto mesoporous carbon was demonstrated using aryl diazonium salts. Ion-exchange capacities of the resulting materials were relatively low (less than 0.2 meq/g) and fuel-cell performance of MEAs fabricated using Pt/carbon having grafted aryl fluorosulfonimide electrolytes was not greatly different from that of MEAs prepared using carbon without the grafted electrolyte. We believe this reflects the relatively small amount of electrolyte that was ultimately grafted.

We desired access to a simpler chemistry for grafting larger amounts of electrolyte, possible polymeric electrolytes, inside the pores of mesoporous carbon supports. To accomplish this aim, mesoporous carbon supports were prepared using the RF method with both colloidal silica and zirconia added, followed by etching to remove silica but not zirconia. The resulting supports are nanocomposites of carbon containing nanoscale zirconia. Subsequent modification of these supports with the difunctional acid, meta-sulphophosphonic acid, was accomplished. Titration of the resulting supports confirmed incorporation of sulfonic acid groups. Ongoing work seeks to increase the amount of incorporated acid both by increasing the amount of zirconia in the carbon / zirconia composite, and also by utilizing telechelic S-PFCB polymers having phenyl-phosphonic acid end groups (see Future Directions).

**Future Directions**

Future work is planned on several fronts. Ionomer blends will continue to be studies with a focus on combinations of low-EW ionomers that can retain water and provide high conductivity, with high-EW ionomers to provide dimensional stability and limit swelling. Crosslinking strategies will be pursued that can stabilize membranes after casting. One such approach will involve new perfluorocyclopentenyl-based ionomers for which a synthesis is shown in Figure 3. The double bond in the PFCP group is a potential site for crosslinking that may be initiated thermally following membrane casting.
Work on telechelic S-PFCB polymers having terminal phenyl-phosphonic acid groups to provide anchoring sites for zirconia will be pursued to provide a route to nanocomposite carbon / zirconia catalyst supports having high ion-exchange capacities of ionomer integrated into electrolyte pores. Figure 4 presents an illustrative structure of a bound ionomer bound at a terminal phenyl-phosphonic acid group. This work will build upon our prior work demonstrating binding of meta-sulpho-phenyl-phosphonic acid onto zirconia groups in carbon / zirconia composite catalyst supports.

Publications (including patents) acknowledging the grant or contract


Objectives

We are developing first-principles based methods for predicting the solubility and diffusivity of hydrogen in amorphous metal alloys. These methods are being used to seek new alloy compositions that will allow the fabrication of dense metal membranes for hydrogen purification that will exceed the performance limitations associated with well-known crystalline metal membranes.

Technical Barriers

A number of experimental groups have demonstrated that it is possible to fabricate useful dense metal membranes from amorphous metals. Unfortunately, the large number of possible amorphous metal compositions makes experimental screening of these materials for membrane applications impractical. We are developing quantitative modeling methods that can aid in the discovery of new membrane materials by making predictions about membrane performance prior to experimental testing.

Abstract and Future Directions

Within this project, we have demonstrated the development of methods to make quantitative predictions about the performance of amorphous metal films during use as hydrogen purification membranes. The modeling framework for the analogous problem with crystalline metals is relatively well developed, but the disordered nature of the interstitial sites in amorphous metals required extensive method development. In brief, our first-principles calculations for amorphous metals proceeds by (i) using *ab initio* Molecular Dynamics methods to create representative amorphous solid structures within a periodic supercell geometry, (ii) use efficient methods based on empirical forcefields to initialize first principles calculations to find the energy of H in all interstitial sites in the material, and (iii) use efficient methods to initialize first principles calculations to locate all transition states for H hopping between adjacent interstitial sites. Once the binding sites and transition states are known, Grand Canonical Monte Carlo (GCMC) and Kinetic Monte Carlo (KMC) calculations are used to accurately describe the net solubility and diffusivity, respectively, of H in the amorphous material. These calculations include a characterization of the H-H repulsion that occurs at levels of interstitial H at which the interstitial species is not dilute. We have characterized this phenomenon via extensive first-principles calculations.

An important general property of amorphous metals is that the solubility of H in these materials is quite high due to the energetically favorable interstitial sites that are created by the amorphous material. At non-dilute concentrations, the differences that exist between various different diffusion coefficients (e.g. the self diffusion coefficient and the Fickian diffusion coefficient) become significant. Previous studies of H diffusion in crystalline metals had only examined the self diffusion coefficient. We have extended our KMC methods to allow the direct calculation of the Fickian diffusion coefficient. It is this diffusivity that is of the greatest physical interest in describing macroscopic mass transport through a membrane. In general, the Fickian diffusivity is larger than the self diffusivity at the same conditions. At high concentrations of interstitial H, the expansion of an amorphous alloy due to the interstitial H can also have a marked effect on the net solubility of H. We have developed efficient methods that allow us to quantify this effect.

We have demonstrated the validity of our modeling approach by comparing predictions from our models with experimental data that is available for permeation of hydrogen through amorphous ZrNi and ZrNiNb films. Once the effects of hydrogen-induced lattice expansion and concentration-dependent diffusion coefficients are taken into account, our model's predictions are in quantitative agreement with experimental data. Crucially, our approach does not require any experimental data, so it can be used in a truly predictive sense. We are currently using our method to screen a variety of binary and ternary alloys that are known to be good glass formers with high glass transition temperatures with the aim of identifying materials that will exhibit high permeability for hydrogen when used as membranes.

In addition to our work on amorphous metals for hydrogen purification, we have performed work on the related topic of understanding hydrogen diffusion in ionic hydrides. Specifically, we examined the diffusion mechanism of hydrogen in two prototypical ionic hydrides, MgH$_2$ and NaMgH$_3$. An interesting conclusion from this work was that the relevant species that control
the mobility of H in these materials are charged, unlike the neutral species that control interstitial diffusion in metallic systems. Understanding the characteristics of H diffusion in these two materials opened the possibility of finding dopants that would accelerate H diffusion, and we used first-principles calculations to examine a larger range of possible dopants for this purpose. We also performed similar calculations for several light metal borohydrides, including LiBH₄. A surprising outcome from these calculations is that hydrogen diffusion in these materials appears to be mediated by formation of neutral molecular H₂ within the solid.

Publications (including patents) acknowledging the grant or contract

Objectives

It is our objective to develop new theoretical and computational techniques to investigate the structure and transport properties of hydrated ionomer membranes, and thereby to enable the development of new and more useful materials for use in polymer electrolyte membrane fuel cells. Specifically, our aim is to produce a tool to predict both the nanophase structure and the proton transport properties for any given membrane material and level of hydration. In this way we hope to develop a deeper understanding of the dominant factors affecting the nature and magnitude of the proton transport.

Technical Barriers

One of the most significant technical barriers to the improvement of polymer-electrolyte fuel cells lies in our lack of understanding of the formation of the continuous hydrophilic pathways necessary for proton conduction. Another serious obstacle is the difficulty of achieving high proton conductivities in a low-humidity environment. In our research, we face the obstacle of the extremely large computer resources required for an accurate simulation of large volumes of membrane electrolyte material. This necessitates our use of a combination of theoretical analysis with united-atom simulation techniques to reach viable conclusions in reasonably short computation times.

Abstract

We have used a combination of analytical theory and molecular-dynamics simulations to investigate the effect of various material parameters on the structure and proton conductivity of Nafion-like ionomer membranes. This has included the effects of varying the length of the molecular side chains and their spacing along the polymer backbone, as well as membrane stretching, membrane poling by the application of strong electric fields, and inclusion of hydrophilic nanoparticles. Most recently we have studied the effects of confining the ionomer inside cylindrical pore channels penetrating an inert membrane.

Progress Report

During the past year we have used molecular-dynamics simulations to explore the consequences of modifying an ionomer membrane in numerous ways [1,2]. We have extended and solidified our previous preliminary results on the effects of strong electric fields on a Nafion-like ionomer, and have confirmed that an aligned structure consisting of a hexatic array of one-dimensional ion channels is thermodynamically stable. This structure has enhanced proton conductivity through the membrane, as the channels follow the direction of the applied poling field. We determined the role of some ionomer structural parameters in the formation of this ordered hexatic phase in poled membranes. We found that it is the length of the side chains that effectively controls the two-dimensional density of the cylindrical rod-like sulfonate clusters. In membranes with shorter side chains, the lattice constant of the hexatic phase is about twice the length of the sidechain. In this case the backbone matrix does not hinder the formation of rod-like clusters, and there is negligible elastic stress. However, in membranes with longer sidechains, which would give rise to larger cluster formations in an unpoled membrane, the sidechain-polymer entanglements restrict the clustering of sulfonates in the poled material. The number of cylindrical clusters in this case is thus controlled by a delicate balance between the effective sulfonate-sulfonate attraction and the elastic forces resisting backbone deformation. The latter makes the formation of larger clusters unfavorable, thereby making the two-dimensional density of induced cylindrical aggregates in poled ionomers higher than expected from theoretical predictions. We have also shown that ion diffusion in poled membranes is strongly anisotropic, and depends on the structural parameters of the hexatic phase. When the backbone segment length in homologous membranes (membranes with constant sidechain length) is decreased, thicker ionic cylinders with shorter sulfonate separations in them are formed. In this case the diffusion of protons both along the poled structures and perpendicular to them increases as an inverse function of the backbone segment length. Thick cylinders are also formed in constant equivalent-weight membranes with longer sidechains and shorter backbone segments. However, in this case the cylindrical
aggregates are highly tortuous, and this inhibits the diffusion of protons along the poled pathways.

Another area of our research concerned the effects of nanoparticle inclusions in ionomer membranes [3,4]. We first analyzed the distribution of conducting ions in these nanocomposite membranes. Our simulations showed that, in the case of neutral particles, the proton distribution is almost unperturbed. This reflects the fact that the hydrophilic channels are homogeneously distributed in the membrane. When the particle-membrane interaction is hydrophilic, however, all the conducting ions accumulate near the nanoparticle surfaces [3]. When the surface area of a single nanoparticle is insufficient to accommodate the accumulated ions, a second layer of ions is formed. We found that such ‘surface assisted’ proton clustering can drastically affect the membrane conductivity, sometimes increasing it by as much as an order of magnitude. In the case of a hydrophobic particle-membrane interaction, the diffusion pathways formed by the hydrophilic ions are repelled from the nanoparticle surface. Thus proton transport across a membrane can be optimized with the right combination of nanoparticle size and concentration.

We have also analyzed the effect of changing the length of the side chains, and the spacing between them along the polymer backbone, on the shape of the hydrophilic network of sulfonate clusters created by their partial phase separation from the hydrophobic backbone material. Various modifications of a Nafion®-like ionomer have been studied. These include ionomers having a backbone spacing up to twice that of Nafion® and those having side chains with a length up to three times that of Nafion®. We showed in detail how two membranes with the same equivalent weight but different detailed architectures can have completely different morphologies. In ionomers having longer sidechains, we find that larger sulfonate aggregates with a higher sulfonate population are formed. In ionomers with shorter side chains, the ion diffusion in small clusters is mostly based on an ion-hopping mechanism between adjacent sulfonates. Inside the larger clusters found in ionomers having longer sidechains, however, the proton transfer has additional contributions from vehicular and Grotthuss dynamics. In membranes with higher sulfonate concentration and longer sidechains, the nearest-neighbor distance between clusters becomes small enough for temporary inter-cluster bridges to be formed, and this facilitates the overall proton diffusion in the membrane.

In our most recent work we have analyzed the nano-morphology of low-water-content ionomers contained within cylindrical pores [5]. Our results reveal a strong enhancement of ion diffusion [6]. We find that when the pore diameter $D$ is larger than the length $d$ that characterizes the typical sulfonate cluster size in a bulk ionomer, the protons accumulate near the pore surface and in the central area of the pore. When $D = d$, the protons cluster mostly in the vicinity of the pore wall. For $D < d$, the continuity of the proton distribution along the pore axis is disrupted to such an extent that water-ion aggregations form a network of separate clusters aligned along the pore axis. In narrow pores the ions mostly occupy the central pore area. There is also positional correlation between the ion and sulfonate radial distributions. In smaller pores the central area is predominantly occupied by conducting ions. The calculated proton diffusion coefficients for ionomers contained in nanopores of various diameters show a nonlinear dependence on the pore diameter. We have shown that the ion diffusion at first drops and then experiences a steep increase when the pore becomes narrower. This enhancement of the diffusion is associated with the correlated movement of individual ion-water clusters: at any given time all ion clusters move in the same direction. This unexpected result
Future Directions

The goal of our work is to use simulation methods to lead us to the discovery of new morphologies of ionomer membranes that may give enhanced proton transport and robust structures in fuel-cell applications. To achieve this we will pursue several different avenues.

First, we will extend our study of the influence of nanoparticle inclusions on the structure and transport properties of ionomer membranes. We will investigate how spherical inclusions with different sulfonate and water interaction potentials change the ionomer morphology. It is expected that in the case of hydrophilic inclusions their surface can serve as a bridging pathway for facilitated proton transfer between neighboring ionomer clusters. Alternatively, hydrophobic inclusions will most probably accumulate PTFE-rich polymer backbone material on their surfaces, and could distort the shape of ionic clusters towards a more connected topology with branching channels. We intend to calculate how the proton diffusion depends on the size, hydrophilicity, and concentration of inclusions. We also plan to investigate the ionomer reaction to the charge and surface potential of nano-inclusions. It is natural to assume that inclusions with tailored surface groups capable of releasing protons into a hydrated membrane can have the potential to increase its proton conductivity.

Another area of great interest is the structure produced by taking an inert membrane that is pierced by cylindrical holes, which are then filled with ionomer. Our recent results on nanopore-constrained ionomers include the finding that ion diffusion can be strongly enhanced in narrow tubes, and so we intend to put this study on a firmer footing by extending our simulation studies to a wider variety of systems. This is important from a technical point of view, since the ionomer-filled nanopore matrix is a robust and durable platform, and has the capacity to reinforce the ionomer membrane’s mechanical stability against damage from swelling and cracking in operating fuel cells. To understand the physics behind the transition from spherical clusters of sulfonates to wire-like clusters in narrow pores is important for devising new nanocomposite materials with extremely high ion conductivities. We will also analyze how the side-chain flexibility, the length of side chains, and the nanopore-ionomer interaction parameters affect the overall ion diffusion along the nanopore axis.

Finally, we remark that all our poling and stretching molecular-dynamics simulations have so far been carried out at room temperature. We plan to extend our studies to higher temperatures and pressures to explore any possible new phases that might be formed.

References


Publications (including patents) acknowledging the grant or contract


Objectives

The objective of this work is to develop a model capable of describing the molecular mechanisms of proton transport in highly confined and highly acidic environments. Specifically, we seek to develop a molecular-level understanding of how confinement and acidity impact both the vehicular and structural components of proton transport. To this end, we develop a Reactive Molecular Dynamics (RMD) algorithm that is capable of describing both components of proton transport, with sensitivity for each component to the local environment. We apply this RMD algorithm to describe proton transport in four systems: (1) bulk water, (2) bulk HCl solutions, (3) carbon nanotubes, and (4) hydrated perfluorinated sulfonic acid (PFSA) proton exchange membranes (PEMs). These four systems allow us to decouple the effect of confinement and acidity on vehicular and structural components of proton transport.

Technical Barriers

This work is motivated by practical technical barriers and addresses theoretical technical barriers. On the practical side, the structure-property relationships obtained from a fundamental understanding of the molecular mechanisms of proton transport in highly confined and highly acidic environments would provide guidance for the development of next generation PEMs. On the theoretical side, the hydrated PEM in a fuel cell contains phenomena that occur over disparate time scales. At the shortest time scale, there is the description of a single proton hopping event, occurring on the order of femtoseconds (10^-15 s) and best described by quantum mechanical techniques; while at the next time scale, vehicular diffusion may take 10s or 100s of nanoseconds, which requires classical molecular dynamics simulation.

The RMD algorithm provides an efficient procedure for including both structural and vehicular diffusion in a simulation.

Abstract, Progress Report and Future Directions

Proton transport in aqueous solutions occurs through a combination of mass diffusion and structural diffusion. The structural diffusion of a proton, as a reaction, can be given as

\[ H_2O^+ + H_2O \rightleftharpoons H_3O^+ + H_2O \]

Transport of the proton by Grotthuss mechanism was implemented using a newly devised reactive molecular dynamics (RMD) algorithm. In this approach, a three step procedure was incorporated to the existing classical molecular dynamic simulation to allow the explicit proton transfer from a hydronium ion to a water molecule based on quantum mechanical transition and ground state configurations to reproduce macroscopic reaction properties. The reactive part of the RMD algorithm is composed of the following steps:

1. Satisfaction of triggers – checks whether the reactants are in a favorable configuration for the reaction to take place by satisfying a set of geometric and energetic triggers based on the transition state obtained from \textit{ab initio} calculations.
2. Instantaneous reaction – coarse grains out the reaction path and the proton gets transported instantaneously from the hydronium ion to a water molecule.
3. Local equilibration – satisfies the target heat of reaction and ensures the products are in correct ending configuration.

The algorithm was validated by modeling structural diffusion of proton in an extensively studied system for which the most reliable data are available, namely bulk water. The determination of the functional form of the triggers were based on the structure of the predominant hydrated models (Zundel and Eigen cations) necessary for the structural diffusion of protons and were parameterized to reproduce the experimental rate constant and activation energy. Using this procedure, 150 replicates of a single hydrated proton in a system of 650 water molecules were studied as a function of temperature from 280 K – 320 K. By fitting the reaction rate the model predicts the transport property of the proton. A detailed study of the two components (structural and vehicular) of the total charge diffusion was conducted. Other systems were also modeled with the new algorithm to study its sensitivity and
the adaptability to different environments. The RMD algorithm endeavors to have a valid starting and ending configuration for the structural diffusion by mapping the transition state onto a set of triggers without having to dynamically describe the transition state structure. Therefore, the algorithm is generalized by the environmentally sensitive geometric and energetic triggers.

The pH dependence of proton transport was investigated by implementing the algorithm for bulk aqueous HCl solutions with different concentrations (0.22 M – 0.83 M). The presence of the chloride ion disrupts both the structural and energetic environment for the occurrence of the reaction and was effectively captured by the triggers. Proton diffusion in water confined in carbon nanotubes of radii ranging from 5.42 Å – 10.85 Å was studied to analyze the effect of confinement on structural and transport properties of a proton. The model shows that enhanced confinement drastically reduces structural diffusion by disrupting the energetic balance around the Zundel ion.

Having independently examined the effect of acidity (HCl solution) and confinement (carbon nanotubes), we next apply the RMD algorithm to proton transport in a system that contains both confinement and acidity, namely hydrated PFSA PEMs. The structural diffusion of proton in hydrated membrane can take place via three classes of reactions.

\[
\begin{align*}
H_3O^+ + H_2O &\rightleftharpoons H_2O + H_3O^+ \\
H_2O^+ + H_2O &\rightleftharpoons nH_2O(4\alpha-n)SO_3H + nH_3O^+ \\
SO_3H + H_2O &\rightleftharpoons 2H_2O + SO_3^- + H_3O^+
\end{align*}
\]

The prevalence of each reaction is dependent on the degree of hydration of the membrane, which the first reaction being most important at high water contents and the last reaction being least important at high water contents. Equation 1 is similar to proton transport in bulk water and will take place along the center of the aqueous channels and reactions as shown in equations 2 and 3 will occur at the interface of the hydrophobic and hydrophilic regions. RMD algorithm can accommodate all the above reactions and the triggers can register the presence of the sulfonic acid groups and other environmental factors like confinement (as shown in the earlier systems). These reactions are individually implemented in three different stages to better understand the contribution of each reaction to the structural diffusion of proton in the PEM at different hydration levels. Thus the algorithm will allow us to measure the diffusivities in the hydrated membranes and provide a molecular level understanding of how the environment in the nano-aqueous regions impact proton mobility.

Publications (including patents) acknowledging the grant or contract


V.P.5 Surface-Directed Fabrication of Integrated Membrane-Electrode Interfaces

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Objectives

Current fabrication approaches\textsuperscript{1,2} for proton exchange membrane (PEM) fuel cells rely on ill-defined, planar interfaces that reduce the performance of the system. The departure from planarity to 3-D interfaces with porosity should provide a boost in power\textsuperscript{3} due to additional surface area for catalysis to support higher mass transfer rates.\textsuperscript{4} In this project, we are investigating the integration of electrode/catalyst support, gas diffusion pathways, and ionomer into a single network based on a bottom-up, surface-directed approach. Our efforts are focusing on (1) the preparation of surface-initiated ionomer that can be grown from electrodes of essentially any geometry and is chemisorbed to the active electrode surface, and (2) the integration of this ionomer with both planar and porous electrodes that are atomically modified by Pt catalysts.

Technical Barriers

The departure from planarity to porous systems creates difficulties in integrating ionomer and catalyst uniformly throughout the porous electrode structure. We are developing an approach where the electrode surface directs the deposition of catalyst and the growth of ionomer, monomer by monomer, to achieve an exceptional level of control over the composition and structure at this vital interface. Focusing initially on the cathode, our system consists of a thin nanoporous gold support that is atomically modified by a Pt monolayer for ultra-low catalyst loadings and is integrated with ionomer through surface-initiated polymerization (SIP). The surface-directed deposition of catalyst and ionomer enables high control over the composition within nanoporous electrodes. Results under the current funding have demonstrated that proton-conducting polymers can be grown from various surfaces by surface-initiated ring-opening metathesis polymerization (SI-ROMP) of 5-(perfluoro-n-alkyl)norbornenes and subsequent rapid sulfonation of the internal olefins. These films can be integrated with Pt catalysts at interfaces for high performance in the oxygen reduction reaction.

While much of our initial work has focused on materials synthesis and integration, our most recent work is utilizing these systems to gain fundamental insight on the effects of materials composition and properties at 3-D interfaces to optimize cathode performance. Specifically, we seek to (1) establish greater versatility in the preparation of nanoporous electrodes to control pore size, porosity, and electrode thickness; (2) develop new “interfacial” ionomer systems from surface initiation, grafting, and self-assembly to fundamentally assess the effects of interfacial bonding, ionomer composition and structure, as well as free volume within the pores, on the performance of the electrode; and (3) extend these strategies to commercial carbon supports. The successful completion of these objectives will yield well-defined and molecularly integrated materials systems to achieve high utilization of catalyst/electrode surface area with ultra-low catalyst loadings. This research will improve the basic understanding of the complex reaction and transport processes that occur near the triple interface in a fuel cell environment.

Progress Report

Our initial efforts reported the surface-initiated ROMP of n-alkylnorbornenes to control film thickness and composition at electrode surfaces\textsuperscript{3} and the sulfonation of these films to facilitate proton transfer.\textsuperscript{6} More recently, we have developed an approach for the SI-ROMP of partially fluorinated films from
I. Growth of Partially Fluorinated Ionomer Films.

A major emphasis of this project has been to prepare partially fluorinated ionomer films through a surface-initiated polymerization (SIP). SIPs provide the ability to grow films of controlled thicknesses from substrates of nearly any geometry, such as 3-D, porous catalyst/diffusion layers. However, SIP of fluorinated monomers has been historically difficult due to the steric hindrance of the fluorocarbon functionality. In an important innovation, we have developed the surface-initiated ring-opening metathesis polymerization (SI-ROMP) of (perfluoro-n-alkyl)norborenes (NBFn) to form partially fluorinated polymer films (pNBFn) of tunable thicknesses ranging from tens of nanometers to microns on various substrates. The polymers are tethered to the surface on one end and upon sulfonation, have the general repeat structure as shown in Figure 1. By varying the fluorocarbon side chain of the monomer, we can tune the structure (SEM and infrared spectroscopy), transport properties (electrochemical impedance spectroscopy), and critical surface energies (contact angles) of the films. Our results indicate that the fluorocarbon side chains self-organize into fluorocarbon-rich regions. Structuring of the polymer in this manner should be highly effective for PEM fuel cell applications since O₂ would transfer through the fluorocarbon regions and protons would transfer through the sulfonated regions. We have recently published methods to sulfonate hydrocarbon and fluorocarbon films prepared by this method.

II. Extension of SI-ROMP to Carbon Paper.

To demonstrate that pNBFn films can be grown from various substrates, including those with technological relevance, we have developed an approach to grow these films from graphitic carbon paper, which has 3-D fibrous structure. Since graphitic fibers are relatively inert, we expose the carbon paper to an oxygen plasma for up to 1 min to create a few dispersed oxygen-containing surface sites across the fiber surface before attaching the polymerization initiator, which enables SI-ROMP from the fiber surface, as shown in SEM images of Figure 2. These pNBFn-modified carbon paper electrodes exhibit superhydrophobic surface properties, meaning that an impinging stream of water bounces off the surface and that a water drop on the surface will exhibit a contact angle of > 150°. Conformal, hydrophobic coatings such as these can greatly aid water management at PEM cathodes. These films can also be sulfonated to provide surface-attached ionomer to the graphitic carbon surface.

III. Integration of Ionomer Films at Pt-Modified Electrodes.

The direct wiring of ionomer films to electrode surfaces is beneficial to reduce interfacial resistances and boost electrochemical performance in many energy-related applications. However, a key issue regarding the direct chemical wiring of ionomer to electrode/catalyst interfaces is the possible deactivation of the catalyst by the chemisorption event. We have reported the surface-initiated growth and sulfonation of polynorbornene (pNB), poly(n-butylnorbornene) (pNBH₄), and poly(perfluoro-n-butyl)norborene (pNBF₄) to prepare ionomer films on gold electrodes that are pre-modified by an atomic layer of Pt. Our goal here was to demonstrate proof-of-concept systems for the integration of chemisorbed ionomer and catalyst at model electrode surfaces. In this manuscript, we have made some important conclusions. First, the ionomer films can be grown from Pt-monolayer-modified surfaces without compromising the performance or integrity of the Pt. Second, sulfonated films derived from NBF₄ and NBH₄ yield more anodic potentials for oxygen reduction than those derived from NB or unfunctionalized electrodes. These improvements are consistent with hydrophobic structuring by the fluorocarbon or hydrocarbon side groups to generate pathways for enhanced O₂ permeation near the interface. Third, we demonstrate a method to electrochemically “clean” ionomer/electrode interfaces. For example, in surface-initiated polymerizations, only a small fraction (often < 10%) of the surface sites typically yield polymer. For electrochemical applications, these inactive adsorbates can block catalyst sites on the surface and hamper the performance of the electrode. Here, we demonstrate the ability to electrochemically reduce and desorb these short, non-polymeric adsorbates from the surface without affecting the surface-attached ionomer.
We show that desorption of these short molecular components from the polymer/electrode interface reduces interfacial impedance and greatly improves the performance of the Pt/Au electrode toward oxygen reduction.

IV. Growing Ionomer Within Nanoporous Electrodes.

A key element of this project is to grow ionomer films within nanoporous electrodes to ultimately integrate ionomer, catalysts, and pores for gas diffusion into a single network. We have developed a simple fabrication scheme to prepare nanoporous electrodes\(^{12}\) with several adaptations to the technique developed by Ding et al.\(^{13}\) that makes use of a graphite roller. Successful SI-ROMP of pNBF\(_6\) throughout the nanoporous electrode has been achieved by controlling the monomer concentration in relation to the average pore size as evidenced by a combination of SEM (Figure 3), infrared spectroscopy, and electrochemical impedance spectroscopy.

**Future Directions**

For the next period, we will build on our successes with surface-initiated, partially fluorinated ionomers and nanoporous electrode films to investigate the following issues:

- Examine the effect of fluorocarbon side chain length and sulfonation levels on the transport of O\(_2\) and protons through the membranes.
- Synthesize short pNBF\(_n\) oligomers that are terminated in thiol functionality for directed self-assembly at both planar and nanoporous Pt/Au interfaces. Sulfonate these oligomers after assembly and investigate their effectiveness in promoting oxygen reduction.
- Combine the most successful approaches from the preceding two objectives with carbon paper electrodes and back-fed O\(_2\) to investigate cathode performance under realistic operating conditions.

**References**


**Publications (including patents) acknowledging the grant or contract**


Objectives

In this project, Shao-Horn examines whether fundamental knowledge of electrocatalytic activity established on single-crystal surfaces can be applicable to understanding of nanoparticle activity by studying the influence of surface steps and near-surface composition of Pt-based nanoparticles on electrocatalytic activity. In addition, the stability and the mechanism by which Pt alloy nanoparticles lose activity for oxygen reduction in PEMFCs are studied. Marzari at MIT investigates the effects of applied electrochemical potentials on the adsorption energies and reactions rates of fundamental electrochemical processes, respectively. The overall goal of the modeling work of Morgan at UW is to model oxidative processes on Pt in order to understand and control their influence on Pt-based-nanoparticle stability and electrocatalytic activity.

Technical Barriers

The estimated cost of PEM fuel cell systems for automotive applications is significantly higher than existing, internal combustion technologies (~$35/kW for advanced technologies). In addition, the lifetime of PEM fuel cell systems is limited to 2000 hours, significantly shorter than the required 5500 hours of operation in a vehicle. This work help identify near-surface chemical compositions of Pt-based catalysts that can provide 1) high activity to reduce catalyst and PEM fuel cell cost, and 2) stability to overcome long-term catalyst degradation problems in aggressively corrosive and oxidizing environments (e.g. PEM fuel cell cathode).

Abstract, Progress Report and Future Directions

Abstract. Our recent experimental work has shown that near-surface compositions but not surface steps, can greatly influence ORR activity. We have obtained direct evidence of near-surface compositions of Pt-Co alloy nanoparticles, which exhibit specific ORR activity 2-4 times relative to Pt. The stability of these Pt and Pt alloy nanoparticles will also be discussed. On the other hand, surface steps do not appear to influence activity for oxygen reduction unlike for methanol oxidation, from which the origin responsible for this difference will be discussed. Our recent theory work has revealed some stable hybrid Pt-O surface structures, which can play an important role in the stability and activity of Pt-based catalysts.

The influence of near-surface compositions of “Pt3Co” on oxygen reduction activity. Acid-treated “Pt3Co” supported on carbon (46 wt% Pt) with an average atomic Pt/Co ratio of 3.6 (having a number-averaged particle size of ~4 nm), was prepared from leaching of a “PtCo” sample in acid. Acid-treated nanoparticles were subsequently heat-treated at 1000 K for 3 hours in vacuum (~10^-2 Torr). Annealed “Pt3Co” was found to have a number-averaged particle size of ~5 nm. ORR activity of “Pt3Co” and Pt nanoparticles was measured by sweep voltammetry in O2 saturated HClO4 electrolyte using a rotating disk electrode at room temperature. Cyclic voltammetry of “Pt3Co” nanoparticles was performed in O2 free electrolyte, from which the electrochemical active area was obtained from integrating the charge associated with hydrogen desorption. Specific ORR activity of acid-treated (with Pt-enriched surface in Figure 1) and annealed “Pt3Co” nanoparticles normalized to the Pt surface area was compared with that of Pt nanoparticles as a function of potential in. At 0.9 V vs. RHE, the activity of acid-treated “Pt3Co” nanoparticles is ~0.74 mA/cm² ( ~2 times of Pt), which is comparable to acid-leached Pt alloy nanoparticles reported previously. On the other hand, the specific activity of annealed “Pt3Co” at 0.9 V vs. RHE (with surface-sandwich-segregation of Pt-enriched and Co-enriched, not shown here, Shuo et al., JPCC 2009) was increased to ~1.39 mA/cm² (~4 times of Pt) after annealing, which could be attributed to surface Pt sandwich-segregation structures (not shown here).
The influence of surface steps of Pt nanoparticles on oxygen reduction activity. ORR activity of Pt/MWNT samples was measured using a rotating disk electrode (RDE) and linear sweep voltammetry in O₂-saturated HClO₄ electrolyte. The electrochemical surface area (ESA) of Pt nanoparticles was obtained from integrating the charge associated with hydrogen desorption in the O₂-free electrolyte. Specific ORR activity normalized to the Pt ESA is independent of heat-treatment temperature, which indicates that surface steps on Pt nanoparticles do not greatly influence intrinsic ORR activity. Specific ORR activity of Pt nanoparticles at 0.9 V vs. RHE is ~200 mA/cm²Pt, which is in good accordance with reported specific activity.

**FIGURE 1.** Atomically resolved structures and compositions of Pt alloy nanoparticles (acid-treated), which was correlated to specific ORR activity based on electrochemically active Pt surface area. The enhanced specific ORR activity (~2 times relative to Pt) of acid-treated "Pt₃Co" nanoparticles can be related to composition variation at the atomic scale and the formation of a Pt enriched skeleton structure within individual particles (Shuo et al. JPCC 2009).
for Pt nanoparticles of comparable sizes in HClO$_4$. In addition, projecting the reported activity of stepped single-crystal surfaces onto nanoparticle surfaces of Pt/MWNT samples, no ORR activity difference was noted for Pt/MWNT samples. It is interesting to compare the role of surface steps on Pt nanoparticles on the intrinsic activity of ORR with that of MOR. Specific ORR activity at 0.85 V and specific MOR activity at 0.5 V (current density in the positive-going cyclic voltammetry) is plotted as a function of area fraction of surface steps normalized to that of 548 K (Figure 2). Specific ORR activity at 0.85 V is independent of normalized area fraction of stepped surfaces while MOR activity linearly increases with the amount of stepped surfaces on Pt nanoparticles.

Future work in Shao-Horn’s group will focus on varying near-surface chemical compositions of Pt-based alloy nanoparticles (e.g. PtAu) and studying its role in the activity and stability for oxygen reduction.

**Oxidation of Pt on Pt Nanoparticle stability.**

Pt oxidation plays an essential role in the long-term stability and catalytic properties of Pt based nanoparticle catalysis used in PEMFC cathodes. However, at present the structure, thermodynamics and kinetics of oxide phases on Pt are not known. As a first step in understanding Pt oxidation it is necessary to establish the stable Pt-O surface phases as a function of oxygen coverage. Due to the challenges of experimental determination of these complex and near monolayer surface structures we are pursuing an approach based on *ab initio* energy calculations. We have integrated previous *ab initio* studies that treat specific oxygen structures and their energetics, adjusting results to a consistent reference (see Figure 3). These results consider three major classes of oxygen surface phases, including surface, place-exchanged, and buckled oxygen structures. We have now explored a wide range of new oxygen surface structures with an intent to understand the key mechanisms (e.g., electrostatic interaction, oxygen subsurface vs. surface energetics, etc.) governing stability of oxide phases. In particular, we have developed a set of hybrid place-exchanged and buckled phases with some of the key stabilizing features of each phase. Certain hybrid structures we identified are in fact more stable than previous structures at near one monolayer composition, as can be seen by their residing on the convex hull of all the calculated energies (dark line in Figure 3). These hybrid structures are therefore likely to be the stable form of oxide on Pt near one monolayer. Our future work will further investigate additional new Pt-O structures to establish the correct stable phases that are expected during Pt oxidation.

**References**


Publications (including patents) acknowledging the grant or contract


Objectives

The objective of this work is to develop an understanding of mechanisms of the Oxygen Reduction Reaction (ORR) and to use this understanding to develop new, non-precious metal containing catalysts for this reaction. A particular focus is to mimic the active site of laccase, a protein that performs near thermodynamic four electron reduction of oxygen to water.

Technical Barriers

The slow kinetics of the ORR have long been identified as a major impediment to the development of PEM fuel cells. Consequences of these slow kinetics include a substantial reduction in the thermodynamic efficiency of fuel cells and the requirement for considerable precious metal usage in practical implementations. Our work is directed to designing new materials that will exhibit low overpotentials without the use of expensive precious metal catalyst.

Abstract, Progress Report and Future Directions

Electrocatalysis of the oxygen reduction reaction (ORR) is currently of widespread interest due to its application in fuel cell cathodes. Slow ORR reaction kinetics significantly impact the efficiency of fuel cells, resulting in cell potentials well below (ca. 0.35 V) the reversible potential for oxygen reduction of 1.229 V vs. the reversible hydrogen electrode (RHE). These lower potentials substantial degrade fuel cell thermodynamic efficiency which obviate fuel cell use. The catalyst for the ORR is usually based on Pt or another precious metal, such as Pd. The costs associated with these materials can be prohibitive. Thus, there is a search for non-precious metal ORR catalysts.

The focus of our research is to understand the mechanisms of the oxygen reduction reaction (ORR) on different electrode surfaces and then use that understanding to develop new catalysts which feature the use of materials other than Pt or other precious metals.

Substantial previous work from our group strongly suggests that the four electron reduction of oxygen in the electrochemical environment proceeds according to the so-called series mechanism in which dioxygen binds to the catalyst surface and then through a series of coupled proton electron transfers is reduced to the peroxide level. Coupling between two metal atoms then leads to spontaneous decomposition of the peroxide to form two metal hydroxides, as shown in Figure 1. These hydroxides are then reduced, forming water in acid. This understanding leads us to expect that new catalysts exhibiting four electron ORR activity will features at least two metal centers. Interestingly, the active site in the protein laccasse, which exhibits four electron reduction of water at overpotentials substantially less that found on Pt features three Cu atoms bound in close proximity to each other.

The efficacy of laccase led us to wonder if Cu coordination complexes/polymers composed of CuII coordinated with bridging azole-type ligands, such as the 3,5-diamino-1,2,4-triazole (Hdartz) ligand (Figure 2), and with other weakly coordinated ligands (such as...
water, sulphate etc.) might provide stability in addition to multi-Cu sites that could potentially bind and activate O₂. We developed a method to immobilize insoluble transition metal complexes on Vulcan and other carbons in order to evaluate their activity toward the ORR. Figure 3 shows the activity of the coordination complex formed between Cu and Hdartz in neutral solutions. The figure shows that the onset of four electron ORR activity occurs at potentials significantly more positive than that afforded by the bare carbon. We found that both the Cu metal and the Hdartz ligand were necessary for ORR activity. Figure 4 shows the variation of the onset potential for ORR activity from electrodes modified by Cu and Hdartz. The figure shows that while the onset potential of the complex is low in acid, it increases as a function of pH and is quite high (850 mV vs. RHE) in basic electrolytes.

The structure of the Cu/Hdartz complex shows that Cu forms a dimer coordinated by two of the three heterocyclic nitrogens of the triazole moiety. We thought that suitable modification of the Hdartz ligand at the 4 position might afford a more positive onset potential relative to the unmodified Hdartz ligand. The best derivative so far characterized in our group exhibits an onset potential some 150 mV more positive than that reported for the Cu/Hdartz.

The performance of the Cu/Hdartz catalyst in basic electrolyte appeared good enough that we thought to compare it with Pt. Figure 5 shows a comparison of the maximum power density achieved by four different catalysts in the alkaline (pH 14) electrochemical environment. The figure shows that while Pt particles on C are still more active than any other catalyst examined here, the Cu/Hdartz sample is second most active, and considerably better than Ag; a material previously used in alkaline fuel cell applications. The comparison with Pt is more broadly made in Figure 6, which compares the peak power generated per metal atom. The Figure shows that the Cu/Hdartz sample is considerably better than Pt on a per metal atom basis. We are presently evaluating the stability of the Cu catalyst in both the alkaline and acidic environments. A full suite of synthetic and computational approaches is coupled to this project.

Future directions involve further exploration of the Cu dimer and trimer motifs for their efficacy in the ORR. Modification of the Cu catalyst we've developed through the agency of ligand synthesis allows for modification of properties and correlation of reactivity with structure.
References


FIGURE 5. Comparison of peak power density from four different catalysts evaluated in this project. The Pt/C loading is 2 mg/cm².

FIGURE 6. Comparison of peak power densities per metal atom for three different ORR catalysts.
Objectives

- Fundamental atomic/molecular level understanding of metal-electrolyte interfaces required for efficient transformation of chemical energy of hydrogen, hydrocarbons and oxygen into electrical energy in fuel cell systems.
- Use and develop state-of-the-art ex situ and in situ surface sensitive probes and spectroscopy, in combination with density functional theory calculations to determine the most active and stable sites for adsorption of reactants, reaction intermediates and spectator species.
- From experimental and computational studies on well-characterized single crystals, form the basis for synthesis of nanoscale surfaces to have optimal catalytic properties for the O-O, H-H, O-H, and C-H bond making and bond breaking events in environments of interest for fuel cell technologies.

Technical Barriers

- Fundamental understanding of metal-electrolyte interfaces will transform electrocatalysis from a largely phenomenological subject into a discipline that will be able to address many challenges, opportunities and research needs in the areas of basic science of materials for clean and efficient energy conversion.
- The novel concept of tailored nanoscale oxygen reduction catalysts will significantly reduce noble-metal loading necessary to make the fuel cell technology economically competitive and sustainable.
- New materials will revolutionize catalyst performance in fuel cell systems, not only for the oxygen reduction reaction, but also for a wide range of reactions that are required for the implementation of a hydrogen-based economy, thereby leading the nation to more secure energy independence and a cleaner environment for future generations.

Abstract

The low rate of the oxygen reduction reaction in low/moderate temperature fuel cell systems is the main limitation for a wide application of this technology. We present here a science-based approach that will allow obtaining predictive understanding of the factors that determine the reactivity and stability of the ORR at electrified metal-solution interfaces at nanoscale dimensions. This approach is based on (i) fine tuning of the electronic properties of metal surface atoms; (ii) systematic alternation of the interfacial properties that constitute the entire electrochemical double layer structure; and (iii) molecular patterning of metal surfaces, aimed at the design of surfaces where the sites of poisonous spectator species are blocked, while providing the sufficient number of free metal sites needed to chemisorb the reactant and reaction intermediates. We demonstrate that depending on the geometric/electronic properties of the catalyst as well as supporting electrolytes (including the nature of anions and cations, temperature and pH) the activities of the ORR and oxidation of small organic molecules can range from 50 fold increase to 50 fold decrease. This behavior is discussed in the light of the role of covalent and non-covalent interactions in controlling spectators’ coverage which determine the number of free active sites for high turnover rates of the electrochemical reactions.

Progress Report

(i) Fine tuning of the electronic properties of metal surface atoms; importance of covalent bonds.

(a) Catalytic activity.

Much of the art and science of catalyst development has been based on understanding chemisorption trends of oxygenated species, considering that the kinetics of both the oxygen reduction reaction and of the oxidation of small organic molecules is governed by the nature of metal-oxygen covalent bonds. This approach we used in the development of PtNi and PtCo catalysts for the ORR. The rate of the ORR, expressed in terms of turnover frequency (TOF, defined as the number of electrons produced per active-site per second), on various of cathode materials (Figure 2) demonstrate that if grown
into “gigantic” 30 nm octahedra our Pt$_3$Ni nanoparticles with TOF=2800 s$^{-1}$ would be expected to yield 10-fold higher Pt mass activities than current Pt/C. The mechanism of improvement/deactivation occurs through the change of electronic properties ($d$-band center and work function) of the nanosegregated Pt-Ni surface alloys. By studying the ORR on Pt$_3$Ni(1099)=20(111) x(100) and Pt$_3$Ni(1077)=8(111)x(100) stepped surfaces (Figure 2) we find that to preserve the TOF of Pt$_3$Ni(111) minimum width of (111) facets should be 20 Pt atoms.

(b) Stability.

The design of cathode catalysts must be guided by two equally important fundamental principles: optimization of their catalytic properties as well as the ability of their surfaces to preserve nobility in hostile electrochemical environments. In our experiments, stability of bimetallic surfaces is monitored as the potential-induced relaxation and disordering of the surface structure, which is examined by utilizing a combination of surface x-ray scattering, scanning tunneling microscopy and electrochemical methods. Figure 2 summarizes electrochemical measurements, which show that Pt$_3$Ni(111) and stepped surfaces are stable up to 1.05 V.

(ii) Fine tuning of the electrochemical double layer structure: importance of non-covalent bonds.

Classical models of metal electrode-electrolyte interfaces have generally focused on covalent interactions between adsorbates and the corresponding solid surfaces (see previous section). Recently, we have demonstrated that these traditional models for describing the catalytic activity of the electrochemical interfaces is not sufficient[3], and to understand electrocatalytic trends in the oxygen reduction reaction (ORR), the hydrogen oxidation reaction (HOR), and the oxidation of methanol on Pt surfaces in alkaline electrolytes, noncovalent interactions, such as hydrogen bonding, cation-water, and cation–OH$_{ads}$ bonding, must also be taken into consideration. All these systems are generally applicable in alkaline fuel cells.

We used a combination of experimental and theoretical techniques to find that cation-specific noncovalent interactions between hydrated alkali-metal cations $M^+$($H_2O)_x$ and adsorbed OH species increase in the same order as the hydration energies of the corresponding cations and likely result in an increase in the concentration of OH$_{ads}$–$M^+$(H$_2$O)$_x$ or (H$_2$O)$_{x+1}$–$M^+$–H$_2$O–OH$_{ads}$ clusters relative to the bulk (Figure 2). These trends are inversely proportional to the activities of the ORR, the HOR and the oxidation of methanol on Pt: Cs$^+ > K^+ > Na^+ >> Li^+$.

(iii) Molecular patterning of metal surfaces.

We developed a new approach that can be used for the rational design of cathode catalysts for phosphoric

![FIGURE 2](image)

**FIGURE 2.** The rate of the ORR on Pt$_3$Ni(111), Pt$_3$Ni(1099) and Pt$_3$Ni(1077) and factor of improvement vs. Pt(111). Potential window of stability is around 1.05 V, exemplified as the “grey zone.”

![FIGURE 3](image)

**FIGURE 3.** Left: Models for noncovalent interactions between hydrated alkali-metal cations and adsorbed OH and the formation of OH$_{ads}$–$M^+$(H$_2$O)$_x$ or (H$_2$O)$_{x+1}$–$M^+$–H$_2$O–OH$_{ads}$ clusters. Right: DFT activity mapping. Nature Chemistry 1 (2009) 466-472[3]
acid fuel cells. This approach is based on molecular patterning of metal surfaces with inert CN adsorbates\cite{4}. We find that on Pt(111) modified by irreversibly adsorbed CN activities of the ORR can go from 25-fold increase in the presence of sulfuric acid anions and 10-fold increase in the presence of phosphoric acid anions (Figure 4 left), to no effect in the presence of weakly adsorbing perchloric acid anions. Interestingly 50-fold decrease is observed in alkaline solutions (Figure 4 right). This enormous increase in activity suggests that the CN$_{ad}$ molecules can block the sites for adsorption of spectator phosphoric acid anions but still provide sufficient number of free Pt sites needed first to chemisorb the O$_2$ molecule and then to break the O-O bond (Figure 5b). Equally dramatic deactivation in alkaline solution is rationalized based on anticipated blocking effect of CN$_{ad}$-M$^+$($\text{H}_2\text{O}$)$_x$ clusters for adsorption of O$_2$ molecule and reaction intermediates\cite{4} (Figure 5c).

**Future Directions**

We will continue to (i) create novel states of catalytic materials by manipulating both covalent and non-covalent interactions at electrochemical interfaces; (ii) characterize, electronic properties of nanostructured interfaces by developing and using ex-situ and in-situ surface characterization techniques and theoretical...
methods; (iii) understand fundamental principles that
govern efficient bond making and bond breaking events
at electrochemical interfaces; and (iv) optimize the active
sites by an iterative process, guided by the fundamental
understanding of electrochemical interfaces.

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V.P.9 Engineering Catalytic Nanoporous Metals for Reactions Important to the Hydrogen Economy

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Objectives
The goals of this program include (a) fabrication of new nanoporous electrocatalytic metals by electrochemical dealloying, (b) development of methods to tailor the surface chemistry and composition of nanoporous metals, (c) tailoring the activity of nanoporous to optimize hydrogen oxidation and oxygen reduction, (d) integration of nanoporous metals into fuel cells as low precious metal loading catalysts.

Technical Barriers
Implementation of low precious metal fuel cells in the commercial sector will require new approaches to the materials design of catalytic materials, particularly toward the inefficient oxygen reduction reaction at the cathode. Dealloying as a chemical route to the production of ultra-high surface area conductive metals allows facile synthesis of highly active nanostructured core-shell and composite catalysts with a wide variety of compositions that may lead to large decreases in loading at fuel cell cathodes.

Abstract
The development of new catalysts for hydrogen fuel cell reactions is a critical step in the development of this technology. Factors for which there is room for improvement include improving the catalyst activity, particularly toward oxygen reduction, and the development of carbon-free catalyst layers in the membrane electrode assembly that are not prone to corrosion. A materials system that may be a potential solution for both of these problems simultaneously are nanoporous metals made by selective electrochemical dissolution of one component of a multi-component alloy (dealloying). More specifically, alloys are chosen such that as the majority alloy component is dissolved, the secondary component diffuses along the alloy/electrolyte interface, reconstructing the material into a high surface area crystal with open porosity, high surface area/volume (ligament and pore sizes 5-10 nm), and intrinsic electrical contact to all surface area. In the last year, we have focused on the formation of core/shell nanoporous NiPt (np-NiPt) and related alloys. By impregnating the matrix np-NiPt of with a protic, hydrophobic ionic liquid that absorbs oxygen from the external environment, we have created a composite catalyst that geometrically confines oxygen in the catalytic region and leads to orders-of-magnitude increases in that mass activity of the composite over nanoparticle-based catalysts.

Progress Report

Formation of nanoporous metals by dealloying that are suitable for electrocatalysis. Nanoporous metals made by dealloying require the fabrication of single-phase multi-component alloys from which the majority component is electrochemically dissolved. During dissolution, the remaining alloy components diffuse along the metal/electrolyte interface and re-form as a porous metal. The porous metal, notably, occupies the same lattice as the parent material, so porosity exists on a scale much smaller than the grain size, and grain boundaries do not play a role in its properties. The lack of grain boundaries also adds to morphological stability because sintering (for instance, of nanoparticles) is usually driven by grain boundary energy reduction. This year we have been closely studying dealloying of Ni(Pt)x (x > 0.75) alloys (Figure 1), for which we find a the average pore and ligament size to be nearly 2 nm. This yields specific surface areas of 44 m2/g, essentially equal to that of nanoparticles, and a baseline requirement for fuel cell catalysis.

One important reason we have focused on the NiPt system is that we have found that the remaining porous metal composition usually sits near the NiPt3 composition. This suggests that during dissolution there is accumulation of a passivating Pt layer over a porous NiPt ligament core, i.e., it is a core/shell nanoporous metal with a composition close to that of the most active catalyst for oxygen reduction known. This was a prediction based on earlier work (DOE7,8) in this program, and electrochemical assays back up this hypothesis.
Assessment of nanoporous NiPt toward oxygen reduction. The assessment of np-NiPt in half-cell reactions toward oxygen reduction are consistent with the core/shell hypothesis. By extrapolating the surface kinetic current of np-NiPt to a roughness factor of 1 (by examining oxygen reduction on samples with different depth of porosity), we find the kinetic current to sit in-between the values associated with single crystal low-index surfaces (Figure 2A), again, consistent with the geometric picture of the (functionally single crystal) porous metal having multiple facet orientations within the porous matrix.

Highly enhanced oxygen reduction activity in composite nanoporous NiPt/Ionic Liquid composite catalysts. Although np-NiPt is highly active toward oxygen reduction, obviously its mass activity drops off as the pore depth becomes deeper (Figure 2B). Part of this is due to the extra mass, and some of this is due to the reactants not effectively penetrating deeply into the pores. That is, the active area for oxygen reduction is actually smaller than the geometric surface area measured by hydrogen underpotential deposition; in fact, we've shown that there is a dependence of the active surface area with the overpotential (DOE1). On one hand, this is a challenge for all nanoporous metal electrodes unless they can be fabricated as
ultra-thin membranes (such as we did with Pt-plated nanoporous gold leaf, DOE4), but it has also turned into an opportunity to make a brand new kind of oxygen reduction catalyst.

The presence of nanoporosity allows a secondary phase to be impregnated into the porous matrix. We hypothesized that if this second phase were an ionic liquid (IL) that is protic (proton conducting), hydrophobic, and contained a high oxygen solubility (higher than aqueous solution), then the composite np-NiPt/IL catalyst would have higher mass activity to oxygen reduction than np-NiPt alone because oxygen that approached the composite would be chemically biased to remain near the catalytic surface until it was reduced. Two ionic liquids (MTBD-beti, MTBD-Tf2N) were found to have these characteristics, and composite catalysts could be made simply by dripping the IL onto the porous metal. Figure 3 shows representative oxygen reduction curves in O₂-saturated 0.1 M HClO₄, and shows that the composite catalyst shifts the oxygen reduction curve nearly 50 mV to lower overpotentials. This is a huge shift, and the mass activity of the composite catalyst (Figure 2B), while still dependent on pore depth, at 2.3 mA/microgram at 0.9 V vs. RHE, is still over 20 times more mass active than Pt nanoparticles (0.1 mA/microgram at 0.9 V). At these low overpotentials, the np-NiPt/IL composite catalyst may be the most mass active catalyst toward oxygen reduction yet discovered.

**Future Directions**

**Integration of nanoporous metal/ionic liquid composite catalysts into fuel cells.** The promising results of oxygen reduction on the np-NiPt/IL composite catalysts were found in idealized half-cell electrochemical studies. The obvious next step is to integrate such catalysts into fuel cells. We have already integrated unsupported np-NiPt ground-up powders into PEM MEAs, and shown good results (namely, identical performance to supported Pt/C down to 0.7 V). To date, to make more efficient composite catalysts, we have synthesized particles of Ni₈₀Pt₂₀ that are ~20 nm in diameter and tested these for oxygen reduction. We see a large increase in activity when the particles are dealloyed, and are working toward impregnation of the particles with IL.

**Electrochemical and surface science investigations of the oxygen reduction reaction in nanoporous metal catalysts.** So far, it is just a hypothesis that the mechanism of enhanced oxygen reduction in the composite catalyst is due to higher oxygen solubility (and the ensuing retention of oxygen near a catalytic surface). The detailed reaction kinetics of oxygen reduction in this material as a function of oxygen and proton concentration and temperature, as well as the physical characteristics of the IL (viscosity, oxygen solubility) must be examined.

**Publications (including patents) acknowledging the grant or contract**


Objectives

The goals of this work are to: 1) determine the controlling elementary reaction pathways and intrinsic kinetics involved in the oxygen reduction reaction over Pt and Pt based alloys and their potential dependent behavior, 2) establish the influence of the extrinsic reaction environment including the surface coverage, alloy composition, solution phase and electrochemical potential and 3) understand the mechanisms that control metal dissolution.

Technical Barriers

Electrocatalysis is controlled by the complex interplay between the active catalytic sites and the influence of their complex environment at the electrified aqueous/metal interface.[1-3] The most active electrocatalytic materials exquisitely integrate the atomic assembly of the active metal sites responsible for the elementary bond making and breaking steps, together with the carbon support to carry out efficient electron transfer, and polymer electrolyte and water to facilitate proton transfer, thus establishing an optimal three-phase interface. Understanding the elementary catalytic processes along with the atomic scale features that control them, however, is obscured by the complexity of this three phase interface and the dynamic changes that occur to it under operating conditions. We are developing a first-principles framework and simulations tools that can be used to elucidate the elementary molecular catalytic transformations that occur in the oxygen reduction reaction (ORR) and the distinct role of the surface structure, alloying surface coverage, solution phase and applied potential on ORR and dissolution.

Abstract and Recent Progress

The ability to follow the molecular level transformations that control electrocatalysis and the mechanisms responsible for metal dissolution are obscured by the complex nature of the water/solution interface.[1-3] In addition to the complexity of the interface, there are a number of challenges in appropriately simulating electrochemical systems which require calculations carried out at constant potentials as they involve grand-canonical ensembles. Current ab initio methods, however, are based on a canonical formalism whereby the number of electrons is held constant. We have recently developed an ab initio approach based upon density functional theory that can be used to simulate different electrochemical and electrocatalytic systems that we describe as the double reference method.[3-6]

The DFT double-reference method is used in this work to simulate the electrochemical double-layer and calculate the elementary reaction energies and activation barriers over a range of potentials applicable to a working PEM cathode. In the first phase of this work, we have focused examined the oxygen reduction reaction (ORR) over different single surfaces Pt and Pt-based alloys and are beginning to transition to Pt nanoparticles in order to explore structure sensitivity.

The initial reduction of molecular oxygen (O\textsubscript{2,ads} + H\textsuperscript{+}_\text{aq} + e\textsuperscript{-} → OOH\textsubscript{ads}) was found to proceed through a proton-coupled electron transfer step followed by the addition of hydrogen to the bound O\textsubscript{2}* to form the surface OOH* intermediate. The transition state for this step is shown below in Fig. 1A. The calculated activation barrier was found to be strongly dependent on potential as is shown in Fig. 1B. The resulting barriers were found to be in good agreement with measured activation barriers over a range of potentials reported in the literature.[7-9]

Over the potentials of interest, the barrier was found to be nearly equal to the overall reaction free energy for this step. At a potential of 1.2 V-NHE, the first reduction barrier (0.7 eV) is close to that calculated for O\textsubscript{2} dissociation (0.77 eV). However, the reaction energy, and likely the activation barrier, for O\textsubscript{2} dissociation is not a strong function of electrode potential. At 0.8 V-NHE, the barrier to the first reduction step (0.3 eV) was calculated to be substantially
lower than that for $O_2$ dissociation. Therefore, at operating potentials, the dominate reduction pathway is expected to proceed through the initial reduction, in agreement with previous experimental and theoretical suggestions. [10-11] The subsequent dissociation of the $OOH^*$ intermediate that forms to $O^*$ + $OH^*$ occurs with an activation barrier of less than 0.1 eV. A detailed reaction path analysis indicates that the ability of the catalyst to break the O-O bond should not directly relate to the ORR performance.

At potentials above 0.8 V, the reaction is limited by reduction of the $OH^*$ intermediates that form on the surface. Below 0.8 V, the reaction was calculated to be limited by the initial reduction of $O_2$ to form the peroxo intermediate. Through a series of calculations carried out over different pseudomorphic Pt overlayers, we defined the optimal oxygen binding energies to carry out both the initial $O_2^*$ and subsequent $OH^*$ and $O^*$ reductions. This defined a series of different Pt-alloys which can meet the optimal binding energies. The results are consistent with previous reported work for $O_2$ reduction.[12-13]

Our more recent efforts have focused on the effects of $OH^*$ coverage on each of the elementary steps in the ORR mechanism and analyzing Pt dissolution for different Pt and Pt alloy surface structures.

Coverage Effects

The presence of surface hydroxyl intermediates were found to significantly alter the adsorption energies for all intermediates and their reaction energies and activation barriers. We examined the influence of coverage on: $O_2^*$ dissociation and $O_2^*$, $O^*$, $OH^*$ and $OOH^*$ reduction. The results for all of these reactions clearly show a linear relationship between the changes in the strength the initial adsorbed intermediate and the changes in their barriers for reaction. The adsorption energies for these intermediates are guided by the complex interplay between both attractive and repulsive interactions with $OH^*$ surface intermediates which result from hydrogen bonding and lateral repulsive interactions. These interactions are functions not only of their relative distances to one another but also in their specific orientation with respect to one another as hydrogen-bonding is directional. While the activation barrier for the reduction of $O^*$ is found to have the highest activation barrier especially at higher potentials, the coverage of $OH^*$ can considerably reduced the barrier as a result of stabilizing the calculated transition states.

Activation of Water and Dissolution of Pt

We have used the double reference approach to map out the surface phase diagrams for water, hydride, hydroxide, oxygen-covered surfaces, as well as solvated Pt ions and their corresponding passivated oxide over Pt(111), Pt(100), and Pt(110) and PtCo alloy surfaces in order to establish the lowest energy surface structures and the energies required to transition between one another phase to another over a range of potentials. The results have been used to show that the more coordinatively unsaturated surfaces more favorably activate water and subsequently undergo dissolution than surfaces comprised of more coordinatively saturated metal atoms. The introduction of Co appears to enhance the reactivity of Pt when Co is in the surface layer but decreases its activity when it's located below the surface.

Simulating Electro catalytic Kinetics

We have constructed a 3D kinetic Monte Carlo simulation algorithm that can begin to simulate the kinetics of the oxygen reduction over different sized cuboctahedral Pt particles as function of potential, temperature and reaction conditions. The simulations track the elementary molecular transformation that occur and as such can follow the changes surface coverages, the rate of water and hydrogen peroxide...
production as well as the potentials at which reactions proceed. The initial simulations reveal that at potentials about 0.8 V the surface is predominantly covered with surface hydroxyl intermediates. We are beginning to extend these initial efforts to provide relevant information on particle size effects on the kinetics for ORR.

Future Work

We are currently extending the work to other Pt-based alloys (Pt-Ni, Pt-Fe), and Pt nanoparticles. More specifically we have focused on the activation of water and its dissolution over large 201 atom Pt nanoparticles in a box of over 450 water molecules. These have been very difficult calculations as there are tremendous challenges in converging the lowest energy water structure at a given potential at the surface of the nanoparticle. An appropriate water surface structure is critical in establishing the appropriate electrochemical and electrocatalytic behavior. We will complete these studies and examine the O2 reduction mechanism as a function of potential.

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Publications (including patents) acknowledging the grant or contract

Objectives

The long-term objectives of our research effort are two folds: 1. Advance significantly our fundamental understanding of sulfur poisoning of Pt-based mono- and bi-metallic nanoscale electrocatalysts through careful interrogation of long and short range electronic effects caused by the poisonous sulfur-metal bonding. 2. Investigate and establish correlations among the surface d band center, the frontier orbitals of the metal surface as represented by the surface local density of states at the Fermi level (E_f-LDOS), and the associated electrochemical reactivity.

Technical Barriers

Lack of detailed molecular level information on how sulfur-metal interaction poisons heterogeneous catalysts in general and electrocatalysts in particular impedes significantly the pace of developing practically viable sulfur-tolerant catalysts. Achieving the aforementioned objectives should help in a significant way the development of sulfur-tolerant catalysts by providing much needed molecular level electronic/geometric structure – functionalities relationships.

Progress Report

**In situ Spectroscopic Development.** Over the last year, we have developed capability of electrochemical (EC) in situ surface-enhanced IR adsorption spectroscopy (SEIRAS) and surface-enhanced Raman spectroscopy (SERS), as shown respectively in Figure 1 and 2. These spectroscopic developments have broadened significantly our molecular level investigative power in achieving a deeper mechanistic understanding of sulfur poisoning of Pt based electrocatalysts.

**Adsorption and Oxidation of Sulfur on Pt Nanoparticles.** We have carried out a detailed EC investigation of the adsorption and oxidation of S on commercial Johnson-Matthey (J-M) Pt black (Pt-B) and carbon-supported Pt (Pt/C). These two samples have different size (7 nm vs 4 nm), different boundary condition (inter-grain boundaries due to NP segregation in Pt-B vs NP isolation in Pt/C), and different surface roughness. By carefully analyzing the EC data obtained on 10 consecutive S-electro-oxidation (S-EO) strippings of 7 samples prepared with different S adsorption times, we were able to identify a Pt-S₂ to Pt-S absorption structural transformation.

**In situ EC ¹⁹⁵Pt NMR Investigation of Ru@Pt and Au@Pt/C NPs.** The first step to delineate how S adsorption alters the structural and electronic properties of bimetallic NPs is to establish what are the starting structural and electronic properties of these NPs. To this end, we have carried out the first in situ EC ¹⁹⁵Pt NMR investigation of Ru@Pt and Au@Pt/C NPs that will enable us to move in this direction. The former sample was prepared by scaling up the EG based wet chemistry synthesis we had developed[1] from 5 mg to ~ 100 mg. The starting Ru black had an average particle size of 3 nm. The targeted Pt packing density (PD) was...
0.4. TEM, XRD, CO stripping and MOR measurements showed results that were in good agreement with the results of the 5mg synthesis[1], demonstrating the feasibility of the scaling-up synthesis. The latter Au@Pt sample was prepared by first synthesizing carbon-supported 30% mass Au NPs. The Au NPs had an average size of 3.5 nm. The Pt was then added in the second step in which the starting Pt ions were reduced by ascorbic acid[2]. The sample studied here had a Pt PD of 3.8. About 80 mg of the NPs were used for NMR measurements.

Figure 3 shows the area-normalized $^{195}$Pt NMR spectra of as-prepared and EC-cleaned samples for Au@Pt (a) and Ru@Pt (b) respectively. The spectrum of a 2.5 nm commercial Pt/C is also shown for comparison. The as-received Au@Pt sample had been on shelf for very long time (>12 months) so the spectrum shows clearly a Pt oxide peak at 1.089 G/kHz. After EC-cleaning (by the setup shown in Fig.1), the Pt oxide peak disappeared and the whole spectrum moved up field as happened to pure Pt/C sample[3]. Although still lacking direct spectral evidence, we think that the peak appeared at the low-field side at 1.0975 G/kHz after EC-cleaning is from the surface Pt atoms. The fraction of the area under this peak can be estimated by a Gaussian deconvolution as indicated by the dashed blue line, which gives a value of 0.53, a value of fraction for Pt surface atoms in Au@Pt NPs that is in good agreement with that estimated electrochemically. However, the peak position is low-field shifted from 1.1000 G/kHz, the peak position for the surface Pt atoms in Pt/C NPs. The up-field part of spectrum is compressed towards low field as many alloyed systems do and also is more structured that that of Pt/C.

On the other hand, the as-prepared Ru@Pt sample was very fresh (only had a shelf life of a couple days) so no clear Pt oxide peak appeared. After the EC-cleaning, the spectrum also did not show spectral change as dramatic as that of the Au@Pt NPs. However, as that of the Au@Pt sample, it is very different from that of the pure Pt/C, with a broad dominant peak centered at 1.1053 G/kHz. Assuming that this is the surface peak, the ratio of the area under this peak can again be obtained by Gaussian deconvolution that gives a value of
The peak is high-field shifted from 1.1000 G/kHz, in the opposite direction from that of the Au@Pt. The origin of the remaining 26% signals is still unclear but clear difference in spectrum between Ru@Pt and Au@Pt highlights different electronic effect caused by the underlying Ru and Au cores.

If the deposited Pt atoms form mono-atomic islands on the surface of the core NPs, then they should have very similar electronic properties and coordination numbers. This is indeed the case for the Ru@Pt NPs as demonstrated by the spin-lattice and spin-spin relaxation times $T_1$ and $T_2$ measurements taken at four different spectral position of the dominant peak centered at 1.1053 G/kHz (Figure 4). As can be seen, the four $T_1$ and $T_2$ data sets are statistically the same with each other. The solid curves are the fits of all four data sets to an exponential saturation-recovery function $A_\infty - (A_\infty - A_0)\exp(-\tau/T_1)$ for $T_1$ and to a J-coupling modulated exponential decay function $[4] S(\tau)/S_0 = \exp(-2\tau/T_2)\left[P_0 + \exp(-\tau/T_{2J})\left[P_0 \cos(\tau/T_2) + P_2 \cos^2(\tau/T_2)\right]\right]$ with $P_0 + P_1 + P_2 = 1$ for $T_2$ respectively. In the former equation, $A_\infty$ is the fully relaxed NMR amplitude, $A_0$ is the residual amplitude after the saturation pulses, and $\tau$ is the time interval between the saturation pulses and the signal reading pulses. In the latter equation, $J$ is the nuclear-nuclear spin J coupling constant, $P_0$, $P_1$, and $P_2$ are the probability for a $^{195}$Pt nuclear spin having zero, one, and two neighboring $^{195}$Pt nuclear spins respectively, $T_{2J}$ is the time constant accounting for the spread in J values due to environmental heterogeneity, $S_0$ is the equilibrium NMR amplitude (the same as $A_0$), and $\tau$ is the time interval between two Hahn echo pulses. The fits give $T_1 = 1.05\pm 0.05$ ms, $T_2 = 348\pm 22$ $\mu$s, $T_{2J} = 209\pm 79$ $\mu$s, $J = 5.9\pm 0.3$ kHz, $P_0 = 0.69\pm 0.04$, and $P_1 = 0.19\pm 0.03$. Using a local Knight shift gradient parameter $[4] \delta = 0.15$, the local Pt atomic fraction estimated from the $P_1$ value is about 0.37 $[5]$. Since for a pseudo-morphic Pt monolayer on a Ru(0001) surface, the Pt fraction among all the next-nearest neighbors is 6/9, a local Pt atomic fraction of 0.37 is thus consistent with a Pt PD of 0.4 of mono-atomic Pt islands.

On the other hand, it is a quite different story for the Au@Pt sample whose results of $T_1$ and $T_2$ measurements are shown in Figure 5. They are qualitatively different from those of Ru@Pt and varied substantially from a spectral position to the other. Table 1 lists the fitted parameters that give the solid curves in Figure 5. The local Pt atomic fractions estimated from the $P_1$ values at 1.0975 G/kHz, 1.1001 G/kHz, and 1.1105 G/kHz are 0.14, 0.53, and 0.59 respectively. The $T_1$ and $T_2$ were also shorted as the spectral positions moved up-field, indicating that a substantial part of the Pt atoms went inside the Au NPs through exchange with the underlying Au atoms.

Using the two-band model $[6]$, we calculated the s-like and d-like $E_F$-LDOS for surface Pt atoms in Ru@Pt and Au@Pt. They are $D_{s,EF} = 3.7$ Ry$^{-1}$-atom$^{-1}$, $D_{d,EF} = 13.3$ Ry$^{-1}$-atom$^{-1}$ for the former and $D_{s,EF} = 4.3$ Ry$^{-1}$-atom$^{-1}$ and $D_{d,EF} = 10.1$ Ry$^{-1}$-atom$^{-1}$ for the latter respectively. Namely, Pt on Au has higher s-like but lower d-like $E_F$-LDOS. How these differences in the $E_F$-LDOS are related to the observed electrocatalytic activity is still unclear at this moment and the Pt PD dependence study should be revealing. Nonetheless, the above EC-NMR investigations demonstrate again the unique investigative power of the technique.

**FIGURE 4.** The spin-lattice relaxation $T_1$ (a) and spin-spin relaxation $T_2$ (b) data of the EC-cleaned Ru@Pt sample measured at different spectral position. The solid curves are the fits to the exponential recovery (a) and J-coupling modulated slow-beat (b) equations.
Future Directions

The immediate future directions of research include, but are not limited to, detailed in situ spectroscopic (NMR/SEIRAS/SERS) investigations of Pt/C, Ru@Pt, and Au@Pt NPs as functions of Pt PD and sulfur coverage.

References


V.P.12 Investigation of the Oxygen Reduction Reaction Activity of Heteroatom-containing Carbon Nano-structures

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Objectives
The main goal of the proposed work is to undertake a fundamental investigation of the ways of modifying the nanostructure of precious metal-free carbon catalysts and their functional groups to enable their use as oxygen reduction reaction (ORR) catalysts in proton exchange membrane (PEM) fuel cells and direct methanol fuel cells (DMFC). The project targets investigation of the nature of active sites and the ways to create these active sites for oxygen reduction reaction by molecular tailoring of the carbon nanostructures and surface moieties.

Technical Barriers
Platinum supported on carbon is the current catalyst used for ORR at the cathode in PEM and direct methanol fuel cells. The cost and availability of platinum is a barrier in wide-spread applications of PEMFC and DMFCs. Carbon-based ORR catalysts offer an alternative. The role of heteroatoms and the nature of the active site in these catalysts are heavily debated and need to be better understood before increased activity, current density and stability of these catalysts can be achieved. The work we are doing aims to develop a better understanding of the role that heteroatoms play in these catalysts, especially in terms of the active site.

Abstract
Heteroatom-containing carbon nanostructures are being investigated as catalysts in the oxygen reduction reaction (ORR) for PEM and direct methanol fuel cells. Heteroatoms including nitrogen, phosphorus and sulfur are being incorporated into various carbon nanostructures to study the role that heteroatoms and nanostructure play in ORR activity and selectivity. It has been found that sulfur can be used as a growth promoter in nitrogen-containing carbon nanostructures (CN_{x}), but does not participate in ORR and introduction of phosphorus can increase ORR activity in CN_{x}. Oxygen surface groups can increase the selectivity of CN_{x} catalysts. Additionally, nanostructure control is being developed to study the role of graphitic edge planes plays in ORR. Work is also ongoing in examining the corrosion characteristics of the catalysts developed. Full fuel cell tests with the most active catalysts are also in progress.

Progress Report

Investigation of the role of sulfur in CN_{x} catalysts.
Commercially, carbon nanofibers are produced using a sulfur growth promoter to increase yield. The impact of sulfur use on the end-use of nanofibers is not commonly discussed or understood. When we introduced sulfur, in the form of thiophene, into the acetonitrile pyrolysis feed used to produce nitrogen containing carbon nanostructure (CN_{x}) catalysts, the CN_{x} yield increased. Through X-Ray Photoelectron Spectroscopy (XPS), temperature programmed desorption (TPD) and temperature programmed oxidation (TPO) experiments, it was found that sulfur was both adsorbed to the CN_{x} surface and incorporated into the graphitic matrix. As long as acetonitrile was still in the fiber growth feed, ORR activity was unaffected by the growth promoter concentration or the amount of sulfur incorporated into the CN_{x}. These results also indicate that sulfur, as incorporated in this study, does not play a role in ORR activity. This work is in press with Applied Catalysis B.

Incorporation of phosphorus heteroatoms into CN_{x}. Phosphorus, when incorporated into CN_{x} has the potential to impact the electrocatalytic ORR activity. Heteroatom incorporation may also affect physical and chemical characteristics, ORR activity and selectivity, as well as, stability. Phosphorus added to the growth media of nitrogen-containing carbon nanostructures was found to dramatically improve the electrocatalytic activity for oxygen reduction. Phosphorus doping was achieved by growing carbon-nitrogen-phosphorus catalyst (CN_{x}P_{y}) over triphenylphosphine- and iron acetate-impregnated magnesia support in N_{2} saturated with CH_{3}CN at 900°C. Catalysts grown in phosphorus-containing media showed improved onset of activity, increased current density and higher selectivity for water formation. The incorporation of both phosphorus and nitrogen into graphite materials allows for the tailoring of the physical and electrochemical properties. Initial results from this study have been submitted to Carbon.
**Oxygen functionalities.** Oxygen functional groups are commonly found on carbons when exposed to an oxidizing environment such as air. Oxygen functional groups affect properties critical for fuel cell catalysts, including hydrophilicity, elicit an activity increase and create anchoring sites for other functional groups or metals. CN_x was subjected to a nitric acid treatment in order to enhance the surface oxygen content and explore the role that oxygen functional groups have on ORR for CN_x catalysts. Nitrogen-containing carbon nanofibers were treated in HNO_3 to impart them with oxygen functional groups. With this treatment, ORR activity was found to increase slightly while selectivity to water formation markedly increased. Work continues with oxygen functional groups to identify the oxygen species that contribute to activity. *Preliminary results from this sub-area are published in Topics in Catalysis.*

**Tailoring the catalyst nanostructure.** The tailoring of nanostructure has been studied using different methods. The most active CN_x catalysts previously made by our research group had a mixture of nanostructures, but contained 60-70% stacked cup nanofibers. Studies were performed to increase the stacked cup nanofiber content. A solvothermal decomposition technique was used for preparing uniform 6nm iron oxide nanocrystals that were deposited on silicon wafers. CH_3CN pyrolysis was performed on the Fe nanoparticles. Unlike carbon nanofibers grown on Fe- or Co-impregnated VC, Al_2O_3, SiO_2, and MgO supports, which led to a mixture of carbon structures ranging from multi-walled nanotubes to nano-onions, this preparation gave exclusively “stacked-cup” structures. Since these stacked cup CN_x catalysts had very low yields because of the low surface area of the polished silicon wafer support, efforts are underway to prepare iron oxide nanoparticles on a silica support, by controlling the size and nanogeometry of the particles through organometallic synthesis techniques. Acetonitrile pyrolysis will, then, be performed, followed by washing, leaving behind the nitrogen containing carbon nanostructures.

Another avenue we followed was the synthesis of stacked platelets. This nanostructure was studied because of its increased edge plane exposure, hypothesized to be the location of the ORR active sites. Stacked platelets were made by passing a stream of CO:H_2 over an Fe:Cu unsupported catalyst. These stacked platelets were post-treated to incorporate oxygen and nitrogen functional groups into the nanostructure. They were oxidized in concentrated HNO_3:H_2SO_4 to add oxygen functional groups to the more active edge planes. The oxidized platelets were treated at two different temperature levels with ammonia to incorporate nitrogen into the nanostructure. It was found that oxidation of the platelets increased activity, but not as significantly as treatments in ammonia did.

**Electrochemically accelerated carbon corrosion.** Accelerated electrochemical corrosion of CN_x catalysts was performed through a chronoamperometric hold of 1.2V vs. NHE in 0.5M H_2SO_4 electrolyte utilizing a rotating disk electrode system. The progression of carbon corrosion was monitored by measuring the intensity of an oxidation intermediate, the hydroquinone/quinone electrochemically active redox couple. Half-cell testing of CN_x oxygen reduction catalyst materials showed superior carbon corrosion resistance compared to Vulcan carbon, the most commonly used material as cathode catalyst support. CN_x materials grown over an iron-impregnated support at 900°C in an acetonitrile atmosphere had a higher oxygen reduction activity than materials without an iron growth catalyst. When oxygen reduction activity was monitored before and after carbon corrosion testing, carbon corrosion resilience trended with oxygen reduction activity. Electrochemical ORR testing was observed to promote the corrosion resistance of highly active CN_x catalysts, but have no impact for materials that have low ORR activity. *This work has been submitted to Electrochimica Acta.*

**Examination of the parameters that impact RRDE measurements.** The parameters that impact the measurement of activity and selectivity through voltammetry techniques, such as rotating ring disk electrode (RRDE), were examined. The selectivity values measured using the RRDE technique for different catalyst loading levels on the disk were compared. A positive correlation between the selectivity and catalyst loading was observed for both CN_x catalysts and commercial Pt/VC.

Another parameter which affects the RRDE measurements is the aging of the catalyst ink before being applied to the electrode. A dramatic decrease in the ring current with aging coupled by a more modest increase in the disk current was observed with RRDE ink aging. The onset of activity does not appear to change with ink aging. When experiments were repeated with Pt/VC catalysts, similar changes in selectivity were observed, indicating that this was not a phenomenon specific to CNx catalysts. *This work is in review with Electrochemical and Solid-State Letters.*

**Full PEM fuel cell testing of heteroatom-doped carbon materials.** Procedures for fabricating membrane electrode assemblies (MEAs) have been modified from those used for Pt-based catalysts reported by Los Alamos National Laboratories for our CN_x catalysts. Method optimization for enhanced performance for non-noble metal catalysts is ongoing. With the addition of an Arbin 50W hydrogen/direct methanol fuel cell test stand, CN_x catalyst MEA performance and stability are being explored.
Initial computational chemistry studies: Computer exploration of heteroatoms in graphite materials. As a collaborative effort with Professor Christopher Hadad, density functional theory (DFT) calculations have been initiated for nitrogen 1s orbital energies in polycyclic aromatic hydrocarbons (PAHs), which have a similar electronic structure to carbon-nitride catalyst materials. A strong correlation between DFT B3LYP method N 1s energies and experimental XPS N 1s energies was established for the PAHs studied. Additionally, experimental ionization potentials trended strongly with the DFT adiabatic ionization potentials. This calibration will be extended to larger and more complex molecules that are more like CN\textsubscript{x} catalysts.

Correlation between activities of CN\textsubscript{x} catalysts in ORR and ODH reactions. There have been reports in the literature citing the activity of carbon-based materials in oxidative dehydrogenation (ODH) reactions. Although the source of activity in these materials was not clear, the pre-treatments that involved O\textsubscript{2}, N\textsubscript{2}O and HNO\textsubscript{3} suggested possible oxygen and nitrogen functional groups playing a role in catalyzing the reaction. While some research has been conducted connecting carbon nanostructure to ORR activity, there is far less literature connecting carbon nanostructure to ODH activity. We initiated a study to examine the activity nitrogen-containing carbon nano-structures in oxidative dehydrogenation of lower alkanes and explore if any correlations existed between the ODH and ORR activities over this group of catalysts. There was a strong correlation between ODH and ORR activities observed. XPS analysis demonstrated that ORR and ODH activity trends between catalysts followed the percentage of oxygen present as quinone groups as well as the pyridinic nitrogen groups. The correlation may suggest a shared active site between the ORR and ODH reactions although alternative explanations cannot be ruled out. This work is in press with Catalysis Letters.

Future Plans

Work on all sub-areas mentioned in the above progress report will continue. Some specific areas of particular interest are listed here:

- Determination of the role of phosphorus carbon-nitrogen nanostructures: Phosphorus was shown to impact the electrocatalytic ORR activity when incorporated into CN\textsubscript{x}. The phosphorus content and local bonding environment will be probed to ascertain what the role of phosphorus is.

- Poisoning CN\textsubscript{x} catalysts: The nature of activity in non-noble metal CN\textsubscript{x} materials is still debated in the literature. To determine if the activity is imparted by a Fe-N\textsubscript{x} type active site, activity testing will be performed on the CN\textsubscript{x} material before and after exposure to several common catalyst poisons that bond strongly to iron.

- X-ray Absorption Spectroscopy (XAS) characterization. The XAS techniques are powerful tools to provide information about the coordination chemistry, formal oxidation state of a selected element being studied as well as the species, distances and coordination number of the atoms surrounding it. These techniques can be very useful in elucidating the molecular structure of the CN\textsubscript{x} catalysts. Heteroatom-containing carbon nanostructures grown on different transition metals will be characterized using XAS techniques. Our recent proposal to Advance Photon Source (APS) of Argonne National Laboratory was accepted and we are given beam time at Sector 10.

- Computational chemistry studies to complement the experimental work. A collaborative effort is in progress to gain insight into the oxygen reduction reaction over the nitrogen-doped carbon catalysts using computational chemistry. It is planned to use both cluster models and periodic boundary models to explore the possible ORR mechanism over the nitrogen-doped carbon catalysts in acidic solution. Experimental techniques will be used in tandem to refine the ORR mechanistic pathway.

Publications acknowledging the grant


V.P.13 *In-Situ* Studies of Active Sites and Mechanism for the Water-Gas Shift Reaction on Metal/Oxide Nanocatalysts

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**Objectives**

The design and optimization of novel water-gas shift catalysts for the production of pure hydrogen depends on a better understanding of catalyst structure and function. We are carrying out a coordinated research program to understand the active sites and reaction mechanism for the water-gas shift on promising metal-oxide catalysts for industrial applications.

**Technical Barriers**

Our goal is to develop the ability to predict, and ultimately design, improved cost-effective water-gas shift low temperature catalysts. These catalysts and the knowledge gained about their behavior will improve the performance and operation of industrial processes used for the production of pure hydrogen.

**Abstract**

The water-gas shift reaction (WGS: CO + H₂O → H₂ + CO₂) is a critical process in providing pure hydrogen for catalytic processes in the chemical industry and fuel cells. High purity hydrogen is needed in massive quantities for the synthesis of ammonia and nitrogen-based fertilizers and for essential hydrogenation processes within the food industry. Furthermore, improved air-tolerant, cost-effective WGS catalysts for lower temperature processing are needed to enable mobile fuel cell applications in a hydrogen fuel economy. The design and optimization of WGS catalysts depends on a better understanding of catalyst structure and function. We are carrying out a coordinated research program to understand the active sites and reaction mechanism for the WGS on promising metal-oxide catalysts. In the initial funding period, our studies with inverse oxide/metal catalysts have shown the crucial role that an oxide can play in the WGS process. By combining nanoparticles of noble metals (Cu, Au and Pt) and ceria over a titania support, we have obtained extremely active WGS catalysts. Our work indicates that highly active WGS catalysts are bifunctional with the metal and oxide catalyzing different parts of the reaction. In the future, we will be working with three different types of catalyst configurations: metal/oxide, oxide/metal and mixed-metal oxide, with the aim of optimizing the performance of the metal and oxide phases. Our goal is to develop the ability to predict, and ultimately design, improved cost-effective WGS low temperature catalysts. Our approach exploits unique capabilities available for *in-situ* studies in the BNL catalysis programs, and at BNL facilities such as the National Synchrotron Light Source (NSLS) and the Center for Functional Nanomaterials (CFN).

**Progress Report**

Since the start of this project 2.5 years ago, seventeen articles have been published by members of the research team examining different aspects of the WGS on metal/oxide catalysts (see separate list of publications). Work was done with high-surface area powders and model catalysts, combining sophisticated techniques for bulk and surface characterization with state-of-the-art theoretical calculations. We have strategically directed part of our efforts to develop synchrotron-based techniques useful for *in-situ* characterization of catalysts and mechanism studies: Quick XAFS, combined XRD/XAFS and combined XAFS/IR.

A. *In-situ* XRD and XAFS studies of the WGS reaction on CuFe₂O₄, CuMoO₄ and Ce₁₋ₓCuₓO₂.

Cu-Fe oxides are used as WGS catalysts in several industrial processes. The structure of CuFe₂O₄ is known as an “inverse spinel” (Figure 1). Copper ions sit predominantly on octahedral sites and iron atoms alternate between octahedral and tetrahedral sites. XRD data collected while performing the WGS on CuFe₂O₄ showed that up to ~ 200 °C, there were no changes in the tetragonal structure of CuFe₂O₄ and no WGS activity was detected. From 200 to 300 °C, CO attacks the oxide and partial reduction leads to the segregation of metallic Cu with the onset of WGS activity. At 350 °C, one has an active WGS catalyst which contains a mixture of Cu, CuFe₂O₄ and/or Fe₂O₃. A Rietveld refinement gave a mole ratio of ~ 1 for the diffraction lines of copper and the CuFe₂O₄/Fe₂O₃ spinel. *In-situ* experiments of x-ray absorption spectroscopy at the Cu...
K-edge indicated that essentially all the Cu\(^{2+}\) initially present in CuFe\(_2\)O\(_4\) was reduced to metallic Cu\(^0\).\(^2\) Our XRD and XAFS results point to metallic copper as an active species for the WGS.\(^2\) This is consistent with studies performed in our group for the water-gas shift on CuMoO\(_4\), Ce\(_{1-x}\)Cu\(_x\)O\(_{2}\), and CuO-ZnO powder catalysts.\(^1,3\) In all of these systems, catalytic activity was seen only after a Cu\(^{2+}\) → Cu\(^0\) transformation. A highly active phase consists of metallic Cu dispersed on a partially reduced oxide support (MoO\(_3\), Ce\(_{2-x}\)O\(_x\), Fe\(_3\)O\(_4\)).\(^1,3\) These studies help to solve a long debate about the oxidation state of Cu in oxide-based WGS catalysts.\(^3,15\)

B. WGS activity of Cu nanoparticles supported on well-defined oxide surfaces. Since CuFe\(_2\)O\(_4\), Ce\(_{1-x}\)Cu\(_x\)O\(_2\), CuO-ZnO, or CuMoO\(_4\) show significant water-gas shift activity only when the Cu cations in the mixed-metal oxide are reduced to metallic copper, Cu nanoparticles were deposited on a series of well-defined oxide surfaces and their WGS activity was measured in a batch reactor.\(^4,10\) The WGS activity of the Cu nanoparticles supported on MgO(100) was 2-3 times larger than that of Cu(100).\(^5\) Even better WGS catalysts were obtained when Cu was deposited on CeO\(_2\)(111) or TiO\(_2\)(110).\(^6,9\) An apparent activation energy of 13.8 kcal/mol was found for the WGS on Cu/MgO(100).\(^6\) This is smaller than the value of 15.2 kcal/mol observed on Cu(100), and substantially larger than the values of 7-9 kcal/mol seen for the apparent activation energies of the Cu/ CeO\(_x\)/Cu(111) and Cu/TiO\(_2\)(110) catalysts.\(^6,9\) Post-reaction surface characterization pointed to the lack of O vacancies in the Cu/MgO(100) catalysts.\(^6\) This is in contrast to results found for Cu/ CeO\(_x\)(111) and Cu/TiO\(_2\)(110), where the oxide support exhibits a significant concentration of O vacancies as a consequence of the WGS reaction.\(^6,9\) The oxygen vacancies present in Cu/ CeO\(_x\)(111) and Cu/TiO\(_2\)(110) could help in the dissociation of the water molecule and reduce the apparent activation energy for the WGS process.\(^9\)

C. WGS reaction on inverse CeO\(_x\)/Cu(111) and CeO\(_x\)/Au(111) catalysts: Active role of the oxide. Several studies dealing with metal/oxide powder catalysts and the WGS indicate that the oxide plays a direct role in the reaction,\(^15,16\) but due to the complex nature of these systems there is no agreement on what exactly this role is. To address this issue, we performed experiments on inverse CeO\(_x\)/Au(111) and CeO\(_x\)/Cu(111) catalysts.\(^7\) After depositing Ce atoms on Cu(111) under an atmosphere of O\(_2\), one obtains CeO\(_x\)/CuO/ Cu(111) systems.\(^5\) Upon reaction with CO, the CuO is easily reduced and one obtains CeO\(_x\)/Cu(111) inverse catalysts.\(^5\) The oxidation state of Ce in these systems is a mixture of Ce\(^{3+}/Ce^{4+}\). The deposition of ceria nanoparticles on top of Cu(111) produces a phenomenal increase in the WGS activity.\(^5\) A comparison of the WGS activities of CeO\(_x\)/Cu(111) and Cu/CeO\(_x\)(111) shows that an optimization of the physical and chemical properties of the oxide component is as important as the optimization of the properties of the metal component.\(^5\)

D. Controlling the nature of mixed-metal oxide catalysts at the nanometer level: High WGS activity of M/CeO\(_x\)/TiO\(_2\)(110) surfaces (M= Au, Cu, Pd). Recently, there has been a strong interest in understanding phenomena associated with the deposition of oxide nanoparticles on the surface of a second (host) oxide.\(^7\) At BNL, STM, photoemission, and density-functional calculations were used to study the behavior of ceria nanoparticles deposited on a TiO\(_2\)(110) surface.\(^4\) The titania substrate imposed non-typical coordination modes on the ceria nanoparticles. In the CeO\(_x\)/ TiO\(_2\)(110) system, the Ce cations adopt a geometry and an oxidation state (+3) which are quite different from those seen in bulk ceria or for ceria nanoparticles on metal substrates.\(^4,10\) The results of STM show the formation of CeO\(_x\) dimers which form small linear arrays on top of the TiO\(_2\)(110) substrate (see Figure 2). An increase in the stability of the Ce\(^{3+}\) oxidation state leads to an enhancement in the chemical and catalytic activity of the ceria nanoparticles.\(^4,10\) The co-deposition of ceria and gold nanoparticles on a TiO\(_2\)(110) substrate generates catalysts with an extremely high activity for the production of hydrogen through the water-gas shift reaction (see Figure 3). Au/ CeO\(_x\)/TiO\(_2\)(110) was found to be much more active than Au/TiO\(_2\)(110) or even Au/CeO\(_x\)(111).\(^4\) On the TiO\(_2\)(110) surface, the ceria nanoparticles help to disperse the Au atoms and to dissociate the water molecule.\(^4,10\) While Au surfaces and nanoparticles interact poorly with water,\(^4\) density-functional calculations predict an exothermic process for the dissociation of water on CeO\(_x\)/TiO\(_2\)(110) with almost no activation barrier.\(^8,11\) The enhanced stability of the Ce\(^{3+}\) state in CeO\(_x\)/TiO\(_2\)(110) is an example of structural
promotion in catalysis documented for the first time on the atomic level.4 Thus, the exploration of mixed-metal oxides at the nanometer level may open new avenues for optimizing catalysts through stabilization of non-conventional surface structures with special chemical activity.4,10,18 The Cu/CoOx/TiO2(110) and Pt/CoOx/TiO2(110) systems are also excellent WGS catalysts.10 In the future, we plan to extend this type of studies to high-surface area powders. A first set of studies for a Pt/CoOx/TiO2 powder shows a very good WGS catalyst.18

Future Directions

The studies described above indicate that highly active water-gas shift catalysts are bifunctional with the metal and oxide catalyzing different parts of the reaction. To optimize these complex systems one must understand the nature of the active sites in each component of the catalyst and determine how they interact with the reactants (CO, H2O) and possible intermediates (OH, HOCO, HCOO, CO3, and HCO3) of the WGS.19 In the future, we plan to work with catalysts in which the oxide phase contains or combines ceria, titania and molybdena. Cu, Au, Pd or Pt will constitute the metal phase. This selection of oxides and metals is based in our previous studies. The high WGS activity of ceria- and titania-based catalysts is well documented in the literature.13,16,20 They are expected to be the next generation of WGS catalysts for industrial applications. We will identify methodologies for developing highly efficient WGS catalysts optimizing the performance of the metal and oxide phases. The scheme at the left shows the three different configurations in which a metal and an oxide will be combined in our catalysts. The most complex and promising is the mixed-metal oxide configuration in which nanoparticles of a metal and an oxide can interact with the reactants.4,10,18 Our experience indicates that a coordinated approach is necessary to address fundamental issues for the WGS on metal/oxide catalysts. Thus, we propose three research thrusts: (i) in-situ studies; (ii) model system studies; and (iii) theoretical calculations. The overarching questions of catalyst state, reaction mechanism, and nanoparticle size and morphology interconnect these thrusts. As in the past, we will be taking advantage of a unique set of techniques available at BNL for in-situ studies (XRD, XAFS, TEM, IR, XPS). The experiments will closely coupled to theoretical studies on the chemisorption of the reactants, the stability of possible intermediates, and activation barriers for elementary reaction steps, providing critical guidance in developing a complete picture of structure and mechanism in this important process.
References

V.P.14 Bio-Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production

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Objectives

Electrocatalysts based on inexpensive, earth-abundant metals are needed since most fuel cells are based on platinum, an expensive, precious metal. Our objective is to design and synthesize biologically inspired functional model complexes that catalyze the oxidation of hydrogen and the production of hydrogen. Our research focuses on molecular complexes containing ligands bearing pendant amines that function as proton relays.

Technical Barriers

The Basic Energy Sciences workshop report, Basic Research Needs for the Hydrogen Economy, emphasized the need for “developing catalysts that rely less on noble metals, which will become a limiting resource in large-scale hydrogen energy systems.” Because of limited supplies and the high cost of platinum, alternatives that use abundant, inexpensive metals are being studied in our research. We seek an understanding of how molecular complexes of nickel, cobalt and manganese can function as catalysts for oxidation of H₂ and for production of H₂ by reduction of protons. The challenges involve synthesis and design of ligands and metal complexes, obtaining an understanding of mechanistic details of the reactions, and development of highly active electrocatalysts with low overpotentials.

Abstract, Progress Report and Future Directions

Renewable energy sources such as solar, wind, or geothermal provide the possibility of large amounts of carbon-free energy, but the temporal variation in electricity output from these sources will require energy storage. Studies of H₂ are a critical part of efforts to rationally design electrocatalysts for energy storage as fuels. Low-temperature proton exchange membrane (PEM) fuel cells require platinum, an expensive noble metal of low abundance. Lower costs for fuel cells are expected to lead to broader and more diverse applications of fuel cells for conversion of H₂ to electricity. The cost of Ni, Co, or Mn is typically about three or four orders of magnitude less than the cost of Pt, so dramatic cost savings may be obtained by development of catalysts using these inexpensive, earth-abundant metals. This goal has already been achieved by biological systems that oxidize and produce H₂ using iron and nickel under exceedingly mild conditions.

Our objective is to synthesize biologically inspired functional models that provide high catalytic activity with low overpotentials, by recognizing that some of the most salient features enabling the remarkable capabilities of Nature’s catalysts can be replicated synthetically. In the [FeFe] enzyme, it is thought that an N atom near the iron assists in the heterolytic cleavage of H₂, and that this pendant amine shuttles protons from the catalytically active metal site to the proton conduction channel. Our efforts focus on the design of biologically inspired complexes that use abundant metals and have a pendant amine; we seek functional rather than structural models of the [FeFe] or [FeNi] hydrogenases.

Our work has demonstrated that complexes based on nickel, an inexpensive, abundant metal, can be used as electrocatalysts for H₂ production with rates (up to about 800 s⁻¹ at 22 °C) comparable to those of [NiFe] hydrogenase enzymes, and with overpotentials of 100-300 mV. Another important need is for catalysts with improved tolerance to CO, since the Pt catalyst in fuel cells is sensitive to CO impurities at the ppm level. The nickel-based hydrogen oxidation catalysts developed by our group have been demonstrated to have remarkable tolerance to CO; they function under 5% CO, with no detectable loss of activity.

Pendant amines in the diphosphine ligand can lead to a profound acceleration of the catalytic rates in nickel electrocatalysts for oxidation of H₂. In our series of electrocatalysts for oxidation of H₂, the thermodynamic driving force for the addition of H₂ increases in the order [Ni(dp^3)₄N₂]⁺⁺ < [Ni(dp^3)₂(dp)₂]⁺⁺ < [Ni(dp^3)₂(dp)₂N₂]⁺⁺ < [Ni(dp^3)(PNP)₂]⁺⁺ (PNP = Et₂PCH₂N(Me)CH₂PEt₂). The turnover frequencies, which correspond to the rates of H₂ addition, show the reverse order. These rates correlate with the number of amines positioned near the metal ion in the second coordination sphere of each complex (not the total number of
pendant amines). These comparisons indicate that two positioned pendant bases are important for achieving the fast catalytic rates observed for \([\text{Ni}(\text{PCy}_2\text{NBz}_2)_2]^{2+}\) in the oxidation of \(\text{H}_2\), and for \([\text{Ni}(\text{PPh}_2\text{NPh}_2)_2]^{2+}\) in the production of \(\text{H}_2\). The role of the two amines positioned in close proximity to the metal serves to stabilize, through hydrogen bonding interactions, both the binding of the dihydrogen ligand on nickel and the heterolytic cleavage of \(\text{H}_2\).

Nickel catalysts for reduction of oxygen to water were also discovered, again with pendant amines on the ligands facilitating these reactions involving transfers of multiple protons and electrons. No activity for catalytic reduction of oxygen was found for related complexes lacking the proton relay in the ligand.

Our progress on cobalt complexes shows that our approach of using pendant amines in the second coordination sphere of nickel complexes can lead to the development of new classes of catalysts based on other earth-abundant, inexpensive first row metals. Catalytic reduction of protons by \([\text{Co}(\text{PPh}_2\text{NPh}_2)(\text{CH}_3\text{CN})]^{2+}\) occurs with a turnover frequency of 90 s\(^{-1}\) for production of \(\text{H}_2\) and essentially 100\% current efficiency. This reaction occurs at the half-wave potential of the \(\text{Co(II/III)}\) couple (-1.00 V vs. \(\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}\)). The overpotential of this reaction was calculated to be 285 mV, so this cobalt catalyst operates at a fast rate and with a relatively low overpotential. In contrast to the nickel complexes, where two relays were found to be optimal, the cobalt catalysts need only one ligand containing a positioned pendant amine. Much remains to be done in terms of future catalyst development. These discoveries point to new directions that we propose to study in detail, since our knowledge of the mechanistic details of these cobalt complexes is scant compared to the understanding we now have for the nickel complexes.

We recently began a new study of manganese complexes. Manganese is not normally even considered in studies of catalytic oxidation of \(\text{H}_2\) or for production of \(\text{H}_2\), but we believe that with appropriate ligands, a new class of catalysts could result. We have synthesized a series of Mn complexes of general formula \([\text{(P-P)}(\text{P’-P’})(\text{CO})\text{Mn}]^{n+}\) and have studied their binding of \(\text{H}_2\). The reaction of \(\text{H}_2\) with \([\text{PPh}_2\text{NPh}_2]^{n+}(\text{dppm})(\text{CO})\text{Mn}]^{n+}\) produces an \(\eta^2\)-\(\text{H}_2\) complex. A related complex with electron-withdrawing aromatic groups on the second
diphosphine reacts with $\text{H}_2$ (1 atm) to give *heterolytic cleavage of H}_2 at room temperature*, with the H$^-$ being located on the Mn and the H$^+$ being transferred to the N.

In proposed future work, we will focus on the design and development of Co, Mn, and Fe complexes; we seek to obtain an understanding of the molecular reactivity that will allow us to design and discover new, robust, highly active catalysts for oxidation and production of $\text{H}_2$. We propose new studies of how changes in the first and second coordination spheres will alter catalytic activity and the mechanism. New studies on iron complexes are being initiated; iron is a very attractive metal since it is cheap, non-toxic, and the metal used by the biological catalysts that have the highest rates for $\text{H}_2$ production/oxidation. We propose the synthesis of a new series of ligands with enhanced hydrogen bonding capabilities.

**Publications acknowledging DOE Hydrogen Fuel Initiative Funding**


Objectives

The research is geared toward fundamental understanding of composition/structure/function relationships in supported, heterogeneous catalysts for reactions that produce hydrogen from hydrogen-rich molecules. The role of particle composition, size, and structure and the effect of supports and promoters on adsorptive and catalytic properties are investigated. A particular goal is to determine if the catalytic activity for hydrogen production from methanol can be significantly improved by preparing catalysts which only partially adsorb CO under reaction conditions. The catalysts are supported metal, alloy, carbide, and nitride nanoparticles and clusters with an emphasis on clusters in the size range <1 nm, i.e., ~2-50 atoms.

Technical Barriers

Catalysts for the reforming of hydrogen rich organic molecules, such as methanol, to produce molecular hydrogen exhibit poor activity at low temperature due in large part to poisoning by CO, an inevitable byproduct of the chemistry. We hypothesize that catalyst performance can be improved greatly by using subnanometer size metal and alloy clusters on suitable supports. Advanced techniques for synthesis, stabilization, characterization, theory and testing are employed to investigate and understand the chemical and catalytic properties of these materials.

Abstract

The objective of the research is a fundamental understanding of composition/structure/function relationships in supported, heterogeneous catalysts for reactions that produce hydrogen from hydrogen-rich molecules. The focus of the work over the last two years has been the synthesis, stabilization, characterization, catalytic evaluation and computation of supported metal cluster catalysts in the size range <1 nm, i.e., ~2-50 atoms. New synthetic and stabilization strategies and computational understanding have been achieved for ultra-small, supported metal particles. The research integrates efforts in: 1) synthesis and stabilization of uniform, supported clusters and oxide promoters; 2) characterization of cluster size, atomic structure, stability, and electronic structure during synthesis, pretreatment, and catalytic reaction; 3) investigation of catalytic and chemical events on the clusters that are relevant to hydrogen production; 4) computational quantum chemical modeling to understand and predict experimental results. Future work will emphasize experiments and computations of alloy, carbide, and nitride nanoparticles and clusters.

Progress Report and Future Plans

Experimental Catalyst Synthesis, Characterization and Reaction Studies

Pd nanoparticle catalysts were synthesized and stabilized by atomic layer deposition (ALD). [1] Alternating exposures of palladium (II) hexafluoracetacetonate (Pd(hfac)_2) and formaldehyde (HCOH) produce well dispersed, discrete Pd nanoparticles on high surface area mesoporous silica gel supports. The average Pd particle size by TEM and EXAFS is ~2 nm. Smaller particle sizes have been achieved using lower reaction temperatures and by depositing support layers prior to metal particle reduction with HCOH. Additional layers of support serve to stabilize the particles against sintering and deactivation. Other ALD noble metal systems, including Pt, Ru, and Ir, were targeted for achieving sub-nanometer particles for hydrogen production. In-situ EXAFS revealed details of the Pt nanoparticle formation. [2] Supported sub-nm Ir nanoparticles (<0.5 nm, Fig. 1a) were prepared, the smallest reported to date. A detailed study of ALD Pt-Ir alloys has also been performed, representing the first study of ALD metal mixtures. [3] Finally, a variety of ALD noble metal alloy nanoparticles including Pt-Ir, Pt-Ru, Ir-Ru, and Pt-Pd (Fig. 1b) were prepared.
Size-selected cluster synthesis of various sized cluster catalysts using a mass-selected ion beam has been combined with the development of an in-situ reaction cell and surface-sensitive tools at 12-ID of the Advanced Light Source. Catalysts can be characterized by synchrotron-based X-ray absorption and scattering and simultaneously monitored for catalytic activity. [4,5]

The performance for methanol decomposition by the ALD catalysts is shown in Fig. 2. The methanol conversion increases monotonically with increasing temperature reaching ~100% at 280°C. At all temperatures the selectivity was nearly 100% to CO and H₂. Catalysts prepared using ALD ZnO as the underlying support showed much lower conversion and rapid deactivation at the higher temperatures due to Pd “dissolving” into the ZnO substrate. By applying one cycle of ALD Al₂O₃ on top of the Pd/ZnO catalyst, the activity was enhanced, and the catalyst deactivation was mitigated. This Al₂O₃ over-coating method stabilizes the Pd/ZnO and effectively prevents the dissolution of Pd into the ZnO substrate. [1]

Smaller Pd₈₋₁₂ clusters formed by ion beam deposition were found to promote decomposition to CO and hydrogen but suffered from poisoning. Larger Pd₁₅₋₁₈ clusters preferentially produce dimethyl ether and formaldehyde, without signs of poisoning. A thin ALD titania overcoat applied on Pd₁₅₋₁₈ improves the sintering-resistance via a mechanism involving partial encapsulation of the Pd. [6] It also changes the selectivity so that CH₂O prevails.

Future synthesis and catalytic experimentation efforts will target subnanometer alloy and nitride particles with weaker bonds to CO. Guidance in the selection of particle size and composition will be provided by computations as described below.

**Computational Catalysis Studies**

Periodic plane wave calculations were employed to determine the activity and reaction pathways of supported and unsupported M₄ and M₈ (M=Pd, Cu, and Co) clusters for methanol decomposition. [7,8] The structures of oxidized Cu clusters have also been studied. [9] For Pd (primarily Pd₄) clusters, the decomposition of methanol begins with C-H bond breaking to form hydroxymethyl (CH₂OH), followed by steps involving formation of hydroxymethylene (CHOH), formyl (CHO), and carbon monoxide (CO). This pathway is shown in Fig. 3. O-H bond breaking as the first step, followed by formation of methoxy (CH₃O) and formaldehyde (CH₂O), was slightly less favorable. C-O bond cleavage is much less energetically favorable, and
no feasible pathways involving C-O bond formation to yield dimethyl ether (CH₃OCH₃) were found. All reaction intermediates bind slightly more strongly to clusters than to extended surfaces. The effects of an alumina support were also calculated. [7] Overall, the results indicate that larger Pd clusters and inclusion of the alumina support did not significantly affect the reaction pathways. The combination of bare and supported cluster results clearly shows that CO adsorbs in a deep well (Fig. 3) that can poison the methanol decomposition reaction, supporting the proposal in the experimental studies of Vajda et al [6] where little product is observed until the temperature is high enough for CO desorption. The reaction pathways on Cu₄ and Co₄ clusters are distinctly different from the Pd₄ clusters. [8] Methanol decomposition to form CO and H₂ is shown in Fig. 3 for Cu₄ and Co₄ along with that of Pd₄. The overall trends are not affected by adding the support. The Co₄ cluster pathway is very favorable both thermodynamically and kinetically for dehydrogenation, but since CO adsorption is also very favorable, it is likely to poison methanol decomposition at low temperatures, similar to the result for Pd clusters. In contrast, CO poisoning of the Cu₄ cluster is less of a problem, but the dehydrogenation steps are not favorable. This strongly indicates a need to find other clusters that combine the favorable aspects of the Co and Cu clusters for methanol decomposition while, at the same time, not suffering from the deficiencies of these elements. Pathways involving C-O bond cleavage are less energetically favorable for the Cu₄ and Co₄ clusters.

The data on adsorption energies and activation barriers can be analyzed in terms of Brønsted-Evans-Polanyi (BEP)-type curves. BEP relations are often implicitly assumed to hold for surface reactions, but to the best of our knowledge, this kind of relationship has not been considered for subnanometer clusters. Fig. 4 shows a BEP plot for all elementary reactions studied for Pd₄ and Pd₈ clusters. According to this BEP relationship, the thermodynamically most endothermic step should have the highest activation barrier and vice versa. C≡O dissociation is the most endothermic step in Fig. 4, C–O, O–H and C–H scission have intermediate energetics, and C–H dissociation is the most exothermic. The equation relating transition and final state energies is provided in Fig. 4 and has a slope of 0.85; this value, close to unity, suggests that the transition states in the reaction networks are final state-like in character, where the final state is defined in the exothermic direction for each elementary step. This type of analysis has also been carried out for the reactions on Cu₄ and Co₄ clusters. The relationships derived will be utilized in screening studies in our future plans to identify promising systems.

**Publications**


Objectives

- Provide fundamental understanding of hydroxide conducting systems.
- Explore stability and basicity of cations.
- Relate cation chemistry and structure to stability and conductivity.
- Elucidate importance of carbonate in hydroxide conducting systems.

Technical Barriers

Alkaline membrane-based electrochemical systems have been limited by: 1) the poor stability of tetraalkyl ammonium ions employed as covalently tethered cations in current anion exchange membranes; 2) the decreased conductivity of hydroxide compared to protons; and 3) the role of carbonate/hydroxide equilibrium in these systems. Alkaline systems have shown improved electrocatalysis and the ability to operate without precious metal catalysts (like platinum). If systems based on alkaline membranes could achieve good stability and conductivity, they would play a major role in enabling commercial competitiveness of fuel cell systems.

Abstract

The advantages of an alkaline system for fuel cells are improved efficiency, and the enablement of non-precious metal catalysis, a critical showstopper to widespread implementation of traditional (acidic) fuel cells. Alkaline systems have seen much less research interest by the fuel cell community compared to competing technologies due to concerns with carbonate formation and the inability to produce membranes of acceptable stability. Still, no fundamental investigations quantifying the role of carbonate formation have been made and investigation of cations other than those based on quaternary ammonium has been very limited. This project addresses both of these points, and probes fundamental aspects of hydroxide conductors for conductivity and stability. We will emphasize the investigation of families of cations that show promise, but have been largely overlooked by the ion exchange community. The project includes quantum mechanics (QM) and molecular dynamics (MD) modeling which allow us to probe the chemical stability and conductivity of target cations, the functional component of anion exchange materials. This modeling work will be closely tied to the characterization of traditional cations and the synthesis and characterization of non-traditional cations potentially suitable for incorporation into anion exchange membranes. Finally, the role of carbonate (or bicarbonate) versus hydroxide anion in these systems will be elucidated. The team we have assembled is eminently and uniquely qualified to successfully achieve these goals. The results of the work proposed here will provide a greater understanding of the fundamental aspects of hydroxide conductors for fuel cells and electrolysis applications, and the development of hydroxide-stable cations may lead the way for the next generation of fuel cells and electrolyzers.
trimethylammonium (BMTA) cation. The best of these, an ether-linked ammonium showed more than a 3x improvement in stability, a meaningful increase when considering applications.

Significant advances in this project have come from studies of cation stability and center on the role of water and solvation in cation stability. In hindsight, the fact that water availability (eg., # of waters per hydroxide) would play a role in cation stability seems fairly obvious, yet this phenomenon had been only minimally reported in the literature and not in the context of membranes (although many vendors of these materials ship them hydrated with instructions to keep wet). Our results demonstrate that the impact of solvation is greater than what many would have expected, and show that under many conditions hydration is far more important than temperature for degradation. The importance of ylide formation (which may also be related to water content and solvation) as a degradation pathway has been highlighted by our chemical and computational studies.

Our studies have involved both experimental and computational studies of cation degradation. In our computational work, all reaction energies and free energies of energy barriers for transition states were estimated by Gaussian 03 software, with B3LYP/6-311++G(2d,p) level of theory and the polarizable continuum model (PCM) to account for the solvent. We have also made qualitative and quantitative findings from ab-initio MD simulations performed with VASP software and the rPBE functional. These studies have shown that by treating the water molecules in the hydroxide solvation shell explicitly and the bulk water molecules implicitly, the calculated reaction barrier free energies are in much better agreement with experimental values. We have recently demonstrated the utility of a QM-molecular mechanics (MM) hybrid algorithm and umbrella sampling technique for faster calculation of reaction energy barriers, and shown that in carbonate or bicarbonate form, reaction barriers for decomposition are significantly (>10kcal/mol) higher than in hydroxide form.

Our thermal analyses of crystalline TMAOH pentahydrate used EGA (evolved gas analysis) to probe degradation chemistry. The results from these studies have allowed us to benchmark mechanistic details and correlate the results with our computational studies. The identity and quantities of the gases that were evolved upon decomposition of TMAOH pentahydrate were analyzed by a combination of thermogravimetry (TG), FT-IR spectroscopy and mass spectrometry (TG-FTIR and/or TG-MS). We have focused primarily on ammonium based cations: BMTA, tetramethyl ammonium, ethyltrimethyl ammonium and phenyltrimethyl ammonium have received the most attention. Mechanistic studies using partially deuterated or judiciously substituted alkyl ammonium cations has allowed us to study the interplay of the various decomposition mechanisms; Hoffman degradation, nucleophilic attack and ylide formation. Furthermore, an ether linked ammonium, and two other literature referenced nitrogen-centered cations have shown increased stability compared to BMTA.

**Future Directions**

Our primary focus remains on fundamental investigations into the mechanisms and reaction barriers associated with cation degradation. This involves both quantifying and understanding the rates of current materials, and the pursuit of advanced cations with improved durability. Additional studies will include investigation into conductivity (basicity) and the role of carbonate. We have already begun modeling studies of carbonate and bicarbonate solutions of the cations under investigation and will use these alternate salt-forms to better probe stability and durability experimentally. Now that we have verified our ability to quantitatively assess cation stability under well hydrated conditions, we can and will include many other cations, including phosphonium, and expand our studies of phosphazenum and sulfonium which had been limited due to the surprisingly high stability we had observed with ammonium based cations. The calculations on reaction energies and free energies of reaction barriers for these cations are already under the way based on our established computational models. Preliminary result shows that the degradation of trimethyl amino sulfonium by hydroxide has a more negative reaction energy than ammonium cations such as TMA or BMTA (-48 kcal/mol vs. -25~29 kcal/mol). We have already received other advanced cations that have been shown to have good performance and durability in fuel cell applications in a collaborative agreement from Yushan Yan’s group.

Our experimental studies will incorporate fixed humidity into our thermal gravimetric analysis (TGA) studies. To date we have focused either on liquid based cation degradation (primarily in NMR tubes at elevated temperatures) or decomposition under drying conditions where degradation of cations is greatly impacted by the loss of water (typical TGA). As water content is critical in the degradation of cations, by including controlled humidity in our studies we will be more able to probe the sensitivity of durability on water content and better isolate degradation products.

Our synthesis of novel cations will focus on triaminosulfonium, triaminosulfoxonium and phosphazenum derivatives because these materials have demonstrated the potential to be much more stable to attack by hydroxide ion than the more conventional trialkyl ammonium ions. We will also expect to expand our studies to include oligomers and polymers such that we can study the stability of the cation tether, the role of polymer architecture on properties and durability.
and the role of carbonate/bicarbonate on the stability and conductivity of these systems. Advanced NMR techniques, including magic-angle spinning (MAS), $^1$H-$^{13}$C cross polarization, nuclear spin-relaxation time, and two-dimensional NMR techniques will be utilized to obtain information about the ionic structure, mobility of the charge carriers (conductivity), and polymer – cation interactions.

References


Publications (including patents) acknowledging the grant or contract

V.P.17 Transport Phenomena and Interfacial Kinetics in Planar Microfluidic Membraneless Fuel Cells

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Objectives

Our research aims to achieve a fundamental understanding of the transport behavior in planar microfluidic membraneless fuel cells and to take advantage of their unique properties, including the lack of a physical membrane and the ability to utilize different pH solutions in fuel and oxidant streams to optimize power output and efficiency. We have identified the borohydride/cerium ammonium nitrate fuel/oxidant combination as one capable of delivering over 0.25W/cm². This was only enabled by detailed fundamental studies of the redox reactions of sodium borohydride as fuel and numerous potential oxidants.

Technical Barriers

While membraneless fuel cells have numerous attractive features, their performance has been limited by a low utilization efficiency of fuel and oxidant as well as relatively low energy density. In our investigations we have been able overcome these limitations through the use of “structured” electrodes (herringbone micromixers) and the identification of high-energy (and high solubility) fuel and oxidant couples. While the scale-up of these devices to deliver 2-10 watts remains a challenge, we have begun studies that we feel will overcome this limitation.

Abstract

Unconventional fuel cell technologies are combined to create a system that not only avoids most typical fuel cell drawbacks, but also achieves the highest power density yet recorded for a non-H₂ fuel cell. Rigorous electrochemistry is used to characterize the high-energy-density fuel BH₄⁻, providing important mechanistic insight for anode catalyst choice and avoiding deleterious side reactions. All major fuel cell oxidants used in place of O₂ are compared in a detailed, uniform manner, and a powerful new oxidant, cerium ammonium nitrate (CAN), is described. The high-voltage BH₄⁻/CAN fuel/oxidant combination is employed in a membraneless, room temperature, laminar-flow fuel cell, with herringbone micromixers which provide chaotic-convective flow which, in turn, enhances both the power output and efficiency of the device.

Progress Report

Previous research centered around a membraneless, laminar-flow fuel cell described earlier, with the goal of creating a high power density device for portable power applications. A transport-enhancing, chaotic-convective flow design was employed to boost power and efficiency. The fuel cell system was studied from both analytical and practical standpoints, with electroanalytical studies of fuel and oxidant accompanying performance testing in this microfluidic fuel cell device.

As a potential fuel, BH₄⁻ has been the subject of intense investigation, as its energy density is superior to that of MeOH, yet its kinetics are much faster, its onset potential is much lower, and it does not poison the anode or any known cathode material. However, BH₄⁻ does suffer from a deleterious, acid-catalyzed conversion to H₂ in aqueous media. This decreases its effective concentration in solution, in turn decreasing its power output.

Our rigorous study of BH₄⁻ oxidation at Pt and Au revealed a number of misconceptions in the literature about BH₄⁻’s reaction mechanism. We found that, unexpectedly and most surprisingly, BH₄⁻ has more problems with hydrolysis to H₂ at Au than at Pt surfaces, and that low-potential current at Pt stems from direct BH₄⁻ oxidation, rather than H₂ produced via BH₄⁻ hydrolysis (Figure 1). Though Au is the literature preferred BH₄⁻ anode, we found that Pt is the superior catalyst, capable of delivering just as much current as Au, but at potentials nearly 0.5V lower. This difference translates to a 0.5V gain in operating voltage for direct BH₄⁻ fuel cells that use Pt rather than Au anodes.
Our fuel cell studies with our new oxidant cerium ammonium nitrate (CAN), showed that BH$_4^-$ was actually the limiting reagent, largely due to its limited stable solubility. BH$_4^-$’s hydrolysis to H$_2$ is first order with respect to BH$_4^-$ and must be stabilized with highly concentrated base, and above 3M NaOH, various fuel cell components were degraded. Since 3M NaOH can hold only 0.15M BH$_4^-$, we studied BH$_4^-$ oxidation in nonaqueous solvents to improve its maximum stable solubility and, therefore, its maximum current/power.

We found that BH$_4^-$ had a solubility higher than 0.4M in DMSO, DMF, diglyme, and EtOH, and higher than 0.3M in MeOH. As literature suggested, BH$_4^-$ will undergo a conversion to H$_2$ in MeOH and, to a lesser extent, in EtOH, similar to its hydrolysis to H$_2$ in water, and it did not appear to be stable in diglyme, either. Thus, DMSO, DMF, and EtOH appeared to be the most promising solvents, but BH$_4^-$ was found to have a disappointing onset potential of around -0.1V vs. NHE in these solvents, which is 0.7V more positive than its onset in alkaline solution. We continue studying these solvent systems to determine if 0.4M BH$_4^-$ in organic solvents has superior performance as compared to 0.15M BH$_4^-$ in 3M NaOH, and whether specific additives can enhance BH$_4^-$ oxidation.

Laminar-flow fuel cells provide the tremendous advantage of fuel cell operation without a membrane, but usually require that the oxidant be dissolved in solution, so as to have fluid fuel and oxidant streams with which to establish laminar flow. Since O$_2$’s solubility in water and other solvents is minimal, highly soluble oxidants with high onset potential and fast kinetics are needed to generate high power density. All fuel cell oxidants with literature precedent were characterized in detail, in a uniform manner, at the common catalysts Pt, Au, and GC, and all oxidants were compared using their best respective catalysts (Tables 1 and 2).

Almost every oxidant was found to have a critical weakness. H$_2$O$_2$ established high current density but catalytically decomposed to form laminae-disrupting O$_2$ bubbles. MnO$_4^-$ produced tremendous voltage and current, but quickly precipitated at its electrodes. VO$_2^+$, used in “vanadium redox battery” fuel cells, has fundamentally low current. ClO$^-$ poisons Pt, Au, and even GC. Only our new oxidant, CAN, performed in a trouble-free manner, exhibiting the highest onset potential of +1.6V vs. NHE, with reasonable current. It was the only practical alternative oxidant found, although its low solubility limits its max current, and higher-power fuel cells will need a better oxidant.

![Figure 1](image)

**TABLE 1.** Oxidant Reactions

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Possible Reactions:</th>
<th>E$^0$ (V vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>O$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$O$_2$</td>
<td>0.498</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>2H$_2$O$_2$ $\rightarrow$ 2H$_2$O + 1/2 O$_2$</td>
<td>1.032</td>
</tr>
<tr>
<td>MnO$_4^-$</td>
<td>MnO$_4^-$ + e$^-$ $\rightarrow$ MnO$_3^-$</td>
<td>0.361</td>
</tr>
<tr>
<td>ClO$^-$</td>
<td>HClO + H$^+$ + 2e$^-$ $\rightarrow$ Cl$^-$ + H$_2$O</td>
<td>1.285</td>
</tr>
<tr>
<td>V$^{2+}$</td>
<td>VO$_2^+$ + e$^-$ $\rightarrow$ V$^{2+}$</td>
<td>0.140</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>VO$_2^+$ + e$^-$ $\rightarrow$ V$^{3+}$</td>
<td>-0.452</td>
</tr>
</tbody>
</table>

**TABLE 2.** Oxidants Performance Parameters Determined or Confirmed by RDE Analysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>$D_{O_2}$ (10$^{-5}$ cm$^2$/s)</th>
<th>max $C_n$ (M)</th>
<th>$i_{max}$ (mA/cm$^2$)</th>
<th>Pt</th>
<th>Au</th>
<th>GC</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>2</td>
<td>2.6</td>
<td>0.0011 $^*$</td>
<td>0.600</td>
<td>0.600</td>
<td>6.25</td>
<td></td>
</tr>
<tr>
<td>FeO$_4^-$</td>
<td>2</td>
<td>1.25 $^*$</td>
<td>42.4 $^*$</td>
<td>0.640</td>
<td>0.640</td>
<td>12.5</td>
<td>217</td>
</tr>
<tr>
<td>MnO$_4^-$</td>
<td>5</td>
<td>1.25 $^*$</td>
<td>7.3 $^*$</td>
<td>1.270</td>
<td>1.120</td>
<td>8.00</td>
<td>593</td>
</tr>
<tr>
<td>VO$_2^+$</td>
<td>1</td>
<td>1.25 $^*$</td>
<td>0.38 $^*$</td>
<td>1.470</td>
<td>1.300</td>
<td>3.00</td>
<td>57</td>
</tr>
<tr>
<td>CAN</td>
<td>1</td>
<td>1.25 $^*$</td>
<td>&lt;3.0 $^*$</td>
<td>0.800</td>
<td>0.800</td>
<td>23.0</td>
<td>43.4</td>
</tr>
<tr>
<td>ClO$^-$</td>
<td>1</td>
<td>1.25 $^*$</td>
<td>10.0 $^*$</td>
<td>1.200</td>
<td>1.010</td>
<td>10.00</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>

$^*$Determined from RDE of VO$_2^+$ at Pt and Au assuming n = 1. See Results and Discussion for details. $^*$Calculated from the density of pure H$_2$O$_2$ liquid. (O$_2$) was studied at its maximum aqueous solubility of ~1.27 mM rather than 5M.
Both BH$_4^-$ and CAN were employed in a membraneless, room-temperature, laminar-flow fuel cell. Electrodes with microfabricated, staggered-herringbone micromixers were employed to separately convect the fuel and oxidant streams, disrupting laminae enough to bring unreacted fuel and oxidant to the anode and cathode, respectively, without allowing the fuel and oxidant streams to mix. We were able to achieve current densities of 0.4 A/cm$^2$ (Figure 2) and power densities of 0.27 W/cm$^2$ (Figure 3).

Comparison with literature values are difficult, as other groups use high-surface area electrodes but normalize to geometric area. By normalizing outputs to catalyst loading, our system achieved the highest power density yet recorded for a non-H$_2$ fuel cell. Whereas MeOH and BH$_4^-$ fuel cells use 1.5-3M fuel at 60°C and provide up to 30 and 220 mW/mg catalyst, our system used 0.15M fuel at room temperature and produced 1,230 mW/mg Pt.

Future Directions

We are continuing to use innovative experimentation to develop fundamentally new fuel cell chemistries and transport. New oxidants are being analyzed to find a replacement for CAN with higher maximum current density. We are testing BH$_4^-$ at less expensive catalysts and in new solvent systems to improve its current output as well. A fuel cell 60 times larger than described above has been built and is undergoing testing to demonstrate that laminar flow fuel cells are scalable. New fuel cell fluid flows and geometries are being investigated to improve the overall device efficiency.

Publications (including patents) acknowledging the grant or contract

Objectives

The proposed project aims to explore enhancements in the electronic and ionic transport properties of nano-scale oxides and surfaces, and to utilize these materials to enhance the performance of reduced-temperature solid oxide electrochemical cells (i.e., fuel cells and electrolyzers). The project is focuses on electrode materials, and the use of nano-scale materials to enhance properties and surface areas to increase electrochemical reaction rates. Also, we are exploring the enhancement of electronic and oxide-ion transport properties, which help limit the reduced-temperature performance. Stability of nano-scale materials is also being explored.

Technical Barriers

Decreasing the operating temperature of solid oxide electrochemical cells is desirable from a number of perspectives including easing seals/interconnect materials issues, reducing balance of plant costs, and enabling applications in portable devices and transportation. However, reduced temperature significantly degrades performance, due to increased electrode polarization resistance and reduced electronic and ionic conductivities. The long-term stability of nano-scale materials needs to be investigated.

Abstract, Progress Report and Future Directions

The goal of this project is to utilize nano-structures, and any enhancements in electronic and ionic transport properties resulting from the nano-scale features sizes and/or high surface density, to address the electrode polarization and conductivity issues currently limiting low-temperature solid oxide fuel cell (SOFC) performance. In this update we highlight recent research results including nano-scale catalysts and effect of grain size on ionic conductivity.

Infiltrated Cathode Materials

On the cathode side, we have studied the effect of solution additives and processing techniques on the phase purity and performance of nano-composite cathodes produced via infiltration. In addition to achieving record low cathode performance from a single infiltration, simple models have been developed to predict the electrode polarization resistance.

Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC) nano-particles with hemispherical radii of ~ 20 nm have been produced by nitrate infiltration Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) scaffolds. Polarization resistance, \( R_p \), predictions were made using the modified Tanner, Fung, Virkar model. The measured polarization resistances for SSC-GDC agreed well with the modified form of Tanner, Fung, Virkar model, as did those of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)-infiltrated GDC cathodes. An exceedingly low polarization resistance of 0.1 \( \Omega \) cm\(^2\) at 600°C was achieved with a single infiltration. We expect that with multiple infiltrations, polarization resistances of this magnitude will be achievable at 500°C.

The coarsening behavior of infiltrated LSCF electrodes, and the associated changes in polarization resistance, have been studied. In order to accelerate changes to manageable time frames (normal cell life times are expected to be > 40,000 h), cathodes were maintained at temperatures higher than expected for operation (700-850°C). Field-emission scanning electron microscope (SEM) and polarization resistance measurements were used to detect changes. With time, LSCF nano-particles were observed to agglomerate together, coating less of the CGO scaffold and growing larger in size. Correspondingly, the polarization resistance increased substantially. The results are being fit to both standard coarsening power-law models and being used to constrain/validate phase-field modeling. The aim is to develop sufficiently detailed mechanistic models to allow accurate prediction of lifetimes at normal operating temperatures (500-700°C) for extended times.

Novel Anode Materials

The mixed conducting oxide, LaSr_{2}Fe_{2}CrO_{9-δ} (LSFCr) is a promising new anode. Ni cermets are the most commonly used SOFC anodes because of their excellent electrochemical performance in hydrogen fuel, but Ni is susceptible to sulfur poisoning and carbon
coking, which are detrimental to anode performance. Oxide anodes have potential for lower operating temperatures, while also being stable to higher impurity concentrations and active to different fuel compositions.

LSGM electrolyte supported fuel cells with LaSr$_2$Fe$_2$CrO$_9$ and LaSr$_2$Fe$_2$CrO$_9$/GDC composite anodes have been fabricated and tested. The LaSr$_2$Fe$_2$CrO$_9$ anode cells typically yielded peak power densities of 400-455 mW/cm$^2$ at 800°C with corresponding electrode polarization resistances of 0.27-0.40 Wcm$^{-2}$. The LaSr$_2$Fe$_2$CrO$_9$/GDC (50:50 wt%) anode cells yielded similar performance as the pure LaSr$_2$Fe$_2$CrO$_9$ compounds with peak power densities 400-480 mW/cm$^2$ and polarization resistances of 0.25 - 0.40 Ωcm$^{-2}$. The similar performance of the anodes with and without GDC suggests that the LaSr$_2$Fe$_2$CrO$_9$ anodes are not limited by their oxygen ion conductivity. Currently, oxygen relaxation experiments are underway to determine the surface exchange rate and oxygen diffusivity of LaSr$_2$Fe$_2$CrO$_9$ under anodic conditions.

This group has also developed a novel class of anodes where nano-scale metal catalyst particles nucleate during cell operation. To investigate the precipitation of Ru nano-particles from (La,Sr)(Cr,Ru) O$_3$ (LSCRu), fuel cells with LSCRu/GDC anodes were operated in an environment of humidified H$_2$ condition at 800°C for 120 hr. Focused ion beam (FIB) cross-sectional TEM revealed that the density of the Ru particles was non-uniform across the thickness of the anode and the particles were only found at the LSCRu surface facing the electrolyte. It was observed that the average size and the area density of the formed Ru nano-particles was 2.9 nm and 5.1 x 10$^4$ particles/μm$^2$, respectively. It was also confirmed that the Ru nano-particles are crystalline, which is in good agreement with the results obtained from reduced LSCRu powders. These results confirm that the performance increases seen in LSCRu/GDC anodes are, in fact, due to Ru nano-particle exsolution.

We have developed models to describe Ru exsolution from LSCRu using phase field methods. The model indicates that as time evolves, the concentration of the Ru atoms in the LSCRu decreases and the Ru nano-particles increase in size and form hemispherical shapes on the LSCRu surface. While most of the growth is taking place through the bulk, the majority of the coarsening takes place via surface diffusion.

Transport In Nano-Scale Materials

Work in the Mason group has focused on continued application of the novel “nano-Grain Composite Model” (n-GCM) to characterize the local properties of fuel cell electrolytes as a function of grain size. As the n-GCM requires independently measured grain core dielectric constants as an input parameter, one side project in the Mason group has been to characterize grain core (or single crystal dielectric constant) behavior over the temperature range of interest.

Using these grain core dielectric constant data, the n-GCM model was then applied to determine local properties of the four electrolyte systems: yttria stabilized zirconia (YSZ), tetragonal zirconia polycrystal (TZP), strontium- and magnesium-doped lanthanum gallate (LSGM), and gadolinia doped ceria (GDC). It was found that in each case, whereas grain core conductivities are not significantly different from that of the microcrystalline counterpart, the local grain boundary conductivities are significantly enhanced at the nano-scale, compared to conventional microcrystalline electrolytes. Despite the consistent increase in local grain boundary conductivity in the nano-grained samples, the total conductivity was seen to decrease monotonically with decreasing grain size in all four systems. This effect is due to the fact that grain boundaries remain barriers to transport (compared to grain cores) at the nano-scale, and there are many more grain boundaries in nano-crystalline samples.

The n-GCM also allows determination of electrical grain boundary widths, calculated from the volume fraction of grain cores. These values have been in excellent agreement with reported acceptor dopant segregation widths at grain boundaries. Furthermore, in collaboration with the Marks group we have shown that electrical grain boundary widths in our nano-YSZ samples agree with yttrium segregation widths measured on those same samples.

The Lattice Monte Carlo methodology has been used to study microstructure and thermodynamic properties of yttria stabilized zirconia, YSZ. Here a topological lattice representing the underlying crystal structure was described by a set of occupation numbers on two distinct sets of sites, defining (Y, Zr) and (O, vacancy) populations which were randomly sampled. A Cluster Expansion (CE) of energy at T=0 was developed as a polynomial in the occupation numbers, with coefficients determined variationally by fitting to a set of ‘training configurations’ whose energy was determined from fully self-consistent geometrically relaxed Density Functional (DF) calculations on supercells. Finite temperature free energy was developed by inclusion of vibrational entropy, in the harmonic approximation, using ensemble averages based upon the cluster expansions. The constant volume specific heat was developed directly as variation of internal energy with T, yielding results in good agreement with experiment. Two-body radial distribution functions were developed, again as ensemble averages at specified T, to display and help understand correlations between Zr-vacancy, vacancy-vacancy, Y-Y, etc site occupancy. The principal observations were that: (1) the oxygen coordination sphere around Zr is less populated than...
that of Y, (2) vacancies tend to associate as 2nd neighbors with Y dopants, just as observed previously for vacancy-Zr association, (3) Y atoms tend to cluster together, and (4) vacancies repulse each other, as expected in terms of Coulomb interactions; however, a noticeable tendency toward vacancy ordering on the 3rd neighbor shells is predicted. Similar analyses for LSM, LSCrRu and LSCF are ongoing.

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Objectives

The overall goal of this project is to elucidate the role of metal ions anchored on oxide supports, and the role of oxide structures in stabilizing the metal ions in their active state for catalyzing reactions of interest to fuel reforming for hydrogen generation. The concentration and types of oxygen defects are strong functions of the size, shape, and composition of the oxide nanoparticles. Novel chemical synthesis techniques are employed to control the size and shape of oxide nanoparticles used to evaluate the structure sensitivity of the reactions of interest; and to design catalysts with optimal metal distribution on the oxide supports.

Technical Barriers

Novel catalysts for the efficient conversion of fuels to hydrogen that possess the required high stability for practical fuel cell application are needed. These catalysts should also be highly active and contain minimum amounts of costly platinum metals to allow rapid development of hydrogen generation and purification schemes for use with low-temperature fuel cells. The current DOE project investigates trace amounts of sub-nm clusters and ions of gold or platinum in nanostructured oxides (ceria, iron oxide, zinc oxide) as potential new catalysts meeting these requirements. Our findings to date point to the importance of the particle size, shape, and oxygen defect density of the host oxide for proper distribution of the active metal sites to effectively catalyze the low-temperature water-gas shift and methanol steam reforming reactions. Abstract

The project follows a comprehensive and complementary approach to elucidate the metal-oxide interaction at the atomic scale for the reactions of interest to fuel processing for hydrogen generation. Accordingly, different activities in the synthesis, characterization, and testing of the catalysts are underway at Tufts and at Columbia. Various oxides, namely; ceria, iron oxide, zirconia, and zinc oxide, are prepared, typically by hydrothermal techniques, as single crystals with nm-dimensions which have moderately-high surface areas and can thus be used as practical metal supports. Such nanocrystals serve as platforms to study how different surfaces can disperse the deposited metals, e.g. Au or Pt, and to identify potential shape effects for the reactions under investigation. The results can be compared to extended single crystal surfaces investigated under vacuum in a systematic way, bridging the pressure and materials gap between surface science and catalysis.

During the past year, several parallel efforts have continued at both schools, and these will be detailed in the annual report. Briefly, we have completed a detailed structural study of Cu-doped ceria for the WGS reaction. We have also completed a comparative study of Pt-metals and Au in ceria nanoshapes for the methanol decomposition reaction, and found that Au on ceria follows the methylformate pathway without any CO production up to 250 °C, while the Pt metals on ceria easily decompose methoxy to CO and H₂. The latter are thus not suitable candidates for methanol steam reforming because their selectivity to H₂ would be limited by the WGS reaction equilibrium. The Flynn group at Columbia has continued the STM/STS study of the structural effects of Au adatoms on Fe₂O₃(111) surfaces and the adsorption of CO and H₂O. As already reported, the CO adsorbs linearly atop the Au adatoms, the latter bound tightly over the uncapped surface oxygens of the Fe-terminated surface. Present data from the H₂O adsorption at 260K indicate that water molecules preferentially adsorb on the Fe atoms neighboring the Au adatoms. To complement this study, nanoshapes of Fe₂O₃ were made and Au was deposited on them by various techniques to examine the Au/Fe₂O₃ interaction and reactivity as a function of the magnetite shape. This work is in progress.

We have also conducted an extensive study of Au on CeO₂ nanoshapes as catalysts for the SRM reaction, and more recently prepared Au/ZnO nanoshapes, and compared this catalyst to Au/ceria. On both oxides, sub-nm gold clusters and atoms are present
on the active catalyst, while gold nanoparticles are inactive. An important mechanistic finding is that the SRM reaction proceeds through the methyl formate route on fully dispersed gold on ceria or zinc oxide. Interestingly, the WGS pathway is not involved in the SRM reaction on Au/CeO$_2$ or Au/ZnO. Methanol dehydrogenation, methyl formate hydrolysis and formic acid decomposition are the steps producing CO$_2$ and H$_2$. While both reactions are catalyzed by Au/ceria at the same low temperatures, we have found that methanol is the preferred adsorbate on gold. Since the water-gas shift reaction is not part of the SRM pathway below 250°C, the selectivity to H$_2$ exceeds the equilibrium value based on the former reaction. The practical implications of these findings are obvious.

Report Highlights

During the past year we have focused on the investigation of potential shape effects of ceria and zinc oxide on the water-gas shift (WGS) and steam reforming of methanol (SRM) at low temperatures. We have found that a small amount (<1wt.%) of gold fully dispersed on ceria single crystals prepared as nanorods (10±2.8 by 50-200 nm) of (110) and (100) crystal surfaces) shows excellent catalytic activity in both the SRM and the WGS reactions at temperatures < 250°C. The ceria nanorods bind and stabilize gold as atoms and clusters (< 1nm, TEM invisible). On the other hand, gold nanoparticles (~ 3nm) deposited on the (100) surfaces of ceria nanocubes (30±11 nm) are inactive for either reaction up to 250°C. On ZnO nanoshapes, we find that gold can be dispersed fully on short nanorods and nanopolyhedra comprised of the polar (0001) surfaces. These are highly SRM- active and selective to H$_2$. Figure 1 compares CH$_3$OH-TPSR results over these two types of catalysts, and a commercial Cu-ZnO catalyst, UCI (G-66B). The maximum hydrogen yield was obtained on the Au-CeO$_2$ nanorods.

Methylformate (not shown) is produced from the coupling of methanol on the gold catalysts. With surface water, this is hydrolyzed to formic acid, which decomposes to produce CO$_2$ and H$_2$. Fig.2 shows SRM-TPSR on the Au/CeO$_2$ nanorods. There is a wide temperature window over which only these two products are measured by mass spectrometry. The production of CO begins above 250 °C. Thus, Au/CeO$_2$ is an excellent prospect for the low-temperature SRM reaction, coupled with PEM fuel cell operation. The water-gas shift reaction is not part of the pathway.$^{2,3}$ This is interesting because this same catalyst is very active for WGS even at 150 °C.$^5$ We have further investigated the catalyst selectivity in steady-state isothermal tests and found that the WGS reaction is suppressed by methanol; i.e. methanol, not CO, is the preferred adsorbate on gold. The results from 1% Au/ZnO nanopolyhedra were similar. Since the water-gas shift reaction is not part of the SRM pathway below 250 °C, the selectivity to H$_2$ exceeds the equilibrium value based on the former reaction. The practical implications of these findings are obvious.

Overall, we have found that the shape effect of the oxide nanocrystals is indirect, i.e. the catalytic activity depends on the number of fully dispersed gold species on ceria or zinc oxide. The shape effect simply means that the (110) surfaces of ceria and the (0001)surfaces of zinc oxide achieve better dispersion of gold than other surfaces. Indeed, in kinetic measurements, we found the same activation energy for Au on any ceria shape. The rates, properly scaled with the amount of dispersed gold are the same, i.e. the TOFs are the same. In conclusion, the Au/Ceria catalyst shows good activity and stability for both the WGS and SRM reactions. Because of its

![FIGURE 1. Methanol-TPSR](image1)

![FIGURE 2. (CH3OH + H2O)--TPSR](image2)
high CO₂ selectivity in SRM below 250°C, this catalyst merits further evaluation for practical applications to future fuel processing and fuel cell systems.

**Future Directions**

All the activities highlighted above are continuing in the near future. A new task in the project, already underway, is the synthesis, characterization and evaluation of surface alloys on nanoscale oxides for the reactions of methanol under study. Of particular interest is the PdAu system, which is being evaluated on ZnO. We will continue to focus a major part of our effort on detailed examinations of the shape effect of the oxide host and propose general catalyst design guidelines as appropriate. The desired outcome is a good mechanistic understanding of the chemistries under investigation, and the evolution of the key catalyst structures.

References and Publications (since 2006) acknowledging the DOE Grant

V.P.20 Strategies for Probing Nanometer-Scale Electrocatalysts: From Single Particles to Catalyst-Membrane Architectures

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Objectives

Primary objectives are to prepare and elucidate the promoting properties of materials that possess high activity for the conversion of H₂ and related small molecules (H₂O, O₂, CO and CH₃OH) in polymer electrolyte fuel cells. One area of research focuses on the study of catalyst materials. Protocols are being developed for probing the structure and benchmarking the activity of Pt and Pt bimetallic nanometer-scale catalyst against Pt single crystal electrode standards. A second area targets fuel cell membrane and the advancement of simple methods based on infrared spectroscopy that can be applied broadly in the study of membrane structure and transport properties.

Technical Barriers

Research aims to identify and overcome factors that limit the stability and performance of polymer electrolyte fuel cell catalyst and membrane materials. Methods are being developed to assess effects of catalyst composition and structure on the rate of electrocatalytic reactions. Techniques are under investigation to assist the design of robust, proton conductive membranes, which resist reactant crossover.

Abstract, Progress Report and Future Directions

A. Fuel Cell Membrane and Catalyst-Membrane Architectures Probed by Vibrational Spectroscopy:

Infrared and Raman spectroscopy were investigated as probes of structures within proton conductive materials that limit or enhance performance in polymer electrolyte fuel cells. The following were primary accomplishments: (a) least squares modeling in conjunction with infrared spectroscopy was demonstrated as a useful approach to detect differences in the response of hydrophilic and more hydrophobic functional groups in ionomer materials undergoing changes in hydration state [1]; (b) strategies developed during the project through studies of model Nafion membranes [2,4] were adapted to investigate new bis(perfluoroalkylsulfonyl) imide [5] and fluoroalkyl phosphonate [6] ionomer materials; (c) the capabilities of Raman spectroscopy were explored for its potential to enable depth profiling of practical fuel cell membrane and in situ studies of fuel cell catalyst-membrane architectures.

In initial work, transmission infrared measurements were performed on thin (~1 µm) Nafion® films [1,3] and freestanding (~50 µm) Nafion® 112 fuel cell membrane [2,4]. Effects of hydration on polymer functional groups [1] and water molecules inside membrane pores and channels [2] were examined. Figure 1 shows a series of infrared spectra recorded during the hydration of a thin Nafion® membrane. The region that encompasses the fundamental ionomer vibrations is displayed. The arrows indicate the shifts in band position and intensity that accompany water uptake. The spectra were examined by applying a least squares approach [7,8]. A diffusion equation that describes molecular transport within a cylindrical pore [9-11] was used to predict the time dependent uptake of water into the membrane [1,3]. The analysis revealed bands for vibrational modes for the more hydrophobic polymer functional

![Figure 1: Infrared spectra of a Nafion® film cast onto a ZnSe optical window recorded during hydration in 100% relative humidity air starting from a dry state. Spectra were recorded at times of 0 min, 0.75 min, 1.5 min, 2.25 min, 6.75 min and 28 min after exposure to humid air. The arrows indicate the direction of band intensity change with increasing hydration time. The inset shows the Nafion® polymer structure. See Ref. 1 for details.](image-url)
groups (-CF₂ and -C-O-C-) changed as predicted by the diffusion equation, whereas the response of the prominent band for the asymmetric S-O stretching mode of the hydrophilic -SO₃⁻ group (near 1064 cm⁻¹ (Fig. 1)) was more complicated. The deviations exhibited by the -SO₃⁻ group vibrations were similar to those that we found for the O-H stretching modes of water inside membrane pores and channels [3]. The different responses observed for the hydrophilic and more hydrophobic ionomer functional groups were ascribed to the more complicated water structures that form in the vicinity of -SO₃⁻ groups, due to neighboring solvated cations. Full details of the study are presented in Ref 1.

Subsequent efforts focused on extending strategies developed for the study of Nafion® membrane to new bis(perfluoroalkylsulfonyl) imide [5] and perfluoroalkyl phosphate [6] ionomer materials. Studies showed the vibrations of the side chain ether groups are sensitive to the nature of the charged end group. In hydrated Nafion®, the symmetric -C-O-C- stretching mode of the ether closest to the -SO₃⁻ group appears as a low energy shoulder on the band for the ether closest to the ionomer backbone at 983 cm⁻¹ (Fig. 1) [12]. The splitting of -C-O-C- modes has been attributed to the different environments experienced by the two side chain groups in hydrated Nafion® [12]. We observed that substitution of the -SO₃⁻ group by a bis(sulfonyl) imide (-SO₂NSO₂CF₃) moiety lifts the apparent splitting of ether group modes leaving only the 983 cm⁻¹ band [5]. Similar effects are being detected with different types of phosphonate end group substitutions [6]. In accord with earlier studies [12], the spectral perturbations are being examined with consideration of the possible differences in the solvent environment in the vicinity of the charged end group.

The project also investigated Raman spectroscopy for applications in the study of ionomer materials. Raman spectra that were recorded from Nafion® materials are displayed in Fig. 2. Ongoing experiments are exploring effects of the Raman excitation wavelength on the spectral signals. The long-term benefits of Raman spectroscopy are its potential to enable depth profiling within fuel cell membrane via confocal measurements and in situ studies of fuel cell membrane-electrode assemblies.

B. Catalyst particle properties and electrochemical activity: A second effort investigated Pt and Pt bimetallic fuel cell catalyst [13-15]. Emphasis was on the use of Pt single crystal electrodes as standards to benchmark catalyst activity [14, 15]. Pt single crystal electrodes were grown in the PI’s laboratory, and building on the group’s earlier investigations of vibrational coupling in CO adlayers on Pt(s)-[4(111) x (100)] and related surfaces [16-18], initial experiments focused on kinetic measurements of CO oxidation. Quantitative electrochemical techniques for determining CO coverage on Pt were applied. Following studies that employed low index Pt surface planes [14], techniques were extended to the stepped Pt(s)-[4(111) x (100)] surface [15]. The saturation coverage for CO on a Pt(s)-[4(111) x (100)] electrode was determined for the first time and found to be consistent with expectations based on ultra high vacuum surface science experiments on the system [19-21]. Our study also included the first kinetic measurements of sub-saturation coverage CO monolayer oxidation. Current-time transients recorded in potential step experiments could be fit by numerically solving the rate equations [22] to the Langmuir-Hinshelwood model of adsorbed CO electrochemical oxidation. Fig. 3 shows the changes that occur in experimental current-time transients as initial CO monolayer coverage is lowered. The comparison to the current-time transients determined by solving the reaction rate equations for CO monolayer electrochemical oxidation is detailed in Ref 15. The experiments laid groundwork for our subsequent benchmarking in kinetic studies of electrochemical reactions for small molecules (O₂, CO, CH₃OH) over practical catalyst materials.

References

Publications (including patents) acknowledging the grant or contract

Objectives

Through a combination of theoretical and experimental methods, we want to identify, synthesize, and test surface-modified materials having desirable properties for hydrogen catalysis and storage. In particular, we are designing and studying new materials with: (i) high catalytic activity and CO resistance for hydrogen fuel-cell anode reactions, (ii) resistance to carbon poisoning for CH₄ reforming, (iii) the ability to catalyze the dissociation and diffusion of hydrogen into the bulk for hydrogen purification and light metal-hydride storage, and (iv) high catalytic activity for hydrogenation/dehydrogenation of unsaturated/saturated hydrocarbons for chemical storage of hydrogen.

Technical Barriers

Succeeding in our scientific objectives should help overcome the following “H₂ economy”-related technical barriers: (i) developing cheaper and more poison-resistant anode catalysts for low temperature fuel cells, (ii) improved efficiency of H₂ production from natural gas, (iii) improved hydrogen purification and storage materials, and (iv) efficient chemical storage of H₂ on chemical bonds found within appropriate “H₂-carrier” molecules.

Abstract

The development of more efficient chemical processes through improved catalyst design has been an important goal for well over a century. Recent developments of new tools in surface science and theory can aid in achieving this goal. One such tool, Density Functional Theory (DFT), can both elucidate reaction mechanisms as well as test novel catalyst architectures for specific reactions. Using these methods, we recently identified a new class of bimetallic alloys that exhibit superior catalytic activity for hydrogen-related reactions [J. Greeley and M. Mavrikakis, Nature Materials 3, (2004) 810]. This class of alloys, namely Near-Surface Alloys (NSAs), is comprised of alloys wherein a solute metal is present near the surface of a host metal in concentrations differing from the bulk. The architecture of these alloys gives them remarkable properties, different from the properties of their constituent metals as well as bulk alloys of the same components. As the catalytic properties of NSAs are directly connected to the precise atomic layer-by-layer structure of their near surface region, we have also needed to develop and implement accurate nanosynthesis techniques for the preparation of the theoretically predicted optimal nanostructures. Our work has been focused in three main areas: (i) the elucidation of fundamental principles of industrially relevant reactions using state-of-the-art DFT, (ii) the application of these principles to discovering novel alloys (specifically, NSAs) with superior catalytic properties and (iii) the synthesis and characterization of these alloys for H-related reactions using innovative chemical and electrochemical techniques.

Over the last few years, we have made progress on these three fronts for a variety of important reactions, as follows:

A. We have theoretically identified and experimentally synthesized and tested for their reactivity Ru-core/Pt-shell (Ru@Pt) nanoparticles that are highly active for the preferential oxidation (PROX) of CO in the presence of H₂ at room temperature. Using DFT, we elucidated the fundamental principles behind this high activity, invoking a novel H-assisted O₂ dissociation mechanism to explain this unusually high reactivity at low temperatures. Other core-shell nanoparticles are currently in the synthetic-protocol design and characterization phase.

B. Using a combination of DFT, microkinetic modeling, and reactivity experiments, we have investigated the kinetics of the water-gas-shift (WGS) reaction on Cu and Pt catalysts; we
proposed a novel mechanism including the formation of a carboxyl (COOH*) intermediate. Additionally, we have begun investigating the promotional effect of iron oxide (FeO) for the Pt-group catalyzed WGS reaction. We also investigated CO₂ chemistry for Cu-Pt NSA systems, relevant for the WGS and methanol synthesis reactions.

C. We predicted the presence of subsurface H in an Au-Ir NSA system. Using electrochemical methods, we have synthesized Au*/Ir (Au overlaid on Ir) NSA catalysts and tested their adsorption of hydrogen, validating such predictions and opening the door to new catalysts with stable subsurface hydrogen.

D. We have begun to extend DFT calculations to electrochemical reactions and study core-shell based catalysts for these important reactions. We have focused on several reactions relevant to fuel cells, including: oxygen reduction (ORR) for fuel cell cathodes; methanol electroxidation for direct methanol fuel cell anodes; and hydrogen electroxidation for H₂-PEM fuel cell anodes. In ORR, we use a new electrochemical model to understand the high activity of Pt overlayers over Pd and other surfaces for this reaction. We also use this model in methanol electroxidation to parameterize the onset potential, allowing us to screen for better electrocatalysts.

Progress Report and Future Directions

Space limitations won’t allow us to expand on any of the topics outlined in the abstract, but (A) and (C):

(A) Core-Shell Nanoparticles for preferential oxidation reactions

Our DFT work identified Ru-core/Pt-shell nanoparticles (Ru@Pt—see Figure 1, left panel) as a promising PROX catalyst. Our experiments showed that these catalysts indeed possess a much lower onset temperature for CO and H₂ oxidation than the constituent metals, physical mixtures or bulk alloys of Pt and Ru. Additionally, the selectivity to CO oxidation on these catalysts at low temperatures is excellent.

One thrust of our work over has been to explain this increased activity using first-principles methods. We find that a Pt skin pseudomorphically deposited on a Ru host provides a different pathway for O₂ dissociation in the presence of hydrogen (H). This novel result highlights the ability of hydrogen to assist in O₂ dissociation on Pt-Ru surface alloys (see Figure 2), thereby lowering the activation energy barrier to oxidation, thereby increasing the activity of the core-shell nanoparticles considerably.

The discovery of this H-assisted path is of interest for several reasons. First, using this new mechanism, we can identify catalysts that may show similar or even better characteristics for PROX by adding a third metal to the alloy. Second, the existence of such H-assisted dissociation may not be limited to O₂ dissociation. We have begun a study of similar dissociation pathways for other relevant intermediates, such as CO₂ which would allow us to better understand the surface chemistry of multiple reactions important to H₂ production and purification, but also for alkane fuels production (e.g.: Fischer-Tropsch synthesis).

(C) NSAs for Hydrogen-related reactions

Another focus of our research has been in synthesizing and characterizing submonolayer alloys for hydrogen-related reactions. Recently, we have deposited submonolayer amounts of Au on an Ir(111) surface and compared the uptake of hydrogen to that of a pure Ir(111) surface using electrochemical techniques. While STM demonstrates that Au is clearly deposited on the surface as a thin film, counter-intuitively, it does not block hydrogen adsorption. Using DFT, we analyzed the interaction of H with this NSA and showed possible reasons for this anomalous behavior. We found that hydrogen at the Au-Ir interface is stabilized as compared with hydrogen on the Au surface (see Figure 3). Such subsurface H has been implicated as

![FIGURE 1. Schematic of core-shell particles, alloy particles and physical mixtures.](image1)

![FIGURE 2. Direct and H-assisted preferential oxidation mechanisms.](image2)
a reaction intermediate in hydrogenation reactions in other systems. Additionally, the subsurface hydrogen may have a promoting effect on further reaction; the presence of subsurface H in the Au-Ir system upshifts the d-band center from -4.10 to -3.02 eV, leading to a significant increase in the reactivity of the pure Au-Ir surface. We plan on continuing this analysis by looking at submonolayer Au alloys on other transition metals to see if this reactivity change is unique to Au-Ir or can be found in other NSA systems. Additionally, we have begun looking at alloy stability and formation on other than close-packed surfaces of transition metals.

References


Publications acknowledging the grant

V.P.22  Multiscale Tailoring of Highly Active and Stable Nanocomposite Catalysts for the Production of Clean Hydrogen Streams

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Abstract

By utilizing a range of different synthesis methods, we were able to demonstrate that through careful tailoring of composition and structure of both the active metal component and the oxide support matrix in nanocomposite catalysts, it is possible to design catalysts that combine exceptional high-temperature stability with high catalytic activity. Activity and stability of these materials was demonstrated through application in catalytic hydrogen production via catalytic partial oxidation of methane and water-gas-shift. Finally, implementation of these nanocomposites into a “macroscopic” support structure was demonstrated.

Progress Report

Below, we will use select examples from the project results to highlight and illustrate major findings from the investigations based on systematic tailoring of composition and structure of the support and the active (metal) component in order to reconcile high thermal stability with high activity in nanocatalysts.

Tailoring for Stability via Embedding: Metal-BHA Nanocomposites

Based on a rather straightforward, single-pot synthesis, a wide range of high surface area metal/oxide nanocomposite materials was successfully synthesized (including Pt, Rh, Pd, Au, Ni, Cu, Fe, Co, and Zn as (active) metal components, and BHA (barium-hexaaluminate), silica, magnesia, ceria, and La2O3 as oxide matrices) and the thermal stability of these materials was demonstrated. In particular BHA-based materials showed excellent high-temperature stability, which could be traced back to a simple “caging” of metal nanoparticles in the highly interconnected pore network of the BHA matrix. This is illustrated in figure 1 (bottom) shows the close agreement between Pt particle size (bars) and BHA pore neck size (blue line) for a Pt-BHA catalyst after calcinations at 600°C. Through a simple dip-coating procedure, it was furthermore possible to anchor this nanocomposite material onto different support structures, resulting in a robust, easy-to-handle catalyst formulation without compromising the carefully controlled nanostructure of the catalyst (see figure 1, top). The resulting catalysts showed excellent activity in partial oxidation of methane (Pt-BHA) as well as in chemical looping combustion (Ni-BHA & Cu-BHA) and chemical looping steam reforming (Fe-BHA). Overall, these results indicate
that it is possible to reconcile activity and stability of nanomaterials via simple nanostructuring.

Tailoring for Stability via Encapsulation: Metal@Silica Core-Shell Materials

As alternate approach for the stabilization of metal nanoparticles, direct encapsulation with porous oxide shells was pursued. This was motivated by the fact that the above described approach is limited with regard to the minimum metal nanoparticle size which can be stabilized: Since the particles are stabilized via a simple mechanical ‘caging’, smaller stable particle diameters require increasingly smaller pores and hence ultimately result in mass transfer limitations. In contrast to that, direct coatings of nanoparticles can be kept sufficiently thin that mass transfer limitations (MTL) should be avoidable.

We were able to demonstrate fine control over key dimensions of silica-encapsulated metal nanoparticles (M= Ni, Cu, Co, Fe, Pd), including size of the metal nanoparticles (from sub-nm clusters up to ~20nm), size of the M@SiO₂ particle, thickness of the silica shell (see fig. 2, top), and presence or absence of a cavity inside the silica shell (see insets in fig. 2). Again, excellent high-temperature stability was demonstrated along with high activity & selectivity in catalytic methane partial oxidation (CPOM, see fig. 2, bottom), and a critical shell thickness for avoidance of MTL was demonstrated.

Tailoring for Stability via Alloying: Bimetallic Nanocomposites

As third alternative for achieving high-temperature stable metal nanoparticles, the alloying of the metal nanoparticles with a second metal was investigated. This was motivated by the aim to increase the stability limits of metal NPs without the use of a stabilizing matrix (as in the two approaches above), i.e. by transitioning from stabilization via structural tailoring to stabilization via compositional tailoring.

One can expect that the addition of a second, higher-melting point metal will result in increased thermal stability, since sintering is known to be strongly correlated with the melting point of a metal. Using Pt-BHA as starting material and carefully adjusting the composition of the metal nanoparticle via step-wise increase in the second metal (for PtRh, PtSn, and PtPd), we found that such stabilization is indeed possible. Unexpectedly, however, it was observed that this stabilization extends to much higher temperatures than predicted by the (initial) composition of the alloy. This was traced back to a sacrificial self-stabilization of the nanoparticles, which bleed out the lower melting point component (M₁) in a continuous, distillation-like process. This results in the formation of larger nanoparticles which are composed of pure M₁, while retaining the entire original population of small metal nanoparticles, which get increasingly enriched in M₂. Overall, this brings about a remarkable self-stabilization of the catalyst, as demonstrated using methane combustion as test reaction. While this stabilization mechanism has limitations due to the fact that the alloying with the second metal must not negatively affect the reactivity of the catalyst, it is remarkable in its simplicity and the fact that it is not dependent on a specific support.

Tailoring for Activity via Composition & Structure: Metal/Mixed-Oxide Catalysts

Finally, the concept of tailoring via composition and structure was applied to a more complex case in which the support takes on a key reactive role (beyond acting as a stabilizing matrix). Water-gas-shift (WGS) over
Au/ceria catalysts was chosen as test system. Based on a similar microemulsion-templated sol-gel synthesis as of the BHA-based materials above, high surface area ceria and ceria/lanthana mixed oxides were synthesized, characterized, and, after Au deposition, utilized in WGS. A strong correlation between composition, reducibility, and activity of the catalysts was observed, were addition of moderate amounts of La (up to ~25%) resulted in significant improvements in WGS activity (see fig. 4).

Utilizing an alternate (hydrothermal) synthesis, ceria and mixed oxide nanorods were also synthesized and compared to the nanoparticulate catalysts. Structuring the catalyst into nanorods results in a strong increase in WGS activity which again can be traced back to the increased reducibility of the oxides (due to predominant exposure of low-stability surface orientations).
Future Directions

The project ended in August 2009, and no extension was applied for. However, the results demonstrate the potential of tailoring catalyst activity and stability via careful compositional and structural control at the “nano-level”, and we are currently extending this concept onto related catalytic reactions.

Publications (including patents) acknowledging the grant or contract

**V.P.23 Metal- and Metal Oxide-Supported Platinum Monolayer Electrocatalysts for Oxygen Reduction**

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### Objectives

This program involves studies of platinum monolayer electrocatalysts for the $O_2$ reduction reaction (ORR) aiming at producing ultimately low Pt content electrocatalysts with high activity and high stability, supported by metal-, alloy-nanoparticles, nanorods, nanowires, as well as oxide-, carbide-, nitride- and hollow metal-nanoparticles, and carbon nanotubes. Theoretical calculations are carried out for a deeper insight into the kinetics of the ORR. Studies using well-defined surfaces are carried out to gain understanding of the atomic-scale phenomena involved in the interactions of Pt monolayers with supporting surfaces, as well as developing new efficient catalysts for ethanol oxidation.

### Technical Barriers

The project is focused at developing several Pt monolayer catalysts that are likely to have the highest Pt mass activity, and excellent potential to overcome the obstacles hindering the broad application of fuel cells. The results will enhance our understanding of the metal monolayer-support interactions for a viable approach for controlling chemical reactivity in the top atomic layer. In addition, we explore the catalyst capable of C – C bond splitting at low overpotentials in the oxidation of small organic molecules.

### Progress Report

**Improved understanding of factors affecting the ORR activity of Pt monolayer**

We examined the effects the thickness of the Pt shell, lattice mismatch, and particle size on specific and mass activities from the changes in effective surface area and activity for oxygen reduction induced by stepwise Pt monolayer (Pt ML) depositions on Pd and Pd$_x$Co nanoparticles. The core-shell structure was characterized at the atomic level using Z-contrast scanning transmission electron microscopy coupled with elementsensitive electron energy loss spectroscopy.

The enhancements in specific activity are largely attributed to the compressive strain effect based on the density functional theory calculations using a nanoparticle model, revealing the effect of nanosize-induced surface contraction on facet-dependent oxygen binding energy. The results suggest that moderately compressed (111) facets are most conducive to the ORR on small nanoparticles and indicate the importance of concerted structure and component optimization for enhancing core-shell nanocatalysts' activity and durability.

In the nanometer range, a particle’s size and shape profoundly affect the ORR specific activity because both the surface fraction of active facets and the facet-dependent binding energy for oxygen vary with size. These results point the way to tailoring a Pt shell’s structure and properties by controlling core particle’s components, size, and shape, for high activity and durability of the ORR electrocatalysts.$^{1,2}$

![FIGURE 1. ORR specific activities at 0.9 V measured at 10 mV s$^{-1}$ (symbols, left axis) and surface fraction of atoms on the (111) facets (solid and dashed lines, right axis) as a function of particle size. The vertical dotted lines mark the sizes of three nanoparticle models that have the BE-O close to the optimal value of 3.89 eV. The blue, red, and green colors are used, respectively, for particles with 1-, 2-, and 3-Pt layers.](image-url)
Improving activity and stability of Pt monolayer electrocatalysts for the ORR

Several methods for improving Pt ML catalysts have been developed based on understanding of the factors affecting the ORR. The new strategies include:
1. Surface and sub-surface modification of cores to tune the interaction with a Pt ML.
2. Reducing number of low-coordination surface atoms by Br- adsorption/desorption.
3. Using smooth surfaces of Pd nanorods and nanowires to support a Pt ML.
4. Contracting Pt-Pt separation with hollow particles
5. Using intermetallic compounds as supports

Sub-surface modification of cores to tune the interaction with a Pt ML

This strategy is based on the expectation that a monolayer of a metal can be driven in sub-surface of support. The subsurface layer of Ir in Pd support, obtained by galvanic displacement of a Cu monolayer by Ir and annealing at 350°C to induce segregation of Pd to the surface and Ir into the particle, enhances the ORR kinetics at Pt monolayer on PdIr nanoparticles (Fig. 2). The subsurface Ir causes a Pd skin to contract, so Pt monolayer on PdIr/C is compressed more than on Pd/C. The Pt-O bond will weaken and ORR activity increased. This was verified by the data in Fig.2.

Modifying surface properties by alloying the core.

Au submonolayer, deposited on a Pd3Co surface by displacing Co atoms in the surface, or AuPd alloy, as a support for Pt monolayer cause a significant increase in the activity of and stability of such catalysts compared with original PtML/Pd3Co/C catalyst. The Pt/Au3Pd/C catalyst has a high activity and durability, i.e., E1/2 =0.901V before and 0.895V after 30,000 potential cycles from 0.75-0.95V, dwell time 30 sec, of an accelerated stability test. The increased catalytic activity and durability originate from the reduced Pt oxidation (PtOH formation), which inhibits the ORR and is a precursor of Pt dissolution, as inferred from in situ XANES spectra of Pt L3 edge.

Ordered intermetallic compound cores

A new class of core-shell electrocatalysts for the ORR consists of a Pt monolayer shell and ordered intermetallic compound cores. We coupled highly stable, inexpensive intermetallics with a Pt monolayer producing electrocatalysts with high activity, low metal content, and very high stability. Our data indicate strategies suitable for selecting the types of intermetallic compounds as the support for a Pt monolayer.

Smooth support surfaces

Smooth surfaces, having a small number of low-coordination atoms, are suitable support for a Pt monolayer for the ORR due to a reduced Pt oxidation that takes place on such surfaces. This assertion has been verified with the Pd surfaces, obtained by removing low-coordination atoms using Br- adsorption/desorption, Pd nanowires (Fig. 3a) and Pd nanorods used as a support for a Pt monolayer. Unprecedentedly high Pt mass activity of 3.4 A/mg has been obtained (Fig. 3b).

Electrocatalysts for ethanol oxidation

Further studies of the ternary Pt-Rh-SnO2/C electrocatalysts capable of splitting the C-C bonds at room temperature involved varying the atomic ratio Pt:Rh:Sn = 3:1:x, where x varies from 2 to 6. The catalysts composed of homogeneous PtRh alloy and SnO2, having all three constituents coexisting in single nanoparticles with the average particle size around 1.4nm and a narrow size distribution. While all the electrocatalysts investigated exhibited high catalytic activity for ethanol oxidation, the most active one had the composition with the Pt:Rh:Sn = 3:1:4 atomic ratio.

Future Directions

We plan to continue with exploring the interaction of Pt monolayers with smooth surfaces of Pd nanorods, nanowires, and nanotubes. This will help in developing of Pt ML catalysts with predominantly high-
coordination atoms deposited on smooth cores of: i) Pd or its alloy nanorods, nanowires or nanotubes cores; ii) Pd or Ir alloy nanoparticles with refractory metals that preclude core dissolution in acid environment. We will study the ternary catalysts for ethanol oxidation using CeO$_2$ instead SnO$_2$. Magnelli phases will be selected as support because they are conductive and stable in acids. Our new method of depositing metal on oxide surfaces will be employed for designing active catalysts.

References


Publications


Book Chapters


Patents

1. Two patents issued; three patent applications submitted in 2009.
Objectives

- Develop new synchrotron radiation based x-ray diffraction and spectroscopy methods that allow in-situ probing of the intermediates in the oxygen reduction reaction (ORR) on the cathode in fuel cells where both species identification, geometric and electronic structure properties can be fully characterized.
- Gain insight into how various catalytic properties on Pt surfaces can be modified due to alloying.
- Perform combinatorial synthesis and high throughput electrochemical screening methodologies of alloy catalyst with different chemical compositions and structures to obtain optimum performance.

Technical Barriers

This project addresses the following technical barriers by understanding the mechanistic pathway of the ORR reaction and by establishing fundamental guidelines to design new low Pt containing catalyst by optimizing the geometric and electronic structure of catalyst along the mechanistic pathway.

- Electrode performance
- Low cost
- Durability

Abstract

We have discovered a new family of Pt-Cu nanoparticle/nanopore catalyst that exhibits the highest ever reported ORR activities of up to 5-6x compared to pure Pt electrocatalysts. The composition of the surface, lattice arrangement and electronic structure of these catalysts have been characterized by synchrotron based x-ray diffraction and photoelectron spectroscopy methods. We discovered an order of magnitude reduction of Cu in near surface region of these catalysts, due to electrochemical leaching and a lattice contraction in the nanoparticle/nanopore structures. This affects the overall reactivity by weakening the bonding of intermediate oxygenated species.

We have undertaken a major effort to obtain in-situ information during electrochemical conditions of the nature of intermediate oxygenated species that controls the rate of the ORR. With high resolution Pt L edge spectroscopy of a single Pt monolayer we have observe the evolution of a surface Pt oxide layer.

Progress Report

While the oxidation of pure hydrogen is not considered a technical hurdle in fuel cells, the power loss at the cathode during the electroreduction of oxygen is found to be significant. Therefore the identification of a catalyst for the electroreduction of oxygen with improved performance is a major scientific priority. Pt has been the only metal which offers a good compromise in terms of performance and durability, and catalyst costs dominate at high Pt loading. Our goal is to understand the mechanistic pathway of the ORR reaction and to design new low Pt containing catalyst by optimizing the geometric and electronic structure of catalyst along the mechanistic pathway.
Dealloying is the preferential dissolution of the electrochemical more reactive component from a bimetallic alloy (precursor) consisting of a less reactive (here Pt) and more reactive metal (here Cu). We have shown that dealloyed Pt-Cu nanoparticles show uniquely high catalytic reactivity for the oxygen reduction reaction (ORR) in fuel cell electrodes (1-4). Dealloyed Pt catalysts, however, meet and exceed the technological activity targets in realistic fuel. Owing to their reactivity, dealloyed Pt catalysts can reduce the required amount of Pt by more than 80%. Despite this importance, the mechanistic origin of their enhanced reactivity remains poorly understood.

We have shown based on a combination of electron microscopy, x-ray photoelectron spectroscopy and anomalous x-ray diffraction studies of dealloyed Pt-Cu catalysts (6) that a core-shell structure is formed during dealloying, which involves removal of Cu from the surface and subsurface of the precursor nanoparticles. X-ray diffraction shows that the resulting Pt-rich surface shell exhibits compressive strain that depends on the composition of the precursor alloy. Based on model electron and x-ray spectroscopy experiments of strained Pt films on Cu(111) the existence of a downward shift of Pt d-band resulting in a weakening of the bond strength of intermediate oxygenated species due to strain (see fig.1). Theoretical simulations of the fuel cell catalytic process also shows that strain enhance the overall reactivity via a weakening of the oxygen adsorption bond strength. The stoichiometry of the precursor, together with the dealloying conditions, provides experimental control over the resulting surface strain and thereby allows continuous tuning of the surface electrocatalytic reactivity – a concept that can be generalized to other catalytic reactions.

To build on the above results and to better understand the structure-activity relationships in dealloyed Pt-alloy electrocatalysts, we have used uniform, single phase, polycrystalline Cu,Pt thin films and single crystal Cu,Pt(111) as model catalysts for accurate characterization of structure and the resulting ORR activity enhancement. Anomalous x-ray diffraction (AXRD) is used to study the structure of the dealloyed Pt-Cu thin film (lattice constant and composition) (7). We have obtained a detailed understanding of the structure and composition relationships in these Pt-skeleton structures prepared by dealloying base metal rich alloy. Compositional inhomogeneity of the dealloyed films is observed with a Pt enriched surface region and Cu depleted interior. The composition of Cu depleted interior is different from that of as-deposited Cu,Pt showing that dealloying of Cu occurs at the surface and proceeds into the interior, leaving a compressively strained Pt-enriched surface region as shown in Fig. 2. Work on single crystal Cu,Pt(111) is ongoing, but qualitatively consistent with the film studies.

Mechanistic understanding of fuel cell cathode reaction

In order to develop more efficient fuel cell catalysts it is essential that we can gain information regarding the nature of intermediate species during oxygen reduction reaction (ORR) that contribute to the sluggish kinetics. Hard x-rays penetrate several millimeters
through electrolyte solutions, thus providing a unique capability for in situ x-ray absorption spectroscopy (XAS) studies of active fuel cell catalysts under electrocatalytic conditions. Of particular interest is determining the nature of Pt–O interactions at high potentials since this is essential for understanding the origin of the overpotential of the electrochemical oxygen reduction reaction (ORR). We have chosen to study a well-defined, simple model system, consisting of one monolayer Pt on a Rh(111) single-crystal surface. By tuning the energy to the Pt L₃ absorption edge this allows for the – intrinsically bulk sensitive – hard x-ray spectroscopy to probe only surface Pt atoms and their interaction with oxygen. Fig. 3 shows the L-edge x-ray absorption spectra (XAS) of a Pt monolayer on Rh(111) detected using High Energy Resolution Fluorescence Detection (HERFD), where the life time broadening of the Pt L-edge has been experimentally removed, resulting in much higher resolved spectral features (8). By using the L₂-edge, the unoccupied Pt 5d-states are probed. The intensity increase, broadening, and shift of the spectra with increasing potential have been identified, through theoretical spectral simulations, to result from the development of a Pt surface oxide. Complementary extended x-ray absorption fine structure (EXAFS) measurements have been carried out under identical conditions. Pt-Pt and Pt-O bond lengths and coordination numbers have been derived, confirming the interpretation of the growth of a surface Pt oxide (8). Weaker changes in the spectral features at lower potentials can be related to adsorbed hydrogen and to the presence of other oxygenated species.

Future Directions

We will continue the in-situ spectroscopy studies of the ORR of a single Pt monolayer to other substrates which are expected to bind oxygen stronger where we expect that the onset of Pt surface oxide formation will occur at lower potentials. We will also extend these studies to nanoparticles of Pt with different sizes since there is a hypothesis that small nanoparticles could induce oxide formation at lower potentials. We will also continue our effort to develop in-situ spectroscopic techniques to the soft x-ray regime. We will extend the studies of the dealloying process to Pt-Cu single crystals. We are currently exploring dealloyed bimetallic Pt systems other than Pt-Cu. Current studies focus on dealloyed PtCo3 and PtNi5. Dealloying behavior of these bimetallic compounds is unknown to date. Preliminary results suggest a similar core shell behavior for PtCo3 as found in PtCu3. PtNi5 showed less susceptibility to leaching. Future experiments will include morphological studies of dealloyed PtCo3 and PtNi5, monitoring of the compositional changes upon extended cycling protocols.

Publications


FIGURE 3. Pt L₃ edge high resolution fluorescence detection XAS spectra of 1ML Pt/Rh(111) in 0.01M HClO₄ as a function of increasing potentials.
V.P.25 Metal dissolution mechanisms in Pt-based alloys: Ideas for advanced PEM cathode design

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Objectives

We aim to develop new understanding that can foster the development of better catalyst materials for proton-exchange membrane cathodes. To achieve this goal, we focus on answering these questions: 1) How the catalytic surface and its environment change as the reaction takes place; 2) What are the effects of the dynamics of the catalyst and that of the surrounding medium on the catalytic activity and stability; 3) What is the effect of important side reactions on the catalytic process.

Technical Barriers

One of the main problems of current alloy cathode electrocatalysts is their strong dissolution trend especially when platinum is combined with less “noble” transition metals. Upon dissolution, metal ions cause other problems such as membrane degradation, or upon ion reduction, particle agglomeration. In this study, we determine the mechanisms that trigger metal dissolution and analyze possible alternative materials that may help mitigate the problem.

Abstract

We present results from a systematic density functional theory study of core-shell alloy surfaces, with monometallic cores of the 3d, 4d, and 5d groups. The analysis reveals that all the 4d and 5d pure cores may serve as relatively stable cores, and their beneficial effect on the Pt monolayer may be further tuned by alloying them to another element, here chosen from 3d or 5d groups. The Pd,X cores enhance the stability of the surface Pt atoms both in vacuum and under adsorbed oxygen; however, the high oxygen-philicity of some of the X elements induces their surface segregation that may cause surface poisoning with oxygenated species and metal dissolution in acid medium.

Based on the above DFT studies, we introduce a new class of catalytic materials with enhanced activity and high stability of the surface and core atoms against dissolution in acid medium. The significant stability improvement found in the new material is due to the addition of a small-radius species that locates in the interstitial sites of the top subsurface layers locking the core transition metal atoms in their positions, thus avoiding their segregation to the surface and posterior dissolution, which is driven by the oxidative acid environment. We illustrate our findings by a detailed analysis of the durability and activity enhancement for the platinum/iron-carbon/iridium system.

Progress Report and Future Directions

1. Surface stability of Pt-monolayers on pure cores. Calculated electrochemical potential shifts (DU) for surface Pt atoms on top of pure 4d and 5d transition metal cores show that the core elements have little tendency to segregate to the surface, and in some cases (Ir and Rh) they have large antisegregation energies. It is interesting that DU decreases as the difference of charges between the surface and the subsurface becomes smaller, indicating that a large charge transfer between the top surface and the subsurface has a stabilizing effect on the surface Pt atoms. We concluded that in principle, these systems could be stable core candidates. Our calculations indicate that the difference in binding energies $B_{O_H} - B_{O}$ that correlates with previous reports on activation energy for OH formation, follows the order Ag > Au > Pd > Pt > Rh > Ir. On the other hand, the O binding energies follow the core order Rh < Ir < Au < Pd < Pt < Ag; this order is the opposite to that of the reported ORR currents: Pd > Au > Rh > Ir; thus, Pt/Pd having an intermediate strength for O adsorption and for OH formation yields the highest ORR activity. It is interesting that the OH adsorption energies (that we shown to be driven by both electronic and geometric effects) follow the core order Ag < Au < Rh < Ir < Pd, and all of the Pt-skin surfaces yield OH adsorption energies weaker than those on Pt(111). In summary, the analysis of stability and activity of the pure cores suggests that combining 4d or 5d elements with 3d elements would provide alternative formulations for core-shell alloys. According to our results, the group of 4d and 5d metals yield weaker O and OH energies, indicating good ORR activities, and their positive DU suggests that if these cores are alloyed with 3d elements
having a large negative d-band center value (such as Co, Ni, Cu), beneficial activity effects may be enhanced.

2. Surface stability of Pt-monolayers on alloy cores. Analysis of segregation trends of Pd and X from the core to the surface as functions of the electronic charge of the atom X in the subsurface for Pt/Pd₃X alloys indicates that the strength of antisegregation of X towards the surface increases with the degree of oxidation of the atom X in the subsurface. On the other hand, Pd has a slight tendency to segregate to the surface that increases with increasing oxidation degree of X in the subsurface. The Pd-segregation data shows two groups: one including elements of the period 6 (Ir and Re), and the other with elements of period 4 of the periodic table. In both cases the less positively charged Pd atoms tend to migrate to the surface, whereas X atoms tend to remain in the core, thus establishing an attractive electronic interaction with the Pt surface atoms bearing slightly negative charges. This polarization of the metal overlayer/transition-metal substrate has been discussed by other researchers based on experimental and theoretical evidence.² ³ Under 0.25 ML of O, the Pd segregation trend is not very different from that found on the clean surface, but a strong segregation pattern is found for Ir, Cr, V, Ti, and Re, and weaker for Co and Fe. We found that the Ir segregation trend changes drastically from that found in the pure Ir core, since the cohesive properties of the pure Ir system are lost in the alloy. Given our findings respect to segregation trends, it is of interest to analyze the stability of Pt atoms against dissolution when Pt is on the surface of these alloys. These trends reveal a clear correlation of the stability of the Pt atoms on the surface and the degree of oxidation of the atom X in the subsurface, reinforcing our earlier conclusion that a strong attractive electronic interaction may be established between the Pt monolayer and the subsurface alloy layer. The calculated binding energies per Pt atom of the monolayer to the core increase in the order Ir < Co < Fe < Re < V < Ti < Cr, that follows (except for Cr) the order shown by the stability of Pt atoms, both for a clean surface and under adsorbed O. Thus the presence of a relatively small concentration of the X elements in the PdₓX core enhances the stability of Pt atoms on the surface of the core-shell alloys. This result is in agreement with previous XPS binding energy shifts and DFT analysis of a metal adlayer on a transition metal substrate revealing heterometallic bond formation attributed to orbital rehybridization effects. With respect to reactivity, although the O binding energies on the Pt-skin surfaces are relatively weak compared to that on Pt(111), these energies increase under segregation of Pd and in some of the surfaces there is a strong increase under segregation of X, especially for Ti, V, Cr, and Re that are known to have strong affinity for oxygen.

Although we have shown that these cores impart high stability to the surface Pt atoms, another factor to evaluate is the trend of the X core elements to dissolve in acid medium inferred from their experimental redox potentials. It is clear that all the elements would dissolve at more negative potentials than pure Pt (1.18 V). In addition, as remarked by Greeley and Nørskov dissolution tendencies follow trends in segregation energies. Based on this, we remark that our calculated segregation trends add significant information regarding dissolution of core elements under oxidation conditions. With respect to the ORR activity of the group of Pt/PdₓX alloys, all the O binding energies are much lower than those on Pt/Pd, following the order Re < V < Ti < Co < Fe < Ir = Cr, the same order is approximately followed by the strength of O adsorbed when Pd segregates. However, on surfaces where the X element has segregated, the binding energies of O to these elements is significantly higher, with the order being changed to Co < Fe < Ir < Cr < Ti < V < Re, that except for small differences is the same order that is followed by the OH binding energies. Thus, within this formulation, Pt/PdₓCo and Pt/PdₓFe stand out as promising alloys in both activity and stability aspects. However, the present analysis also suggests that Pt/Pdₓ,ₓ₅ alloys with 0<y<1 are excellent candidates for ORR catalysis.

3. Design of a core/shell material with an active and durable Pt surface. Based on the above analysis, we inferred that an active surface that is also resistant to dissolution in acid medium requires a stable core that in addition is able to alter the Pt electronic structure increasing its ORR activity. Thus, we investigated a new class of core-shell materials composed by a platinum monolayer over a composite core where an extra element has been added to the transition metals in order to anchor them to the core, thereby retaining their beneficial properties towards the surface atoms and enhancing the stability of the catalyst against dissolution.⁵ We demonstrated the properties for the composite system Pt/Fe-C/Ir depicted in Figure 1.

We first evaluated the effect of the presence of subsurface interstitial carbon on the surface electronic
and geometric properties of the Pt monolayer. We determined oxygen adsorption energy strength (signaling catalytic activity),\(^4\) segregation energy of the subsurface metal atoms on the clean surface and under 0.25 ML of adsorbed oxygen (related to surface stability and activity),\(^4\) electrochemical potential shift on clean surface and under 0.25 ML of adsorbed oxygen (onset of Pt dissolution),\(^5\) and binding strength (per Pt atom) of the top surface to the core (a measure of surface stability). We noted that the largest electrochemical potential shift corresponds to the alloy core in absence of carbon; however this structure has a significant iron surface segregation trend which affects the catalyst durability.\(^6\) Instead the structure where carbon fills the subsurface shows an optimal combination of activity and stability properties.

One of the best characteristics of the proposed composite core-shell material is the antisegregation of transition metal atoms toward the surface even in presence of adsorbed oxygen; this feature is explained from the analysis of the electronic structure as given by the Bader electronic charges.\(^7\) Without carbon, the geometric stress introduced by the Pt overlayer on the core generates a charge transfer that results in an excess of electrons in the surface and a deficit in the first subsurface layer, as found in previous experimental\(^8\) and theoretical studies.\(^3\) A similar charge transfer effect occurs between the Ir and Fe atoms of the 4th and 5th layers. In presence of carbon, the iron atoms transfer charge not only to Pt and Ir but also to carbon, as revealed by the increase of the positive charges on Fe as the C concentration increases. The charge transfer Fe-C denotes their strong affinity and bonding resulting from orbital hybridization, which prevents iron segregation towards the surface, even under adsorbed oxygen. The increased stability is also associated with the polarization of the first two layers, which determines the high binding of the overlayer to the core.

In summary, we have demonstrated the potential durability and activity properties of a new class of core-shell composite materials. The enhanced durability arises from the use of carbon in the interstitial sites of the subsurface that anchors the transition metals in their positions impeding their segregation to the surface while keeping their beneficial properties that favor ORR activity on the top platinum monolayer. We are currently exploring other core-shell designs that may offer similar catalytic and extended durability properties and we expect to address other challenges such as the presence of surface defects on the performance of the new material. Interesting systems include the use of a Pd monolayer (instead of Pt), although Pd dissolution may happen at lower potentials than those of the Pt monolayer, according to the trend of their redox potentials.

Future Directions

We are extending our design of dissolution-resistant catalysts to other core combinations. This extended study will allow us to optimize the cost and feasibility of fabrication. We have been discussing possible fabrication of our proposed new catalytic design with experimental groups and we have some ideas for making the systems more realistic keeping the same basic beneficial features. In addition, we are developing and implementing a kinetic Monte Carlo (KMC) technique to evaluate the evolution of the surface as a function of time, under reaction, and under applied potential. The KMC program requires as input the rates of the diffusion and migration processes from the subsurface and on the surface that we have already obtained in our previous and current DFT analysis.

References

Publications 2009-2010

(1) Sole funding by DOE-BES and this particular grant


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Book chapters


V.P.26  Mechanism of Proton Transport in Proton Exchange Membranes: Insights from Computer Simulation

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Objectives

This project involves the development and application of a unique multiscale computer simulation methodology for studying proton solvation and transport in proton exchange membranes (PEMs) for fuel cell applications. A key component of the project is an atomistic reactive molecular dynamics MD simulation approach that allows for the explicit and accurate treatment of proton shuttling in the MD simulation of complex systems having large system sizes and long MD simulation times. Another key objective is the bridging of the molecular scale proton transport information to mesoscopic models of PEMs that connect the proton transport with the features of the polymer morphology.

Technical Barriers

The computer simulation of the proton conductance behavior of proton exchange membranes must involve a description of the relevant physics over a wide range of length and time scales. These scales range from those involving the breaking and making of chemical bonds at the Angstrom and picosecond scales during the proton shuttling process through mediating water molecules, to the mesoscopic collective proton transport behavior of the polymer membrane behavior at the micrometer and microsecond scales. A systematic multiscale computational approach must therefore be developed and implemented, often within a high performance computing environment, to correctly describe proton exchange membranes.

Abstract

The solvation and transport of hydrated protons in proton exchange membranes (PEMs) such as Nafion® will be described using a novel multi-state reactive molecular dynamics (MD) approach, combined with large scale MD simulation to help probe various PEM morphological models. The multi-state MD methodology allows for the treatment of explicit (Grotthuss) proton shuttling and charge defect delocalization which, in turn, can strongly influence the properties of the hydrated protons in various aqueous and complex environments. A significant extension of the methodology to treat highly acidic (low pH) environments such as the hydrophilic domains of a PEM will be presented. Recent results for proton solvation and transport in Nafion® will be described which reveal the significant role of Grotthuss shuttling and charge defect delocalization on the excess proton solvation structures and transport properties. The role of PEM hydration level and morphology on these properties will also be described.

Progress Report

A. Simulations of Explicit Proton Transport in Nafion® as a Function of Water Loading (Hydration). Novel atomistic reactive molecular dynamics(MD) simulations of 1100EW Nafion® were performed for water loading of 15H2O/SO3- 10H2O/SO3-, 7H2O/SO3- and 6H2O/SO3-. This work has extensively utilized the self-consistent iterative multi-state empirical valence bond (SCI-MS-EVB) method,1 a generalization of the MS-EVB approach which allows for the treatment of solvation and the transport of multiple excess protons under intermediate to high acid concentrations at an affordable computational cost. In addition to its exceptional computational efficiency relative to ab initio molecular dynamics, the SCI–MS-EVB method also scales linearly with the number of protons in the simulation box. The recently developed MS-EVB3 parameterization, which is also based on a more accurate un derlying water model,3 was also employed. These simulations have provided a better understanding of the physics of proton solvation and transport in the Nafion® membrane as a function of water loading. The dynamical evolution of the excess protons, water distributions (cf. Fig. 1), and the cooperative motion of the sulfonate/hydronium ion pairs, as well as their associated solvation structures at different water loading levels, were the focus of this study.

The center of excess charge (CEC)4 of the net positively charged hydrated proton electronic charge defect, which best characterizes the instantaneous location of the excess proton charge and most physically accurately describes the effects of Grotthuss proton
shuttling, was used to characterize the structure and
dynamics of the highly acidic Nafion® environment.
The water distributions were also characterized by
radial distribution functions of the water molecules.
As depicted in Figure 1, water clusters of water loading
level $6H_2O/\text{SO}_3^-$ are characterized by the high peak at
$\sim 0.26\text{nm}$, while the relatively lower peak at the same
position and the slightly larger amplitude at longer
distance for water loading level $15H_2O/\text{SO}_3^-$ indicate
the existence of a water network that can facilitate the
observed higher proton conductance.

The unusual proton transport behavior discovered
previously in this project was further studied at
different water loading levels. The excess proton
CEC displacement vectors were decomposed into a
continuous displacement component due to "vehicular"
(classical Einstein) diffusive motion and a component
due to the discrete "hopping" displacement due to
the identity change of the protonated water molecule
via Grotthuss shuttling. The overall mean squared
displacement (MSD) could then be written as the sum
of the MSD of each component and an overlap term
which describes the correlation of the two displacement
vectors. Figure 2 displays the different components of
the MSD for the two water loading levels, $10H_2O/\text{SO}_3^-$
and $6H_2O/\text{SO}_3^-$. (The diffusion constant is proportional
to the slope of the MSD at long times.) At all water
loading levels studied, hopping (discrete) diffusion
is somewhat faster than the vehicular motion. More
interestingly, as the water loading level increases, the
diffusion constant of discrete motion increases faster
than that for the continuous motion (e.g., at $10H_2O/\text{SO}_3^-$
), indicating the onset of water network formation which facilitates the Grotthuss hopping more than vehicular
diffusion.

B. Large Scale Molecular Dynamics of Nafion®
Morphological Models. Atomistic molecular dynamics
simulations of a very large scale were performed to
study hydrated Nafion® systems. The simulations were
large enough (~ 2 million atoms, ~50 nm box length)
to directly observe several hydrophilic domains at the
molecular level. These systems consisted of six of the
most significant and relevant morphological models of
Nafion® to-date: (1) the cluster-channel model, (2) the
parallel cylinder model, (3) the local-order model,
(4) the lamellar model, (5) the rod network model, and
(6) a ‘random’ model that does not directly assume
any particular geometry, distribution, or morphology.
Each system was initially built to closely approximate
the proposed hydrophilic cluster structure in a given
model. Molecular dynamics simulations were then
used to observe resulting changes from and behavior of
the assumed initial configurations. These simulations
revealed fast intercluster ‘bridge’ formation and network
percolation in all models. Sulfonate groups were found
inside these bridges and played a significant role in
percolation. Sulfonates also strongly aggregated around
and inside clusters. Cluster surfaces were analyzed to
study the hydrophilic-hydrophobic interface. Interfacial
area and cluster volume significantly increased during
the simulations, and radial distribution functions and
structure factors were also calculated. All nonrandom
models clearly exhibited the characteristic experimental
scattering peak, underscoring the insensitivity of
this measurement to hydrophilic domain structure
and highlighting the need for future work to clearly
distinguish morphological models of Nafion®.

C. Proton Transport in Non-Aqueous Electrolytes.
Anhydrous proton conduction media are important
targets for applications in high temperature fuel cells
given the difficulties with water as an electrolyte
under such conditions. The MS-EVB methodology
was therefore successfully extended to simulate excess
proton transport in liquid imidazole, which is a target

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**FIGURE 1.** Radial distribution function of water molecules of water loading level $6H_2O/\text{SO}_3^-$ (black line) and $15H_2O/\text{SO}_3^-$ (red line).

**FIGURE 2.** Mean-squared displacement (MSD) versus time of excess protons in Nafion. Dashed lines are water loadings of $6H_2O/\text{SO}_3^-$ and solid lines are $10H_2O/\text{SO}_3^-$. Black denotes total diffusion, red is the continuous "vehicular" diffusion component, and blue is the discrete (Grotthuss hopping).
non-aqueous electrolyte (or chemical derivatives of imidazole). As in aqueous systems, this approach allows proton transfer to simultaneously occur on both reaction sites (donor and acceptor) of the imidazole molecule. The underlying imidazole and imidazolium models were described by the generalized Amber force field (GAFF), while the imidazole MS-EVB model was parameterized to reproduce the \textit{ab initio} proton shuttling potential energy surface (PES) of a protonated imidazole dimer in the gas phase. In bulk phase at 393K, the MS-EVB simulation yielded a proton diffusion coefficient of 0.20 Å$^2$/ps and a Grotthuss hopping rate of 1/36 ps$^{-1}$, and both results are in good agreement with experiment. Despite the prevalence of a classical-like imidazolium structure with highly localized protonic charge defect, the charge delocalization was found to not be negligible process in the simulations. Rather, it was shown to enhance the rate of proton diffusion by approximately 40\% through Grotthuss shuttling. Analysis of the MS-EVB states revealed that the imidazolium ion’s first solvation shell by imidazole molecules is highly ordered, through the formation of hydrogen bonds, while the second solvation shell is highly disordered. Together with the importance of charge delocalization, this result demonstrated that reorientation of imidazole rings in the second solvation shell is the rate-limiting step for proton transfer.

**Future Directions**

Now that the atomistic-scale reactive MD (SCI-MS-EVB) simulations of proton transport in PEMs are well in hand, the role of polymer morphology in defining the mesoscopic proton conductance behavior can begin to be explored. This effort will involve increasingly larger SCI-MS-EVB simulations for select PEM morphological models, coupled to new mesoscopic simulation methods to describe both the polymer morphology and the proton transport on a unified, larger length and time scale, footing.

**References**


**Publications acknowledging the DOE grant**

Objectives:

The long-term goal of this program is to create materials and methods that can be used to fabricate ultrathin (< 10 nm) membranes for the separation of H₂ from CO₂. The immediate objectives of this research are to examine the feasibility of (i) creating thin films via the layer-by-layer (LbL) deposition method, which exhibit reverse size-selectivity, and (ii) introducing a molecular sieving mechanism into ionically cross-linked (i.e., “glued) Langmuir-Blodgett (LB) bilayers.

Technical Barriers:

Of the three main methods that are currently available for separating gases (i.e., adsorption, cryogenic and membrane methods), it is membrane technology that holds the greatest opportunity for improvement. Based on current technologies, it has proven difficult to prepare membranes that are thinner than ca. 100 nm without introducing major defects and losing selectivity. Thus, the creation of defect-free membranes that are less than 10 nm in thickness, which afford high flux rates and permeation-selectivities that exceed the “upper-bound”, would significantly increase the competitiveness of membrane technology for gas separations. This program seeks to create such membranes for the separation of H₂ from of CO₂.

Abstract.

An ionic linker strategy has been developed for converting poly(ethylene oxide) into a polyanion that can form polyelectrolyte multilayers (PEMs) via the layer-by-layer deposition method. These polyanions have been combined with poly(allylamine hydrochloride) (PAH) to produce 7 nm-thick membranes having modest reverse He/CO₂ permeation selectivity favoring CO₂ by a factor of 1.3, and exceptional CO₂/N₂ size-selectivity, favoring CO₂ by a factor of >200. For these measurements, He has been used as a surrogate for hydrogen for safety reasons. In addition, a calix[5] arene-based surfactant has been synthesized that will be used to test the feasibility of introducing a molecular sieving mechanism into ionically cross-linked (i.e., ‘glued) Langmuir-Blodgett (LB) bilayers.

Progress Report

A. Reverse Selectivity of Layer-by-Layer Thin Films Derived From a Poly(ethylene oxide)-Based Polyelectrolyte. Polymers that contain poly(ethylene oxide) (PEO) are of considerable current interest as membrane materials for the separation of acid gases from light gases and hydrocarbons; e.g., the removal CO₂ from H₂/CO₂ and CO₂/N₂. The main virtue of PEO for such separations is its affinity towards CO₂, which results in relatively high solubility and permeability. In principle, the creation of ultrathin PEO-based films that combine high flux rates with such selectivity properties could lead the way to advanced materials and processes for the purification of hydrogen, as well as the removal of CO₂ from flue gases. While there have been several reports in the literature of gas permeation across polyelectrolyte multilayers (i.e., PEMs), to our knowledge, none have exhibited preferential CO₂ permeation over H₂ with film thicknesses below 10 nm.

We have now shown how poly(ethylene oxide) (PEO) can be converted into a polyelectrolyte using an ionic linker strategy, and that this polymer is suitable for forming polyelectrolyte multilayers (PEMs) (Scheme 1). Specifically, we showed that I can combine with poly(allylamine hydrochloride) (PAH) to form (PEMs) via the layer-by-layer (LbL) deposition method (Scheme 2). We have also shown that such materials, in the form of 7 nm thin films, exhibit reverse size-selectivity favoring the permeation of CO₂ over He by a factor of 1.3. In the course of these studies, we also discovered that the permeation selectivity with respect to CO₂/N₂ (flue gas) has been found to be exceptional, favoring CO₂ over N₂ by a factor >200.
Significance. This work has led to the introduction of a fundamentally new structural motif of polyelectrolytes that can be used for the construction of PEMs based on an ionic linker strategy. It has also demonstrated the feasibility of creating films that are 7 nm in thickness, which exhibit reverse size-selectivity, when poly(ethylene oxide) is converted into a polyanion. While the reverse He/CO₂ selectivity is only modest for such membranes (i.e., ca. 0.8), its size-selectivity for CO₂/N₂ (>200) is exceptional; the latter could be practical interest for membrane-based separations of flue gas.

B. A Calix[5]arene for Glued Langmuir-Blodgett Membranes. During the course of the current grant period, a calix[5]arene-based surfactant, 3, has been successfully synthesized and characterized using the sequence of reactions that are shown in Scheme 3.

Significance. The successful synthesis of 3 now provides us with an opportunity to determine whether a molecular sieving mechanism can be introduced into ionically cross-linked (i.e., “glued”) Langmuir-Blodgett (LB) bilayers. Specifically, since the maximum internal pore diameter of the calix[5]arene framework (0.36 nm) is closer to the kinetic diameter of CO₂ (0.33 nm), as compared to the calix[6]arene framework (0.48 nm), and since H₂ (0.28 nm) has a smaller kinetic diameter, one would expect that molecular sieving could make a significant contribution to the permeation selectivity of calix[5]arene-based, glued bilayers.

Future Directions:

1. Poly(ethylene oxide)-containing Polyelectrolyte Multilayers. Our preliminary results with layer-by-layer thin films made from 1/PAH are sufficiently encouraging that they warrant a detailed examination. Obvious extensions of this work, which will be explored, include a systematic study of the influence of (i) polyelectrolyte concentration, (ii) the size the poly(ethylene oxide) used to form the polyanion, (iii) the molecular weight of the polyanion that is used (iv) the formation of PEMs from polyanions and polycations that both contain poly(ethylene oxide).

2. Introducing a molecular sieving mechanism into ionically cross-linked Langmuir-Blodgett (LB) bilayers. Our expectation is that by decreasing the pore diameter of the calix[n]arene framework from n=6 to n=5, we will observe an intrinsic permeation behavior of this film that crosses the upper bound. Such behavior would lend strong support for a molecular sieving mechanism. To test this hypothesis, we will examine the barrier properties of two types of membranes: LB bilayers that have been glued together with (i) PSS, and (ii) poly(acrylic acid). It should be noted that in
a previous study, we have shown that a calix[6]arene analog of 3, formed glued LB bilayers with poly(acrylic acid) at pH 3.5 having exceptional He/CO₂ permeation selectivity; that is a selectivity of ca. 150, which lies close to the upper bound.¹¹ We think it’s likely that the calix[5]arene analog (3) can “push” the barrier properties of such membranes across the upper bound, but this needs to be confirmed by experiment.

3. A Change from He to H₂. Until now, we have used He, extensively, as a surrogate for H₂ because it has a similar size, similar permeation behavior, and because it is non-combustible. However, we now intend to measure the permeation of H₂, directly, in a fume hood for laboratory safety.

References


Publications


Objectives

Electrodes in solid-oxide fuel cells (SOFC) and electrolyzers (SOE) are typically composites of an electronic conductor and the electrolyte material. The objective of this work is to develop a fundamental understanding of how interactions between the various components of the composite affect catalytic and electrochemical performance. Another objective is to use these insights to design nanocomposites that provide stable, high performance for these applications.

Technical Barriers

A major barrier in the development of SOFC and SOE electrodes is the difficulty in preparing composites that are stable to the conditions under which they will be exposed. Under working conditions, the electrode composites are exposed to high temperatures, low P(O2), and potentially high electric fields at three-phase boundary sites. At the fuel-side electrode, they can be poisoned by sulfur or carbon formation and damaged by redox cycling. Sintering and solid-state reactions between the components are major problems.

Abstract

Oxide-oxide interfaces for fuel and air electrodes in solid-oxide fuel cells and electrolyzers have been studied using cells in which the ceramic-based electrodes were formed by infiltration of porous YSZ with conductive and catalytic components. For the fuel electrodes, it is shown that both a microstructure with porous features and the presence of a catalyst are crucial for good performance. For the air electrode, surface area seems to be the primary factor in determining performance, since cathodes formed from different perovskites, all based on the LaFeO3 but having widely different ionic conductivities, exhibited similar performance. Finally, model studies of perovskite-YSZ interfaces, involving nanoparticles deposited onto a YSZ(100) crystal, show that interactions between the perovskite and the YSZ surface can cause the perovskite to spread over the YSZ surface following high-temperature calcinations.

Progress Report

Work on SOFC and SOE is being carried out in three general areas: 1) Infiltrated SOFC anodes (the cathode for an SOE); 2) infiltrated SOFC cathodes (SOE anodes); and 3) studies of model systems for understanding perovskite-YSZ interfaces.

SOFC Anodes/SOE Cathodes

Most of our recent work in this area has focused on developing ceramic-based anodes because of their stability towards sintering and their tolerance towards carbon and sulfur, relative to the Cu-based anodes that we started with.

A particularly interesting material, developed by a collaborator, Prof John Irvine (St. Andrews University), is La0.8Sr0.2Cr0.5Mn0.5O3 (LSCM), a perovskite that is stable and conductive under reducing conditions. Ceramic anodes were prepared by infiltration with the nitrate salts to produce composites with 45-wt% LSCM in a 65% porous yttria-stabilized zirconia (YSZ) scaffold. SEM micrographs indicate that the LSCM coats the YSZ pores following calcination at 1473 K. Composites produced in this manner exhibited conductivities at 1073 K of approximately 1 S/cm in air and 0.1 S/cm in humidified H2. Although SOFC with LSCM-YSZ anodes exhibited very poor performance at all temperatures, the addition of 0.5-wt% Pd and 5-wt% ceria exhibited maximum power densities at 1073 K of 1.1 W/cm2 and 0.71 W/cm2 in humidified (3 % H2O) H2 and methane, respectively.

To better understand the catalytic requirements of LSCM-YSZ electrodes, fuel-cell performance was measured after the addition of various catalysts to the LSCM-YSZ composite electrodes. The addition of 0.5 to 1-wt% Pd, Rh, or Ni was sufficient to increase the maximum power density of SOFC in humidified H2 at 973 K from less than 100 mW/cm2 in the absence of a
catalyst to above 500 mW/cm². The addition of either 1-wt% Fe or 5-wt% ceria also improved power densities but to a lesser extent. Finally, the use of Pt paste as the current collector increased performance to a similar extent as intentionally adding a catalyst, showing the importance of using inert materials in electrode testing.

Because LSCM has a low ionic conductivity and appears to form a coating over the YSZ, the high electrode performance that we achieved was very surprising; therefore, we made various measurements to understand why this was the case. Scanning electron microscopy (SEM) showed that the LSCM underwent microstructural evolution upon heating and redox cycling. Although the LSCM formed a film on the YSZ scaffold after heating to 1473 K, treating this microstructure at 1073 K in H₂ caused the formation of an interconnected array of ~10nm scale particles, offering an attractive structure with extensive triple phase boundary regions where electrochemical reactions can occur. Thermodynamic measurements (coulometric titration) demonstrated that the reduction of LSCM and La₀.₉Sr₀.₁MnO₃ (LSM) occur over a similar range of P(O₂) and that reduction is the likely cause for formation of the microscale array.

**SOFC Cathodes/SOE Anodes**

Based on the hypothesis that the ionic conductivity of the perovskite is critical in determining the performance of perovskite-YSZ composites when used as the air electrode, we measured the ionic conductivity of La₉Ni₀.₆Fe₀.₄O₃ (LNF) and La₀.₉Sr₀.₁Ni₀.₆Fe₀.₄O₃ (LSNF), as well as LaFeO₃ with Ba, Sr, and Ca dopants. All of these materials are good electronic conductors and but their ionic conductivity differed by more than 10². We then tested fuel cells with cathodes made by infiltration of each of these perovskites, followed by calcinations to either 1123 K (at which temperature each of the perovskites formed small particles on the YSZ scaffold) or 1373 K (at which temperature each formed a film). None of the perovskites underwent solid-state reactions with the YSZ at 1373 K. The performance of the fuel-cell electrodes was found to be indistinguishable for each of the perovskites, raising the question concerning whether ionic conductivity really is a limiting factor in cathode performance.

To determine whether the addition of infiltrated catalysts could influence the performance of cathodes, we examined the effect of adding various dopants to composite cathodes prepared by infiltration of either LSF or La₀.₉Sr₀.₁MnO₃ (LSM) and calcined to either 1123 or 1373 K. The addition of dopants had little influence on the 1123-K composite electrodes but all dopants tested improved the performance of the 1373-K composites. With 1373-K, LSF-YSZ electrodes, the open-circuit impedances decreased dramatically following the addition of 10-wt% YSZ, 0.5-wt% Pd, 10-wt% Ce₀.₈Sm₀.₂O₁.₉ (SDC), 10-wt% CaO, and 10-wt% K₂O. Similarly, the 1373-K, LSM-YSZ electrodes were enhanced by the addition of 10-wt% CeO₂, 1-wt% Pd, and 10-wt% YSZ. Since the improved performance was close to that of the corresponding LSF-YSZ and LSM-YSZ electrodes that had been calcined to only 1123 K, we concluded that the improvement was related to structural changes in the electrode, rather than improved catalytic properties or ionic conductivity.

**Model Perovskite-YSZ Interfaces**

The interaction between LSM nanoparticles and a YSZ(100) crystal was investigated in order to understand the structural changes that occur with increasing annealing temperature. Measurements were performed using AFM, XPS, and SEM/EDX. After depositing nanoparticles of LSM directly onto YSZ(100), samples were annealed from 1123 to 1523 K. The particles gradually decreased in height and eventually disappeared completely. Subsequent reduction in H₂/H₂O at 973 K resulted in the reappearance of nanoparticles. Studies were carried out on identical regions of the sample allowing the same nanoparticles to be characterized at different temperatures. Morphological changes indicate the formation of a thin layer of LSM, and XPS results support that observation by indicating an increase in signal from the La and Sr and a decrease in signal from the Y and Zr with increasing temperature. SEM/EDX was used to verify that the nanoparticles in the reduced sample contained La. The changes in the LSM/YSZ morphology may be important in explaining the non-stationary behavior observed in operating fuel cells.

**Publications Citing DOE Support (1/1/08 to present)**

6. “Relationship between electrical behavior and structural characteristics in Sr-doped LaNi_{0.6}Fe_{0.4}O_{3-δ} mixed oxides”, T. Montini, M. Bevilacqua, E. Fonda, M. F. Casula, S. Lee, C. Tavagnacco, R.J. Gorte, and P. Fornasiero, Chemistry of Materials, 21 (2009) 1768-74.


V.P.29 Charge Transfer, Transport, and Reactivity in Complex Molecular Environments: Theoretical Studies for the Hydrogen Fuel Initiative

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Abstract, Progress Report and Future Directions

We have performed multi-scale simulations of proton transport, water percolation and membrane dynamics in a number of promising fuel cell membranes. Our work takes into account the membrane morphological changes with hydration level, but is also informed by detailed *ab initio* quantum chemical calculations. At the most fundamental scale, our simulations capture the quantum mechanical characteristics of proton transfer as a function of hydration level for models of existing and proposed membranes. This provides us with fundamental understanding of the role of acidic pendants in proton dissociation. At the next higher level, our simulations determine the changes in proton hopping as a function of hydration level using quantum hopping molecular dynamics (Q-HOP MD) that is parameterized based on quantum chemical calculations. We are also using quantum mechanics/molecular mechanics (QM/MM) simulations starting from equilibrated configurations generated by classical MD to examine combined proton and water molecule transport. At higher scales, we use classical MD with reactive and conventional force fields to compare changes in membrane morphology and water network percolation in hydrated Nafion®, Dow, Hyflon, SPEEK and Sulfonyl-Imide-based novel membranes. We are also exploring structure and dynamics in ionic liquids, such as triflic acid and diethylmethyl amine to understand anhydrous membranes. These simulations provided an integrated understanding of the influence of acidity and water network percolation on conductivity of PEMs.

*Ab initio* electronic structure and dynamics of acidic pendants in PEMs: We have examined proton dissociation in acidic units that are the building blocks for several promising polymeric electrolyte fuel cell membranes. Minimum energy structures for four acidic moieties with clusters of up to 6 water molecules were determined using density functional theory at the B3LYP/6-311G** level starting from chemically rational initial configurations. The perfluorosulfonylimide acid group (CF$_2$CF$_2$SO$_2$NHSO$_2$CF$_3$) was observed to be the strongest acid, due to the substantial electron withdrawing effect of both fluorocarbon groups. The hydrophilic functional group (CH$_3$OC$_6$H$_4$OCH$_2$C$_6$H$_4$SO$_3$H) of sulfonated polyetherether ketone (SPEEEK) membrane was found to be the strongest base with the acidic proton dissociation requiring the addition of six water molecules and the hydrated proton being more tightly bound to the conjugate base. Even though both perfluoro sulfonyl
imides and sulfonyl acids (hydrophilic functional groups for sulfonyl imide and Nafion® ionomers respectively) required only three water molecules to exhibit spontaneous proton dissociation, the largest possible solvent-separated hydronium ion was attained only for the sulfonyl imide moiety. These results provide a scientific basis for understanding the improved conductivity of perfluorinated sulfonyl imide-based membranes relative to that of the widely-used Nafion® membrane.

**Water network percolation and proton hopping in Nafion membrane:** We have used percolation analysis following classical MD simulations of Nafion® for a large number of hydration levels \( \lambda = 1, 3, 5, 7, 9, 11, 13.5 \) and 20 water molecules per sulfonate groups) to examine water clustering, connectivity of clusters and persistence of spanning clusters as a function of hydration level in Nafion® membrane. We have also used quantum hopping (Q-HOP) molecular dynamics method to compute the mean residence times (MRTs), rate constants and activation energies for proton transfer. At low hydration levels \( \lambda \leq 5 \), clusters of water molecules and hydronium ions are isolated from each other and proton residence time on a water molecule is about 220 ps at 300 K. The average number of clusters decreases from more than 25 for \( \lambda = 5 \) to fewer than 4 for \( \lambda = 7 \). Multiple SO\(_3^–\) groups confine the H\(_3\)O\(^+\) ion. Vehicular proton transport is hindered by steric hindrance and long-range structural transport is not possible due to the lack of connectivity of H\(_2\)O molecules.

Water network percolation occurs between \( \lambda = 5 \) and \( \lambda = 6 \) in agreement with estimates based on infrared spectroscopy experiments. This threshold was determined based on multiple criteria. In fact, we have proposed a new criterion for detecting percolation based on the relative probabilities of finding water molecules in the smallest and largest clusters. Near the percolation threshold, clusters are linked from time to time by mobile H\(_2\)O molecules, so that transient spanning clusters form and disappear. At high hydration levels \( \lambda \geq 9 \), a persistent spanning cluster permeates the membrane and creates water channels along which the proton can hop. At high \( \lambda \), the proton residence time on a H\(_2\)O molecule drops by two orders of magnitude from the value at low \( \lambda \). At higher hydration, proton transfer is faster due to ease of solvation of the proton, whereas at higher temperatures, protons are more mobile because thermal effects generate a larger number of favorable proton transfer geometries. At high \( \lambda \), the rate constants approach that of proton transfer in bulk water. The proton diffusion coefficient for \( \lambda = 15 \) at 300 K is about 1.1x10\(^{-5}\) cm\(^2\)/s in good agreement with experiment. The understanding of water percolation and dynamics of proton transfer generated by this work could help in the design of future polymer membrane materials that have lower uptake of water and yet offer faster proton transfer and transport.

**Nanophase structural dynamics of phenylated sulfonated poly ether ether ketone (Ph-SPEEK membrane):** We used classical MD to model solvated Ph-SPEEK membranes in the presence of hydronium ions. We characterized the nanophase structure and dynamics as a function of hydration level for \( \lambda = 3.5, 6, 11, 25, \) and 40; where \( \lambda \) is the number of water molecules per sulfonyl group. Pair correlation function analyses reveal that the nanophase segregation increases with salvation. The water and hydronium ion diffusion coefficients also increase with \( \lambda \). While the average number of hydrogen bonds between hydronium ions and sulfonyl groups are dramatically affected by the hydration level, their average lifetime remains constant. The membrane is found to be relatively rigid and its overall flexibility shows little dependency as a function of water content. Compared to Nafion®, water and ion diffusions are considerably smaller at lower hydration levels at room temperature. However, at \( \lambda = 25 \) and 40 these coefficients are comparable to that of Nafion® at

**FIGURE 1.** Perspective projection of H\(_2\)O molecules and H\(_3\)O\(^+\) ions in Nafion for hydration levels of \( \lambda = 3 \) and 13.5. SO\(_3^–\) is shown as a large (yellow) bead. The backbone and pendant are shown as a transparent surface. Both percolation probability and spanning cluster formation probability reach almost 1.0 for \( \lambda \geq 7 \).
the same solvation levels. This study also indicates that solvent diffusion for Ph-SPEEEKK membranes at low hydration levels can be significantly improved at high temperatures.

Future directions include ab initio molecular dynamics of proton transport in model hydrated pendants and ionic liquid systems; extension of QM/MM simulations to novel membranes; and large scale massively parallel reactive force simulations of the anode/electrolyte interface. The proposed work addresses several different length scales and represents the logical progression of effort from the work accomplished to date under this project.

This work is supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). The computations were performed using the Molecular Sciences Computing Facility (MSCF) in the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE’s Office of Biological and Environmental Research (OBER) and located at PNNL. This work benefited also from resources of the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. DOE.

Publications (including patents) acknowledging the grant or contract


Invited and contributed presentations acknowledging the grant or contract


4. Dupuis, M. (Invited Speaker) Colloquium, Department of Materials Science and Engineering, University of North Texas, Denton TX, Fall 2009.


Objectives

The program aims to design, synthesize and test rare earth phosphate materials for proton conducting applications in the temperature region of 300-550 degrees Celsius. The program relies on three major approaches: a theoretical understanding of proton conduction in rare earth phosphates employing quantum chemical computation and molecular simulation; the chemical design, synthesis, and proton conductivity measurement of nano-composite materials expected to exhibit facile proton conduction; and the structural and dynamical characterization of the nano-composite materials using a range of advanced characterization methods including nanoscale structural and chemical electron microscopy, vibrational and x-ray spectroscopy, and nuclear magnetic resonance (NMR).

Technical Barriers

Hydrogen, as well some biofuels, can be advantageously used for electric power generation in fuel cells that can operate between 350-550°C, significantly lowering materials cost, simplifying catalysis, and extending fuel cell lifetimes. An essential component to enable this technology is the development of appropriate proton conducting membranes. However, these membranes are not presently available. This program examines the fundamental aspects of proton conduction in doped rare earth phosphates to provide such membranes.

Abstract

Lanthanum and Cerium phosphates with modified grain boundaries were synthesized and characterized, showing proton conductivity in amorphous, nanometer grain boundary layers as high as 10⁻³ S/cm at 500°C. First principles computation revealed that proton conduction in rare earth phosphates, such as LaPO₄, proceeds by intertetrahedral hopping. Temperature-dependent °H MAS-NMR results below 150°C confirmed computed proton activation energies for local motion. It was shown that dramatic increases in proton conductivity in La-phosphates resulted from the introduction of Al, Sr, and Ca leading to glasses and glass-ceramics conductors with a conductivity of ~10⁻⁴ S/cm at 440°C in dry argon, a record to date. The (LaSrAl)PO₄ glasses have a melting point of about 800°C, and can allow for easy membrane production by common glass processing methods, and may be thermally manipulated further to yield nanocomposite glass-ceramics with even higher expected conductivities. This finding points to way to easily-fabricated thin proton conducting membranes for hydrogen/air fuel cells operating in the technologically advantageous range of 300-500°C.

Progress Report

The electrical properties of [La(1-x)Mₓ]P₃O₉ metaphosphate glasses, where M is Ba, Sr, Ca, and 0≤x≤0.8 were investigated in the 300 – 500°C range. The protonic conductivity increases two orders of magnitude from the unsubstituted to the 60% substituted glass reaching a maximum conductivity of about 10⁻⁵ S/cm at 450°C. The activation energy is found to be approximately independent of concentration though dependent on the type of modifying substitutional cation, and decreases from about 1.04 eV for Ca and Sr to ~ 0.96 eV for Ba. AC impedance measurements were used to find the DC ionic conductivities. Mean ion travel distances at the frequencies, νZ* or νΜ*, associated with the maximum in Z” or M” were found to be up to 30 times larger than the average oxygen spacing in the glasses. While diffusion coefficients derived from conductivities, Dσ, were vastly lower than an uncorrelated diffusion coefficient computed from first principles, the travel distance at νZ* or νM* derived from a simple random walk expression using DΓ were surprisingly close to those derived from the more rigorous statistical treatments. The ratio ξ=Dσ/DΓ<<1 may be interpreted as indicative of highly correlated ion motion and strongly reduced mean attempt frequencies, together with a mean activation energy for motion increased by ΔE=Eσ-EΓ over that of the uncorrelated intertetrahedral motion of an ideal crystal characterized by DΓ.
Al$_2$O$_3$ was added to a 2CaO-La$_2$O$_3$-5P$_2$O$_5$ metaphosphate, to replace 10% of the Ca$^{2+}$ ions by Al$^{3+}$, forming a phosphate with the nominal composition 1.8CaO-0.1Al$_2$O$_3$-La$_2$O$_3$-5P$_2$O$_5$. The effect of Al$_2$O$_3$ addition and heat treatment on the microstructure and conductivity of the resulting glass-ceramics was investigated by XRD, SEM, TEM, and AC impedance spectroscopy. Upon transformation from glass to glass-ceramic, conductivities increased significantly. The glasses were isochronally transformed at 700°C and at 800°C for 1 hr or 5 hrs, in air, following heating at 3 or 10°C/min. With Al$_2$O$_3$ addition, after a heat treatment at 700°C, 100–300 nm nano-domains of LaP$_3$O$_9$ crystallized from the glass matrix. Annealing at 800°C produced a further order of magnitude conductivity increase for the Al-free glass, but less so for the Al-containing glass.

Structural and electronic properties of cerium orthophosphate (CePO$_4$), a mixed electronic and protonic conducting electrolyte, are calculated using density functional theory (DFT) and beyond, and compared with experiments. A Hubbard-like parameter U is employed to reduce the self-interaction for localized Ce 4f states. As U is varied from 1-5 eV, the band structure is found to undergo significant changes, with the Kohn-Sham gap varying between 0.8 and 4.3 eV. Interestingly, the lattice parameters are unchanged, indicating structural properties are far less sensitive to U. The valence band energies and the optical band gap of CePO$_4$ are measured using photoemission and optical reflectance spectroscopy. The structure was determined using XRD. The choice of U = 3 eV provides the best match between the calculated density of states and the experimental photoemission and optical reflectance spectra. The activation energy of the minimum energy path for proton transfer will be calculated and compared to that of LaPO$_4$, another proton conducting electrolyte.

Rare earth phosphate ceramics have been investigated as proton conductors for applications in fuel cells, hydrogen sensors, and hydrogen separation membranes. Protons are incorporated into the materials as charge-compensating defects when the phosphates are doped with aliovalent cations. Protons bond to oxygen atoms on the phosphate tetrahedra and are thought to move through the material via intertetrahedral transfer. Lanthanum orthophosphate (LaPO$_4$), a monoclinic material with space group P21/n, is an established proton conductor. This behavior is thought to be due to mixed proton and hole conductivity. Under reducing conditions, proton conductivity is thought to dominate, whereas under oxidizing conditions, the carrier is thought to be electron holes.

**Future Directions**

- Doped nanocomposite RE-phosphates are synthesized from quenched glass melts, by controlled thermal annealing to manipulate the glass-ceramic nucleation and growth, to exploit conductivity enhancement that can result from such architectures.
- First-principle calculations at NERSC in conjunction with conductivity measurements and heteronuclear correlation and pulsed gradient NMR are used to elucidate the proton conduction mechanisms.
- Advanced high resolution chemical and structural characterization carried out in the facilities at the National Center for Electron Microscopy and the Molecular foundry to support NMR and vibrational spectroscopy studies.
- AC and DC conductivities are measured on the REP glasses and glass ceramics as a function of composition and water vapor exposure, to determine the proton transference numbers.
- Detailed structural elucidation of the nanocomposite materials is done using several multidimensional and multi-quantum NMR techniques, with an emphasis on understanding the impact of aliovalent substitution on proton dissolution in rare earth phosphates.

**Publications**


**Acknowledgements**

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Objectives

We are seeking to understand the connections between the hydrated morphology and the local dynamics of water in polymer electrolyte membranes (PEMs) of different equivalent weights (EWs) at various hydration levels through the measurement of their dielectric response. Dielectric relaxation behavior provides correlations between the polymer environment and the cooperative solvent dynamics, which can unveil important insights into water and proton transport in these membranes.1,2 It is widely accepted that water confined in systems such as reverse micelles possesses different dynamics as compared to bulk/free water.3,4

The choice to conduct measurements at microwave frequencies (1 to 20 GHz) is due to the observation that the principal absorption band, attributed to a Debye type relaxation of molecular origin, in pure bulk water occurs at about 18 GHz.3-5

Technical Barriers

All hydrated PEMs were removed from their equilibration chamber just prior to the dielectric measurement at room temperature in open atmosphere using single post dielectric resonators (SPDR). However, we observed that there is a rapid loss of water in them. As the dielectric properties are strongly dependent on the water content, it is critical to precisely control the RH of the test environment. Also, the SPDRs were unable to yield the dielectric constants for hydrated Nafion® 117 (thickness 185 microns) because the Q factor of the resonator with this sample under test is smaller than 100.

Abstract

EW is an important factor in determining the structure of the membrane and the dynamics of protons and water molecules within the membrane. The behavior of the acid form of the polymer is dramatically affected by the presence of water. The dielectric properties of PEM are dictated by the molecular structure of the system and the physical state of water in these materials. The dielectric spectra can provide insights into both the state of water and indirectly, the hydrated structure of polymer. Thus, knowledge of the state or nature of the water in the membrane is critical to understanding the mechanisms of proton transfer and transport in PEMs.

When hydrated, these membranes exhibit a nanophase-separated morphology with the hydrophobic backbone of the polymer separated from a network of water and ions (both fixed SO3⁻ groups and hydrated protons).6 The rigidity of the backbone and the crystallinity of the polymer confine the water; and with the significant density and distribution of the pendant anionic groups give structural ordering to the water in the membrane.7,8

Project Report and Future Directions

The split-post dielectric resonator (SPDR) technique is a well established and accurate method for characterization of the dielectrics in the laminar forms up to 20 GHz.9,10 Since no electrodes are involved this method, measurements are not affected by electrode/ferroelectric interfacial effects (i.e. dead layer). The split-post resonator consists of two low loss dielectric packs in a metal enclosure. The resonator uses TE01δ mode of the electromagnetic field, which is insensitive to the presence of air gaps between the tested sample and the dielectric resonator. Our SPDRs were custom built to measure the dielectric response frequencies of: 1.9, 5, 10, 15, 18 and 20 GHz. The characterization of a PEM sample consists of two steps through measurement of the resonant frequency and quality factor of the (i) empty resonator, and (ii) resonator with the membrane. The first measurement provides the input for calculation of the dielectric permittivity. The real part of the complex permittivity is computed from the measured resonant frequencies with a SPDR both with and without the membrane sample from the following equation:

$$\varepsilon' = 1 + \frac{f_0 - f_s}{hf_0K_\varepsilon (\varepsilon', h)}$$
where \( h \) is the thickness of the measured substrate, \( f_0 \) is the resonant frequency of the empty SPDR, \( f_s \) is the resonant frequency of the SPDR with the dielectric sample, and \( K_\varepsilon \) is a function of \( \varepsilon_r \) and \( h \). The latter is calculated for a number of \( \varepsilon_r \) and \( h \) using the Rayleigh-Ritz technique. An iterative procedure is used to evaluate the values of \( K_\varepsilon \) and \( \varepsilon_r \) from the above equation.

All the PFSA membranes (including Nafion\textsuperscript{®} 117, Solvay E8705S, etc) were pretreated by cleaning in 1M HNO\textsubscript{3} at 80\(^\circ\)C for 1 hr and in DI water at 80\(^\circ\)C for 1 hour. They were then washed in DI water and stored in deionized water prior to placement in the SPDR for measurement under fully hydrated conditions. The films were weighed after removing any surface water to obtain the wet weight. They were then dried over P\textsubscript{2}O\textsubscript{5} for determination of the dry weight.

The isopiestic equilibration scheme of Pushpa et al\textsuperscript{11} was employed to control the membrane water content, enabling the study of the relative permittivity of the membranes over a range of water contents. Equilibration of the samples over the aqueous LiCl is critical in establishment of reliable and reproducible water contents in the membrane. The dried membranes were then equilibrated over aqueous LiCl solutions for at least 1 week. The concentrations of the LiCl solutions were selected to encompass the different regions' observed on the water adsorption isotherms for Nafion\textsuperscript{®} 117 as shown in Table 1.

**TABLE 1. Water adsorption isotherm data for Solvay films (EW 790 and 870)**

<table>
<thead>
<tr>
<th>LiCl(M)</th>
<th>Water Activity</th>
<th>Water Content, ( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EW</td>
<td></td>
<td>789</td>
</tr>
<tr>
<td>Fully Hydrated</td>
<td></td>
<td>8.2</td>
</tr>
<tr>
<td>1</td>
<td>0.964</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>0.748</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.6</td>
</tr>
</tbody>
</table>

The water adsorption isotherm data for the Solvay films (Table 1) was obtained by measuring the weight of the films under fully hydrated conditions (100% RH), and following 1 week of equilibration in chambers at 96.4% RH and 75% RH. The dry weight of each of the films was also obtained by drying them over P\textsubscript{2}O\textsubscript{5} for a week. The water uptake was calculated from the following:

\[
\lambda = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{18.015} \right) \left( \frac{\text{EW}}{W_{\text{dry}}} \right)
\]

Hence, it is critical that the RH of the samples be controlled precisely during the actual measurements. We have designed a relative humidity controlled glove box for future experiments that will enable us to perform all our measurements under precisely controlled conditions of humidity and temperature. The equilibrated films, SPDRs, and weighing balance will all be placed in the glove box at a previously set RH to coincide with the activity of the LiCl solution and then equilibrated prior to making the dielectric measurements in-situ. The loss from these membranes in air. As the dielectric properties are strongly dependent on the water content, the dielectric constant depends on how long the sample has been out of the chamber as shown in Figure 2.
dielectric response of completely dry samples of Solvay PEM (EW870) was measured at 1.9 GHz, 5.2 GHz and 10 GHz as shown in Figure 3. The values varied from 3.8 to 3 as frequency changed from 1.9 GHz to 10 GHz.

Our SPDRs were unable to measure the dielectric constants for fully hydrated Nafion® 117 with a thickness of 185 µm. From the graph in Figure 4, it is clear that the resonant frequency shifts can be substantial in thick high permittivity samples. The SPDR cannot measure the permittivity of the sample if the Q factor of the resonator with sample under test is smaller than 100. It is recommended to keep resonant frequency with sample within 10% of the resonant frequency of the resonator. If the Q factor < 100 or the resonant frequency shift > 10%, spurious modes, whose frequencies are changing faster with permittivity than for the TE mode, may overlap with the proper mode disturbing measurements. For all our future measurements we will use Nafion® 112 as our standard material. It has the same EW as Nafion® 117 but with a thickness of 51 microns.

We also plan to cast our own films on glass substrates using ionomer solutions of different EWs to achieve the desired thickness.

References:

VI. MANUFACTURING R&D
INTRODUCTION

The Manufacturing R&D (research and development) sub-program supports research and development needed to reduce the cost of manufacturing hydrogen and fuel cell (FC) systems and components. The manufacturing R&D effort will enable the mass production of components (in parallel with technology development) and will foster a strong domestic supplier base. Activities will address the challenges of moving today's laboratory-produced technologies to high-volume, pre-commercial manufacturing to drive down the cost of hydrogen and FC systems.

In Fiscal Year (FY) 2010, manufacturing projects continued in the following areas: novel electrode deposition processes for membrane electrode assembly (MEA) fabrication, high-volume FC leak-test processes, novel assembly processes for low-cost MEAs, gas diffusion layer cost reductions, and fabrication technologies for high-pressure composite storage tanks.

GOAL

Research and develop technologies and processes that reduce the cost of manufacturing FCs and related systems.

OBJECTIVES

- **Fuel Cells** — Presently, FC stacks are fabricated in very small quantities, and the cost of these stacks for non-automotive applications is approximately $5,000/kW (at volumes of tens of units), which is more than 20 times the projected cost of about $140/kW for stacks in 2010 at low volume (1,000 stacks/year) and over 60 times the cost of $25/kW at high volume (500,000 stacks/year) for automotive applications. The projected high-volume cost includes labor, materials, and related expenditures, but does not account for manufacturing R&D investment. The objective of manufacturing R&D is to enable cost reduction in fuel cell stacks for stationary and transportation power systems.

- **Hydrogen Storage** — The objective of hydrogen storage manufacturing R&D is to reduce the cost of making high-pressure carbon composite hydrogen storage tanks by a factor of 10 from 2010 costs, to be in line with the Hydrogen Storage sub-program’s cost targets.

FY 2010 TECHNOLOGY STATUS

This sub-program focuses on the manufacture of component and FC technologies that will be needed in the early stages of 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 goals is measured in terms of the ability of funded research to reduce the cost of producing FCs, and to increase manufacturing processing rates and annual manufacturing capacity.


3 Ibid.

The current costs for hydrogen and FC technologies are about $20/kWh for a 700-bar gas-phase hydrogen storage system (projected to high volume) and about $3,000/kW for polymer electrolyte membrane FC stacks fabricated at very low volume.

**FY 2010 Accomplishments**

FY 2010 saw a number of advancements in manufacturing of FCs and storage systems:

- **Gas Diffusion Layer (GDL) Fabrication:** Ballard developed a process model for controlling GDL coating conditions, resulting in significant improvement in quality yields and GDL cost reduction of 53%.
- **Electrode Deposition:** W.L. Gore demonstrated—using their cost model—that a new three-layer MEA process has the potential to reduce MEA cost by 25%.
- **High Pressure Storage:** Quantum and Boeing demonstrated advanced filament winding and fiber placement processes that reduce storage system costs by 10%.
- **MEA Manufacturing:** BASF developed a predictive model and evaluated electrode variation and defect impacts on MEA performance using their new on-line X-ray fluorescence (XRF) technique.
- **Stack Testing:** UltraCell constructed and tested their leak-test and conditioning stand.
- **Component and Stack Measurement:** The National Renewable Energy Laboratory developed and tested an internal resistance-based test stand for detection of multiple defects such as pinholes, electrical shorts, and electrode thickness variations.
- **Sensors:** The National Institute for Science and Technology developed and tested non-contact sensors for bipolar plate process control.

**Budget**

The President’s FY 2011 budget request for the Fuel Cell Technologies Program includes $5 million for Manufacturing R&D.

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FY 2011 Plans

In FY 2011, activities in the Manufacturing R&D sub-program will reduce MEA cost by 25%, reduce storage system costs by 10%, demonstrate impact on MEA performance through use of on-line XRF techniques, further reduce GDL costs beyond the 53% reduction already achieved, further develop stack leak testing, and further develop NREL’s component and stack measurement capabilities. The Program plans to initiate a solicitation for manufacturing process improvement for high-temperature stationary-power FC systems and will complete a process model for high-temperature stationary FC manufacturing.

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VI.1 Fuel Cell Membrane Electrode Assembly Manufacturing R&D

Objectives

NREL and its collaborators are developing capabilities and knowledge related to in-line quality control that will assist manufacturers of polymer electrolyte membrane (PEM) fuel cell membrane electrode assembly (MEA) components (membranes, coated electrodes, and gas diffusion media) in transitioning to high-volume manufacturing methods. Our main tasks are to:

- 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 R&D section (3.5) of the Fuel Cell 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 Fuel Cell 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:

- Developed a system and techniques to identify by areal infrared thermography various MEA and MEA component defects, such as membrane pinholes, electrode catalyst non-uniformity, micro-cracks in gas diffusion media, and MEA shorting.
- Extended our membrane thickness imaging technique to non-polyfluorosulfonic acid (PFSA) membranes and PEM electrolysis membranes.
- Installed and commissioned a research web-line to simulate continuous roll-to-roll processing of MEA component materials for evaluation of diagnostics under process-like conditions.
• Demonstrated fabrication methods to repeatedly create membrane and electrode defects that simulate real as-manufactured defects to study the effects of defects on MEA performance.
• Used LBNL models to qualitatively explain key behaviors of MEAs with defects and to understand the behavior of MEAs under the different excitation diagnostic techniques.
• Continued collaboration with three of DOE’s competitively awarded manufacturing research and development (R&D) projects, in accordance with our project charter.
• Completed work on a Phase I Small Business Innovation Research project with partner Proton Energy Systems related to quality control measurements on PEM electrolyzer MEAs.

Introduction

In Fiscal Years (FYs) 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 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

Work continued on the NREL-developed optical instrument. We extended the demonstrated capability to image thickness and identify defects of PFSA-based membranes, non-PFSA membranes, and thicker membranes for applications such as direct methanol fuel cells and PEM electrolyzers, an example of which is given in Figure 1. We also progressed in our assessment of using this same general technique to measure catalyst uniformity in an areal fashion. In addition to this optical platform, we evaluated the feasibility of using infrared thermography as a rapid method to check for MEA and MEA component defects. Using work done by several of our industry partners as a basis, we further developed and refined the excitation methods for a variety of target MEA defects. We also assessed the response time of the technique to better understand how it might be applied to in-line process measurements. As examples of the potential of this technique, Figure 2 shows the identification of a void in an electrode coating, and Figure 3 shows the identification of a micro-crack in the microporous layer of gas diffusion media. The inset in Figure 3 shows an LBNL simulation of this defect modeled as a series of discontinuities of thermal and electrical conductivity. With this modeling, we can better understand how to optimize the measurement technique for in-line use. The electrode sample depicted in Figure 2 also is an example of our work to develop fabrication methods for MEA component defects. In this case, we used ultrasonic spraying as a highly repeatable process with excellent control of spray pattern and catalyst loading. The inset graphic

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VI. Manufacturing

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is a validation of the intended loading using X-ray fluorescence. To provide a platform upon which to evaluate these and other diagnostics, we installed and commissioned a research web-line, shown in Figure 4. With this unique capability, and using MEA component roll goods from our industry partners, we will assess the accuracy, repeatability, and resolution of different diagnostic techniques under conditions simulating manufacturing process lines.

**Future Direction**

- Design a prototype in-line configuration for the membrane thickness imaging technique and implement this system on our research web-line.
- Evaluate the feasibility of using infrared thermography as an in-line imaging diagnostic and develop a prototype system to install on the research web-line.
- Complete our evaluation of the NREL-developed optical instrument to measure platinum uniformity of electrodes.

**FIGURE 1.** Two-dimensional image of an alternate membrane material measured with the NREL optical instrument. The image shows bubble and pinhole defects as well as thickness variations (color contrast). An area approximately 3" by 2" is shown.

**FIGURE 2.** Two-dimensional infrared thermography of a 25 cm² electrode fabricated with a 1 cm² void in the center. White indicates higher loading, dark indicates lower loading, with black signifying the absence of platinum. The inset shows a validation of this measurement using an X-ray fluorescence scan from one edge of the sample to the other, through the void.

**FIGURE 3.** Two-dimensional infrared thermography of a commercially-available gas-diffusion layer with a series of micro-cracks in the microporous layer. The inset shows modeling from LBNL simulating this defect as a discontinuity in thermal and electrical conductivity.

**FIGURE 4.** The Research Web-Line
VI. Manufacturing

- Use single and segmented cell test methods to understand threshold sizes for critical MEA component defects like membrane pinholes and electrode voids.
- Study the growth rates of as-manufactured defects in cells.
- Continue to gain critical insights on the electrochemical and thermal behavior of MEAs with defects from the LBNL MEA models.
- Continue to work with our industry partners to ensure the relevance of our studies to their evolving needs and directions.

**FY 2010 Patents**


**FY 2010 Publications/Presentations**

VI.2 Reduction in Fabrication Costs of Gas Diffusion Layers

Objectives

- Reduce the fabrication costs of gas diffusion layer (GDL) products by:
  - Reducing the number of process steps.
  - Replacing batch processes with continuous processes.
  - Utilizing in-line measurement tools to reduce costly ex situ testing.
- Develop and implement new, high volume GDL process technologies.
- Produce high-performance, low-cost GDLs at sufficient volumes for near-term fuel cell markets.
- Research, develop, and implement new in-line process control and measurement tools consistent with high volume manufacturing.
- Advance the understanding of the relationship between process parameters, ex situ GDL properties and fuel cell performance to maximize production of high performance, low-cost GDLs for near-term markets.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Lack of High-Volume Membrane Electrode Assembly Processes
- Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project will contribute to the achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell 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

- Reduced GDL costs by 40% from $36/kW to $21/kW from Fiscal Year (FY) 2008 to FY 2009 by:
  - Increasing the manufactured width from 40 cm to 80 cm wide.
  - Implementing process control tools to improve product uniformity, reduce the amount of ex situ testing and improve yield and scrap rates.
  - Installing new equipment allowing us to process rolls over 800 m long.
- Demonstrated multilayer coating capability on our production line:
  - Produced short rolls of both anode and cathode material.
  - Verified performance of both in a 50 cm² test stand against a commercial baseline material.
  - Addressed issues relating to micro-cracking in the microporous layers (MPLs) by modifying MPL ink properties and modifying process drying conditions.
- Demonstrated the ability to manufacture MPL inks using a dynamic mixer:
  - Produced three separate commercial inks on a 2-inch continuous extruder designed for our process.
  - Produced a short roll of anode material.
Verified performance of this anode GDL in a 50 cm² test stand against a commercial baseline material.

- Identified, purchased and installed new process control tools for multilayer coating, in-line mixing and heat treatment processes.
- Used Raman and Fourier transform infrared (FTIR) spectroscopy to determine the impact of sintering on Teflon® - poly-tetrafluoroethylene (PTFE) distribution in the GDL and are currently developing a link between the size and frequency of PTFE agglomerates and PTFE distribution in the GDL.
- Examined the size and shape of pores in the GDL using high-resolution X-Ray tomography (HRXRT) in an effort to find a link to performance.
- Examined each step of the manufacturing process and found relationships between specific process parameters and critical GDL properties. This will help make a more stable, consistent product and allows for the development of enhanced designs to improve performance in specific applications.

**Introduction**

This project addresses the Manufacturing R&D sub-program’s goal of research, development and demonstration of technologies and processes that reduce the manufacturing cost of proton exchange membrane (PEM) fuel cell systems. Specifically, this project reduces the fabrication costs of high-performance GDL products, while increasing manufacturing capacity and improving product uniformity. The end result of this program will be low-cost, high-performance GDLs for near-term fuel cell markets, such as back-up power or materials handling. A conceptual design of a Greenfield manufacturing plant that is capable of meeting the 2015 GDL target price of $4/kW at specified volumes will also be developed.

**Approach**

The largest barrier to the implementation of fuel cell products is cost. The cost of the GDL was evaluated in 2008 and was determined to be around $36/kW, almost 10 times the DOE cost target for 2015. A breakdown of the cost of the GDL revealed that the majority of BMP’s GDL cost was due to manufacturing labor, specifically for ink mixing, coating and quality control, as shown in Figure 1.

It was determined that much of that cost could be removed by reducing the number of process steps, replacing slow batch processes with faster continuous processes, and utilizing modern on-line tools to improve product quality and reduce the amount of ex situ testing.

**Results**

Throughout the first two years of this project, BMP has been able to reduce the fabrication costs of GDLs by 40% from $36/kW to $21/kW, as shown in Figure 2. This has been accomplished by increasing the manufactured width of the GDL from 40 cm to 80 cm, installing new web-handling equipment to allow for processing of rolls in excess of 800 m long, and implementing better process controls to improve yield and scrap rates. As a result of these efforts, the plant capacity has more than doubled, which allows for production of low-cost, high-performance GDLs at volumes suitable for near term markets.

Ballard has also identified further cost reductions for 2010 and 2011 based on the implementation of multilayer coating and in-line mixing. Initial single cell validation work, shown in Figure 3, has been done to demonstrate that GDLs manufactured with this new technology perform as well as standard baseline materials. For this validation work multilayer coating was performed with standard inks and the in-line ink was applied with standard single layer coating processes, so that each process could be evaluated independently.

In addition to the cost reduction work, Ballard has examined every step in their manufacturing process to find relationships between process variables and critical GDL properties. These relationships have allowed Ballard to make adjustments during processing to meet specific customer targets, allowing for more stable, consistent product leading to improved yield.
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Morgan – Ballard Material Products

rates and cell performance. This work should allow for the development of enhanced GDL designs that are tailored for a specific application and should help in manufacturing parts with tight tolerances.

The Pennsylvania State University, under the direction of Dr. Michael Hickner, is working with BMP to develop an in-line method for measuring the chemical homogeneity of the GDL. Specifically, Penn State is looking at using Raman spectroscopy to determine the PTFE agglomerate size and frequency prior to sintering utilizing one-dimensional scanning, as shown in Figure 4. It is believed that this work will be useful in more accurately controlling the PTFE distribution in the GDL and allow for real-time adjustments of processing parameters to reduce variability both down-web and cross-web. HRXRT is also being used by Penn State to evaluate the effects of pore size and shape on GDL performance. They are also working on actively doping the powders used in the MPL inks, to allow us to determine the amount of penetration or MPL intermixing associated with both of our standard and multilayer coating processes.

Conclusions and Future Directions

BMP was able to significantly reduce the fabrication costs of GDLs, while more than doubling manufacturing capacity and improving product quality throughout Phase 1 of this project. Multilayer coating and in-line mixing technologies have been demonstrated and single-cell validation testing showed no significant performance difference when compared to baseline material. In addition, Ballard has been able to relate critical process parameters to key GDL properties and performance, which will allow for more stable, consistent GDL product, improved GDL design and increased production yields. This work will be beneficial for production of high-performance, low-cost GDLs for near-term fuel cell markets.

The Pennsylvania State University, under the direction of Dr. Michael Hickner, has developed a method for characterizing PTFE distribution in the GDL using Raman scanning. They have also used HRXRT to examine the size and shape of pores in the GDL. This work is important in understanding how variations in the PTFE distribution or pore structure may influence GDL performance.

In the next year, the future activities of this project include:

- Conduct short roll uniformity studies to establish product uniformity with new process technologies.
- Generate a production length roll to demonstrate capability.
- Validate performance of new low-cost GDLs utilizing all new process technologies with both single cell and stack testing.
VI. Manufacturing

• Complete installation of all on-line process control tools including vision system for the coating line.
• Determine manufacturing capability with all new process technologies with a goal of achieving six sigma standards.
• Continue development of process variable, product property, and fuel cell performance relationships to direct new process specifications.
• Continue investigation of Raman scanning and HRXRT work as a method of characterizing GDL properties.

FY 2010 Publications/Presentations


Acknowledgements

I would like to acknowledge the technical leadership and contributions of Don Connors, Guy Ebbrell & Kathryn Rutter at Ballard Material Products, as well as Dr. Michael Hickner & Alfonso Mendoza at Penn State.
VI.3 Modular, High-Volume Fuel Cell Leak-Test Suite and Process

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).
- Performance leak tests in-line during assembly and break-in steps.
- Demonstrate fuel cell stack yield rate to 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 R&D section (3.5.5) of the Fuel Cell 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 sub-section of the Manufacturing R&D section of the Fuel Cell 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 processed for assembling stacks. (4Q, 2013)

Accomplishments

- Developed a specification for the leak-test suite laboratory prototype.
- Designed leak-test suite prototype.
- Fabricated leak-test suite prototype.
- Installed leak-test suite prototype at UltraCell facility at Vandalia, OH.
- Tested and evaluated leak-test suite prototype.
- Created fuel cell stack quality metrics.
- Developed techniques for analysis of dynamic mechanic analysis data from the leak-test suite prototype.
- Characterized individual fuel cell stack components using leak-test suite prototype.
- Developed a finite element model capable of modeling the dynamic mechanical properties of fuel cell stacks.

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.

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. A 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

A specification for the leak-test suite laboratory prototype was developed. 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. The design of a leak-test suite lab prototype was completed. A programmable automation controller, CompactRIO, was chosen to control and acquire data for the leak-test suite and prototype. A personal computer LabVIEW application is used for data display, storage, and analysis. CompactRIO is a low-cost reconfigurable control and acquisition system designed for applications that require high performance and reliability. The human machine interface of the leak-test suite prototype includes nine major screens. The main screen will be displayed when the application is started. From this screen the operator can log in, monitor the status of the peripheral devices and change the operating mode. The setup screen is used to enter the parameter files for the tests. The files are entered in Excel spreadsheets. The parameters are divided into eight groups: general parameters, break-in parameters, performance parameters, alarms, temperature controller, report, summary, and notes. When the screen is first accessed, the operator can select and load the desired parameter file. When changes are made to any parameter, the operator can save the file for future use. The prototype can be operated manually and automatically. When in manual mode, the operator can manually control hydraulic press, gas, pneumatic, temperature, crossover current, and stack height. Diagnostic screen displays inputs and outputs. The test screen displays test results. Notes screen is provided to allow the operator to enter notes that can be referred to in the future. The faults screen displays a list of faults as they occur. The calibration screen is used to scale the various input and output functions. The system screen displays human machine interface operation and real-time error, which is used for debug during installation. The user control section is used to perform maintenance on the user database and the user access levels.

The fabrication of the prototype was completed. The leak-test suite lab prototype was installed at the UltraCell manufacturing facility in Vandalia, OH. The whole leak-test suite is shown in Figure 1, and the detail of the fixture is shown in Figure 2. All the functions of the prototype were tested individually. The sequences of multiple functions were then tested to ensure the logic is correct.

The prototype can perform all manufacturing processes which include inline leak-test, compression, bolting, break-in, and performance test (Figure 3). All these processes except bolting are carried out automatically. The prototype monitors all processes, quickly identifies failures, and provides diagnostic information. Safety features were implemented in the

FIGURE 1. Leak-Test Suite Prototype
prototype to protect the operator. The prototype can be used for both research and manufacturing with a simple change in the test protocol. A leak-test was repeated five times during the fuel cell stack manufacturing process (Figure 3). The leak-test can be added or removed easily. The average time for each leak-test is 9.3 min. This demonstrated that the leak-test can be performed at a rate greater than 5 stacks/hour. The results obtained from the prototype were compared with existing manual test protocols. It was demonstrated that the new instrument can reliably detect individual cell failures.

Techniques for analysis of dynamic mechanical analysis data from the prototype was developed and used in the leak-test suite prototype to characterize individual components in a fuel cell stack. This provides a necessary database for both the modeling effort and in validation of the new instrument capability. The application of a dynamic force to the fuel cell stack during assembly is expected to reveal how the various components press against each other. However, interpretation of the data requires a theoretical framework that can be used to quantitatively interpret the results. To this goal a finite element model has been developed to explore how the assembled materials respond.

Conclusions and Future Directions

The conclusions include the following:

- Developed a specification for the leak-test suite laboratory prototype. 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.
- Designed leak-test suite prototype. The prototype was designed with functions and features for research and development as well as manufacturing uses.
- Fabricated leak-test suite prototype.
• Installed leak-test suite prototype at the UltraCell facility at Vandalia, OH.
• Tested and evaluated leak-test suite prototype. The prototype can perform all manufacturing processes which include inline leak-test, compression, bolting, break-in, and performance test. All these processes except bolting are carried out automatically. The prototype monitors all processes, quickly identifies failures, and provides diagnostic information. Safety features were implemented in the prototype to protect operator.
• Created fuel cell stack quality metrics.
• Developed techniques for analysis of dynamic mechanical analysis data from the prototype.
• Characterized individual fuel cell stack components using the new leak-test suite prototype. This provides a necessary database for both the modeling effort and in validation of the new instrument capability.
• Developed a finite element model capable of modeling the dynamic mechanical properties of fuel cell stacks. This effort is critical in understanding how complex assemblies such as fuel cells actually respond to the applied dynamic forces.

Future directions include the following:
• Fabricate, integrate, test, and evaluate the leak-test suite.
• Modify pilot production line to accommodate the leak-test suite.
• Test run pilot production line with the leak-test suite.
• Validate the leak-test suite.

**FY 2010 Publications/Presentations**

VI.4 Manufacturing of Low-Cost, Durable Membrane Electrode Assemblies Engineered for Rapid Conditioning

Phase 2 Objectives

- New Process Exploration:
  - Investigate equipment configuration for low-cost MEA production.
  - Investigate raw material formulations.
  - Map out process windows for each layer of the MEA.
- Fuel Cell Heat and Water Management Modeling and Validation:
  - Efficiently optimize electrode and gas diffusion media (GDM) thermal, geometric, and transport properties and interactions.
- Multi-Layer Mechanical Modeling:
  - Develop a deeper understanding of MEA failure mechanisms.
  - Use model to optimize mechanical durability of the MEA structure targeted by the new low-cost process.
- MEA Optimization:
  - Utilize modeling results and designed experiments.
- Low-Cost MEA Conditioning Research
- Scale-Up and Process Qualification
- Stack Validation

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section of the Fuel Cell 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 Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing and Fuel Cells sections of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

3.5 Manufacturing R&D

4. Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)
VI. Manufacturing

3.4 Fuel Cells: Membrane Electrode Assemblies
Meeting All Targets

38. Evaluate progress toward 2015 targets. (4Q, 2012)

Accomplishments

- Direct Coating Process Development:
  - Primary and alternative paths for direct-coated 3-layer MEA process development have been determined.
  - Direct coated anodes and cathodes have demonstrated performance which is equivalent to Gore’s current commercial MEAs in ‘current automotive’ operating conditions when paired with control electrodes.

- Gore has demonstrated mechanical durability of a 12 micron expanded polytetrafluoroethylene (ePTFE) reinforced membrane. In previous testing, GORE™ 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.

- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior. Mechanical property experiments which are required to calculate model input parameters are 35% complete. The final model will be used to predict reinforced MEA lifetime for a variety of temperature and relative humidity (RH) cycling scenarios. The model will also be used to explore different reinforcement strategies and optimize mechanical durability of the MEA structure targeted by the new low-cost process.

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 the key component of fuel cell stacks – MEAs.

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. Fuel cell heat and water management will be modeled to optimize electrode and GDM thermal, geometric, and transport properties and interactions. 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 ePTFE membrane reinforcement and advanced perfluorosulfonic acid ionomers which enable durable high-performance MEAs.
- Advanced fuel cell testing and diagnostics.

Results

Low-Cost MEA Process Development

Primary and alternative paths for direct-coated 3-layer process development have been determined. Experiments targeted at both paths have made substantial progress, and direct-coated electrodes have demonstrated performance equivalent with the current commercial electrodes in specific operating conditions (Table 1). Figures 1 and 2 show performance of direct-coated electrodes paired with opposing control electrodes in a range of operating conditions which can be used to assess the viability of an MEA for different applications (automotive, stationary, portable, etc.), or for dynamic operation within a single application.

Future experiments will combine direct-coated anodes and direct-coated cathodes. These direct-coated MEAs will be produced according to the primary and/or alternative paths for process development.

The primary path is to directly coat the cathode electrode on a backer-supported reinforced membrane to form a 2-layer intermediate rolled-good. The next
The alternate path is to directly coat the anode electrode onto a backer-supported reinforced half-membrane to make an anode-side 1.5-layer intermediate rolled-good. The cathode electrode is then directly coated onto a backer-supported reinforced half-membrane in a similar process. In the final step, the backers are removed from the anode-side and cathode-side 1.5-layers intermediates and the webs are laminated together to form the 3-layer product.

Mechanically Durable 12 μm Reinforced Membrane

Gore has demonstrated mechanical durability of a 12 μm reinforced membrane (see Figure 3). The 12 μm membrane construction has also demonstrated high performance due to reduced resistance and increased water back-diffusion (see Figure 3). In previous testing, GORE™ 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. The

### TABLE 1. Operating Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
<th>Tcell (°C)</th>
<th>Inlet RH (Anode/Cathode)</th>
<th>Stoichiometry (Anode/Cathode)</th>
<th>Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stationary</td>
<td>80</td>
<td>100/100%</td>
<td>1.3 H₂/2.0 Air</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Wet</td>
<td>70</td>
<td>152/152%</td>
<td>1.3 H₂/2.0 Air</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Current</td>
<td>80</td>
<td>33/33%</td>
<td>1.3 H₂/2.0 Air</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>Automotive</td>
<td>95</td>
<td>19/19%</td>
<td>1.3 H₂/2.0 Air</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
<th>Tcell (°C)</th>
<th>Inlet RH (Anode/Cathode)</th>
<th>Stoichiometry (Anode/Cathode)</th>
<th>Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Stationary 80 100/100% 1.3 H₂/2.0 Air 0</td>
<td>2 Wet 70 152/152% 1.3 H₂/2.0 Air 0</td>
<td>3 Current 80 33/33% 1.3 H₂/2.0 Air 7</td>
<td>4 Future 95 19/19% 1.3 H₂/2.0 Air 7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 1. Direct-Coated Anode Performance (PL = platinum loading in mg/cm²)
VI. Manufacturing

accelerated mechanical durability testing protocol is summarized in Table 2.

### TABLE 2. Mechanical Durability Testing Protocol

<table>
<thead>
<tr>
<th>Tcell (°C)</th>
<th>Pressure (kPa)</th>
<th>Flow (Anode/Cathode, cc/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>270</td>
<td>500 N₂/1,000 N₂</td>
</tr>
</tbody>
</table>

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).

Multi-Layer Mechanical Modeling

A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior. Mechanical property experiments which are required to calculate model input parameters are 35% complete.

Nafion® PFSA NR-211 membrane is used for the model membrane and the temperature, RH, and time dependant properties are calculated from the ongoing experimental results. The viscous properties are modeled using a 2-layer viscoelastic constitutive model. This material model consists of an elastoplastic “arm” that is in parallel with an elastoviscous “arm.” The elastoplastic arm consists of an elastic spring (stiffness $K_p$) and a plastic component (yield stress $\sigma_y$ and hardening $H'$). Yielding according to the Mises criterion is used here. The elastoviscous arm has two elements, one spring (stiffness $K_v$) and one dashpot (using a time hardening law $\epsilon_v = A \sigma_v^n$). Thus, the instantaneous elastic stiffness of the material the sum of the elastic elements, $K_p + K_v$. In summary, the parameters that are required for this model are $K_p$, $\sigma_y$, $H'$, $K_v$, $A$ and $n$. These properties are determined from the experimental results.

FIGURE 2. Direct-Coated Cathode Performance (PL = platinum loading in mg/cm²)
Tensile testing was conducted for a range of displacement rates to investigate the influence of this parameter on the mechanical response. The rates (0.01 mm/min to 250 mm/min) are selected so that the full visco-elastic-plastic constitutive equations can be determined. The relationships obtained from the MEA testing are “composite properties,” combining the properties of the membrane with the electrodes. The constitutive equations for the electrodes will be obtained via reverse analysis. Figure 4 shows the comparison between the MEA and previously conducted experiments on Nafion® 211 membrane at T=45°C and RH=50%. The mechanical response of the MEA and Nafion® 211 membrane is different at medium or high displacement rates. However, at low displacement rates the mechanical response of the MEA and Nafion® 211 membrane is very similar.

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 heat and water management experience of the University of Tennessee enables a robust approach to development of a new low-cost MEA manufacturing process.

- Low-cost direct-coated electrodes have demonstrated performance equivalent with the current commercial electrodes in specific operating conditions. Future low-cost MEA process development experiments will be focused on improving direct-coated cathode performance in very wet and very dry conditions. Gore will also combine direct-coated anodes with direct-coated cathodes on a durable 12 µm reinforced membrane. This construction will be produced according to the primary and/or alternative paths for direct coating process development.

- Fuel cell heat and water management modeling will be used to efficiently optimize electrode and GDM thermal, geometric, and transport properties and interactions. Direct-coated electrodes will be paired with the most appropriate GDM materials identified in this study. In this way, GDM will enable maximum performance and durability of the low-cost 3-layer MEA.

- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior. Mechanical property experiments which are required to calculate model input parameters are 35% complete. When data collection is complete, the model will be validated with MEA accelerated durability testing. The final model will then be used to predict reinforced MEA lifetime for a variety of temperature and RH cycling scenarios. The model will also be used to explore different reinforcement strategies and optimize mechanical durability of the MEA structure targeted by the new low-cost process.

FY 2010 Publications/Presentations


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VI.5 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: June 30, 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 Manufacturing R&D technical barriers of the Fuel Cell 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 will contribute to achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell Technologies 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

- Validated COMSOL\(^1\) models of both thermal and ultrasonic pressing thermal processes.
- Completed promising initial experiments on the use of alternating current (AC) impedance measurement for adaptive process control of the thermal sealing process, resulting in MEA performance that exceeds specifications.
- Demonstrated major reductions in sealing process cycle time (~90%) and energy consumption (~95%) with the use of ultrasonics.
- MEAs sealed ultrasonically demonstrate a significant (~30 mv) improvement in activation losses when compared to thermally sealed MEAs.
- Initial durability tests of ultrasonically sealed MEAs show no measurable degradation after a 190-hour standard test protocol with 25 start-stop cycles.
- Manufacturing cost models show the potential for significant cost reductions by the use of both ultrasonics (84%) and adaptive process controls (38%) for MEA sealing.
- Submitted 10 publications and conference presentations.

\(^1\) Multiphysics modeling and engineering simulation software
**Introduction**

To realize the tremendous potential that fuel cell 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 fuel cell manufacturing. First, 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. Second, for the current process used to press low-temperature (e.g. Nafion®) MEAs used in both PEM fuel cell and direct methanol fuel cell it is common to thermally press for as long as 1½ - 5 minutes. Even the pressing process for high-temperature (polybenzimidizole, or PBI) MEAs, while much shorter than for Nafion®-based MEAs of about one minute, is still too long for high-volume manufacture. Third is the variability of MEA performance. The component materials, including gas diffusion layers or gas diffusion electrodes, 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.

The research being conducted in this project will help reduce all three of these barriers by reducing the unit process cycle time for MEA pressing by the use of ultrasonic sealing, and by minimizing the variability in performance of MEAs produced using adaptive process control. This will in turn help lead to the reduction or elimination of the practice of burn-in testing of fuel cell stacks. All of these benefits will contribute to a reduction in manufacturing costs for MEAs.

**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 incoming 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 will 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 AC impedance) 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 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 fuel cell applications.

**Results**

We are now in the second year of our research project, and have achieved significant results in all areas of investigation.

We have completed our initial designed experiments of ultrasonic sealing of high-temperature MEAs, and with the use of analysis of variance we have identified the main affects of process parameters on MEA performance. The most dominate process parameter has been identified as the post sealing heat treatment of MEAs in order to eliminate excess water and to achieve a stable acid content and thickness of the MEAs. Using a 95% confidence level criterion we have also identified the anvil backer stiffness, booster amplitude, and applied pressure as having a significant affect on MEA performance. Figure 1 shows representative polarization curves for ultrasonically sealed MEAs, compared to the specification polarization curve provided by BASF Fuel Cell. Initially we were concerned by the steeper slope of the curves in the ohmic loss region. However,
by working with BASF scientists we have confirmed that this is, in fact, the result of the higher contact resistance of the current collectors in our test cells, and the resistance of the flow field plates made of a different graphite material. Of more importance, however, is the fact that all MEAs produced using ultrasonic sealing demonstrates a significant improvement in the activation region of the curve, with a 30 mv improvement being typical. We believe that this is the result of the ultrasonic process resulting in a higher acid content and retention of the acid in the membrane and at the reaction sites in the catalyst layer rather than in the gas diffusion layer. Titration tests have confirmed the higher acid content of ultrasonically sealed MEAs compared to thermally sealed MEAs.

In order to assess whether or not ultrasonic sealing of MEAs may have an adverse affect on MEA durability we have conducted accelerated durability tests on three ultrasonically sealed MEAs. The test protocol used was the standard durability test protocol used by BASF Fuel Cell, consisting of 190 hours of testing during which 25 start-stop cycles were performed, including thermal cycling, load cycling, and reactant shut-off. Figure 2 shows the plot of cell voltage and current density for one such test. In all cases there was no measurable degradation in performance over the test duration. Typically, if there would be a durability problem with an MEA it would be manifested within the first 100 hours of an accelerated durability test.

We have been investigating the potential of applying adaptive process control techniques to the thermal sealing process, coupled with in situ sensing of properties of the MEA during the sealing process that can be correlated to MEA performance. One sensing technique being investigated involves sensing the AC impedance of the MEA during sealing. Figure 3 shows plots of the real value of complex impedance, and also the corresponding phase angle. While we have been unable to correlate the impedance value with MEA performance we have been successful in correlating the...
phase angle of the AC impedance to MEA performance. Using a “man-in-the-loop” technique we were able to use the phase angle measurement to control the sealing process duration based on the time to achieve a target phase angle value, with the objective of achieving more uniform MEA performance. With this technique we were able to produce MEAs that all met or exceeded the BASF performance specification, with an average 60% reduction in cycle time. Next we will implement an automated control scheme on the precision press and then evaluate uniformity of MEA performance.

Our efforts at modeling of the relationships among MEA component materials, manufacturing process parameters, and performance of the resulting MEAs are showing good preliminary results. We have developed thermal models of both the ultrasonic sealing process and the conventional thermal sealing process using COMSOL. Figure 4 shows plots of the temperature distribution within MEAs during ultrasonic sealing, on the top, and thermal sealing, on the bottom. These models have been experimentally verified using miniature thermocouples embedded between each layer of the MEAs during pressing. It is important to note that the two processes are significantly different in that thermal sealing adds heat from the outside in, while ultrasonic sealing generates heat from within the MEA at the interfaces between material layers. This explains why ultrasonic sealing is a much more efficient and effective process at raising the materials to the required critical process temperature. We have also completed preliminary compression models of both thermal and ultrasonic pressing. These models help us to understand exactly what happens to the acid and water during the pressing process. In the future the thermal and compression models will be coupled to better describe the pressing process and how it affects MEA performance.

During Phase I we completed a detailed manufacturing cost analysis that included the following cost factors: capital depreciation, tooling, space, labor, chilled water, heating, ventilation and cooling, maintenance, electricity, and waste disposal. We did not include MEA materials costs in the analysis, nor did we consider any secondary cost savings that might result, such as reduced costs of stack rework due to greater uniformity of MEA performance. The results of our analysis indicate that the use of adaptive process controls for thermal sealing may result in a 38% process cost savings, and the use of ultrasonic sealing may result in an 84% process cost saving. During Phase II we will update this cost analysis prior to our Phase II milestone review.

During the past year we have successfully passed our Phase I milestone review and have been approved to continue into our Phase II research project.

Conclusions and Future Directions

We are very encouraged by the results we have achieved during the past year. We have found the use of ultrasonic sealing to be a very robust process with the potential to significantly reduce unit process cycle time, improve MEA performance, reduce MEA failure rates, and achieve substantial manufacturing cost reductions. Our investigations into the use of adaptive process control to achieve more uniform MEA performance and shorter pressing times is likewise very encouraging. The Phase I manufacturing cost analysis has shown the potential to significantly reduce manufacturing costs for high-temperature PEM MEAs.

Major activities planned for the remainder of Phase II include:

- Completion of our post sealing heat treatment process optimization design of experiments for both thermal and ultrasonic sealed MEAs.
- Continue modeling of the relationships among incoming MEA properties, manufacturing process parameters, and MEA performance.
- Full factorial process optimization designed experiments for ultrasonic sealing.
• Designed experiment for ultrasonic sealing of low-temperature PEM MEAs.
• Cell level testing of MEAs produced using optimized process parameters.
• Continue durability testing of ultrasonically sealed MEAs.
• Implementation of automated adaptive process control on a commercial precision thermal seal press.
• Continue to seek additional properties that can be measured in situ and that correlate to MEA performance.
• Initiation of stack level testing of MEAs.
• Coordinate low-temperature MEA testing support by National Renewable Energy Laboratory personnel.
• Update of manufacturing cost analysis and comparison with our Phase II cost targets.

FY 2010 Publications/Presentations

Conference Papers/Presentations


Journal Articles (in review)


Journal Articles (in preparation)


VI.6 Cause-and-Effect: Flow Field Plate Manufacturing Variability and its Impact on Performance

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Contract Number: DE-EE0001047

Subcontractor: Los Alamos National Laboratory (LANL), Los Alamos, NM

Project Start Date: October 1, 2007 Revised Interagency Agreement (October 1, 2009)  
Project End Date: October 1, 2009 Revised Interagency Agreement (October 1, 2011)

Objectives

Develop a pre-competitive knowledge base of engineering data relating fuel cell performance variation to bipolar plate manufacturing process parameters and dimensional variability.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D – Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Lack of High-Speed Bipolar Plate Manufacturing 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 milestone from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 13 Complete development of standards for metrology of proton exchange membrane fuel cells. (4Q, 2010)

Accomplishments

- Co-developed LANL/NIST statement of work (SOW) including an initial testing protocol to facilitate an official collaborative agreement for LANL through DOE to conduct fuel cell performance testing using NIST fabricated and verified experimental plates (10/2009).
- Initiated experimental plate testing at LANL and completed preliminary testing report with protocol recommendations (4/2010).

Introduction

Based on a workshop organized by the Center of Automobile Research and NIST in December 2004; industry bipolar plate manufacturers identified a need for engineering data that relates geometric bipolar plate tolerances to fuel cell performance. This need is in response to pressure from fuel cell designers to produce lower cost plates, as such, plate manufacturers are being forced to consider potential quality related trade-offs to achieve desired cost targets. To justify these trade-offs, manufacturers are questioning the relevance of stated tolerances on dimensional features of bipolar plates; thus expressed a desire for published engineering data relating performance and dimensional quality of the plates that can be used as a reference when making these decisions. In response to the identified need, this project was conceived in 2004 and partially funded through the NIST Advanced Technology Program Intramural Competition for a period of three years (Fiscal Year [FY] 2005-FY 2007). In 2008, funding was provided through DOE in an attempt to bring this project to a successful completion by the end of FY 2008.

To date, the reference single-cell design has been selected, the fabrication and dimensional verification of all experimental plates has been completed according to a statistically based design-of-experiments, and the NIST single cell performance capability has established and verified. All that remains is the performance testing of the experimental plates. Unfortunately, progress has been delayed due to membrane degradation issues.
followed by difficulties associated with obtaining the required on-site facility safety upgrades needed to permit continuous and sometimes unattended multi-day fuel cell performance operation required to reduce performance variability associated with start-up and shut-down. Due to the potential importance of the outcome of this project the deadline for completion was extended through FY 2010. The facility upgrade difficulties forced us to adopt an alternative and hopefully more efficient plan where LANL will conduct the performance testing. This activity is currently underway.

**Approach**

Using a statistically-based design-of-experiments (Table 1), fabricate experimental “cathode” side flow field plates (Figure 1) with various well defined combinations of flow field channel dimensional variations; then through single-cell fuel cell performance testing using a well defined protocol, quantify the performance affects, if any, and correlate these results into required dimensional fabrication tolerance levels.

**Results**

In the absence of a DOE Annual Merit Review Progress Presentation and Annual Progress Report submission during 2009, the following details results from October 2008 to the present.

- Validated NIST’s single-cell testing performance proficiency to a higher level through successful participation in second single-cell performance intercomparison organized by the US Fuel Cell Council Joint Hydrogen Quality Task Force/DOE North American Hydrogen Quality (Participants included: LANL (Reference Lab), Hawaii Natural Energy Institute, University of Connecticut, University of South Carolina, Clemson/Savannah River).

**TABLE 1. Design of Experiment $2^{4-1}$ Fractional Factorial Design…4 Parameters, 2 Levels, and Replicate Center Point**

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<tr>
<th>Part</th>
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<th>$X_2$</th>
<th>$X_3$</th>
<th>$X_4$</th>
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<th>Measuring</th>
<th>Perf. Testing</th>
<th>Drawing</th>
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<td>1</td>
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</tr>
<tr>
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<td>+1(180)</td>
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**FIGURE 1.** Concept - Reference Single Cell and NIST Fabricated Cathode Flow-Field Plates
• Performed long-term stability testing of the reference single-cell with chosen components and NIST fabricated anode and cathode flow-field plates. For this testing, the fabricated plates for both sides are the reference “optimal geometry” plates having dimensional variations less than 5 um.

• From this testing we concluded:
  – Performance stability can only be achieved through continuous operation during the entire testing process for each assembly of the cell with substitute experimental cathode plates. More specifically, this means that start-up and shut-down introduced variability and a typical testing cycle including a stabilization period takes approximately 2 to 3 days.
  – Although the membrane was chosen based on what were considered sound recommendations, the membrane exhibited substantial and not always predictable degradation. This was independently verified by LANL through testing we requested of the same membrane supplier.

• Facility safety upgrades needed to support unattended continuous operation encountered significant difficulties and delays therefore a SOW was developed in cooperation with LANL where the testing would be conducted by LANL to hopefully ensure a timely completion of this project.

• LANL performed initial testing of the NIST single-cell using their membrane of choice and reached the following conclusions (Figures 2 and 3):
  – Reuse of the same membrane from one single-cell configuration to the next where experimental cathode plates are swapped out between each configuration is not possible, as the disassembly and reassembly process results in significant degradation and sometimes operational failure.
  – The initial range and testing points selected in the testing procedure co-developed by NIST and LANL in the SOW did not extend far enough to show the mass-transport region and subsequently the target point for alternating current impedance investigation did not fall within this region as needed to elucidate plate-to-plate differences.

**Conclusions**

• Progress significantly delayed due to issues involving facility safety upgrades of the NIST Fuel Cell Testing Laboratory needed to support unattended and continuous fuel cell operation.

• Alternative plan formulated with the oversight and assistance of DOE program management where LANL was subcontracted to conduct performance testing thus enabling the quickest possible completion.

• Membrane and protocol weaknesses/limitations, as well as, proposed solutions were identified through NIST and LANL preliminary performance testing.
Future Directions

- Proposed protocol and membrane solutions will be tested by LANL.
- Assuming the solutions prove adequate, LANL will perform and complete performance testing of experimental plates.
- NIST and LANL expect to complete analysis of results and publication of the conclusions by January 31, 2011.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Acknowledgements

The work detailed in this report would not have been possible without the contributions of the following, all are NIST personnel and guest researchers unless otherwise noted: Tommy Rockward (LANL), Ted Doiron, David Bergman, Martin Misakian, Alkan Donmez, Manny Hahn, Brian Pries.

FY 2010 Publications/Presentations


FIGURE 3. LANL preliminary testing using NIST reference cathode and anode plates indicating initial protocol limits were not appropriate for mass transport investigation.
VI.7 Non-Contact Sensor Evaluation for Bipolar Plate Manufacturing Process Control

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Contract Number: DE-EE0001047  
Project Start Date: October 1, 2007 Revised Interagency Agreement (October 1, 2009)  
Project End Date: October 1, 2009 Revised Interagency Agreement (October 1, 2011)

Objectives

- Identify and evaluate the capability and uncertainty of commercially available non-contact, high-speed scanning technologies for applicability to bi-polar plate manufacturing process control.
- Using capabilities identified in the first objective, demonstrate smart assembly concept (new under revised interagency agreement).

Technical Barriers

This project will address the following technical barriers from the Manufacturing R&D – Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Lack of High-Speed Bipolar Plate Manufacturing 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 7.** Develop manufacturing [quality control measurement] processes for graphite resin, natural flake graphite, and metal plates. (4Q, 2010)
- **Milestone 12.** Demonstrate pilot scale processes for assembling stacks. (4Q, 2013)
- **Milestone 13.** Complete development of standards for metrology of PEM fuel cells. (4Q, 2010)

Accomplishments

- Evaluated and concluded that photogrammetry is not a potential measurement solution for this application (9/2009).
- Assessed the capabilities and performance of several in-house instruments for use as a test bed for Phase II Sensor Testing (Accuracy as a Function of Scan Rate) and found only one that was marginally acceptable and most likely not the ultimate setup (12/2009).
- Discovered through initial Phase II testing, using our intermediate test bed with the laser spot triangulation probe, promising performance for some parameters but approach/sensor combined performance limitations for others (1/2010).
- Designed and procured (awaiting delivery) the necessary components to facilitate the fabrication/assembly of a dedicated sensor evaluation platform meeting all desired performance specifications. This dedicated platform is necessary to overcome the limitations identified in the previous two bullets and it will ultimately provide us the translation mechanism to evaluate these sensors over the desired range of scan rates (5/2010).

Introduction

Based on input from numerous bipolar plate manufacturers, we initiated an internally funded project in the summer of 2007 to develop, integrate, and evaluate non-contact, high-speed sensors or system of sensors for application in the dimensional process control of bipolar plates. This effort initially focused on determining the measurement needs of plate manufactures; this included learning what the common plate materials were and the current methods of fabrication and inspection. Using this information,
we attempted to identify what, if any, alternative commercially available measurement technologies existed that would be suitable for in-line high-speed inspection or if a solution needed to be developed. Since 2008, DOE has provided funding support for this project and in 2009 the project scope was modified to include demonstrating the concept of “Smart Assembly.” This additional objective, the concept of “Smart Assembly” is that if plate parallelism is measured and tagged to each plate, then assembly can be done in an automated fashion where plates are configured ideally to minimize the overall stack parallelism. This will allow lower tolerances on individual plate parallelism.

To date, an informal survey of plate manufacturers indicates that they are using vision-based ex situ systems for inspection of plate dimension. With the nature of the plate materials used and features of interest this approach is subjective, potentially not fully automatable, and does not have the accuracy required for evaluating the tighter tolerance demands. Furthermore, plate manufacturers have not yet looked for potential high-speed in-line solutions as high production volumes have not yet been demanded. In regards to measurement technology, numerous well qualified solutions for topography characterization exist but accuracy of lateral dimensions seem questionable for this application as these systems were not originally intended for those types of measurements.

Ultimately this project aims to enable cost reduction and rapid commercialization by providing plate manufacturers with a traceable, high-speed, fully automated solution for process control and intelligent stack assembly along with the information needed to optimize inspection scan rates as a function of the accuracy requirements.

**Approach**

Our approach includes the identification and/or development, integration, and evaluation of high-speed non-contact sensors or system of sensors for application in process control of bipolar plates. The evaluation will include: suitability based on typical plate materials and methods of fabrication, ability to quantify the dimensional parameters of interest to the accuracy required to evaluate those parameters against the tightest tolerance demands, and the flexibility to vary the scan rate (velocity). This variability in scan rate will enable fabrication rate flexibility that can be selected in relation to accuracy required. During this process we intend to develop measurement evaluation protocols for both sensors and plates to support and substantiate our efforts and to support future evaluation efforts as new sensors become available. Inclusive in these measurement protocols will be approaches for achieving contractual traceability requirements to support international product acceptance. Lastly, assuming a suitable measurement solution is obtained; demonstrate the concept of “Smart Assembly.”

**Results**

Although an ongoing effort, we have conducted research to determine the scope of potential measurement solutions, common plate materials, typical high-speed plate fabrication methods, and the plate dimensional parameters of interest along with the associated range of tolerances encountered. In general, the measurement solution must be able to perform lateral and topographical (vertical) measurements on both graphite (diffuse) and metallic (shiny) plates, at high incident angles commonly encounter due to tapered sidewalls (a product of many high-speed fabrication techniques or by design), capable of scan rates of up to minimally 100 linear mm/s (300 mm/s desired), and to an accuracy suitable for evaluating these parameters against tolerances ranging from 0.05 mm down to 0.012 mm.

Our initial efforts resulted in the procurement of two potentially promising structured-light non-contact sensors, both of which were evaluated based on ability to measure both graphite and metallic plates, as well as, their sensitivity or lack of as a function of incident angle (Phase 1). From this testing, one of the sensors, a 30 um diameter laser spot triangulation probe showing the best promise from the initial testing was mounted to the spindle of a 3-axis machine tool where it was tested in a scanning configuration to evaluate its sensitivity to measurements of feature height and to demonstrate the feasibility of lateral measurement by tying profile data to velocity of the translation mechanism.

Over the past year, the testing of this sensor moved to another test bed that provided us with a platform for evaluating the sensor accuracy as a function of scan speed (Phase 2). As part of this process numerous in-house measurement instruments were evaluated for velocity stability and velocity range capability. Unfortunately, none of these instruments satisfied the needed stability of 0.01 mm/s and minimum selectable and stable velocity of 100 mm/s. The coordinate measuring machine (CMM) chosen as an intermediate test bed has a maximum velocity of 70 mm/s and stability of 0.03 mm/s at 30 mm/s as measured using a the velocity output of a laser interferometer. Although this test bed did not meet the desired requirements it did allow us to discover numerous performance limitations and determine their cause based on the sensor and/or the approach used to quantify lateral dimensions.

Using this intermediate test bed for the laser spot triangulation probe we assessed the performance using “gage blocks” for absolute testing and sample fuel cell plates characterized using a more accurate reference
system for repeatability and correlation testing at 30 mm/s (Figure 1).

The laser spot triangulation probe demonstrated a repeatability of 1.5 um and errors on the order of 2 um or less on the width of flow field channels with “sharp” edges such as those produced by machining. Figure 2 shows flow field channel width comparison data between the non-contact laser triangulation spot probe and reference measurements performed on our dual-probe micro-feature CMM. The plate used is a carbon composite plate with machined flow field channels. The flow field consists of three individual channels in a serpentine configuration. This particular plate was a reject from an initial machining process employed to make experimental plates for our other plate manufacturing project. In this instance, as you scan across the plate with the channels oriented perpendicular, each individual channel is measured several times and the data shows each channel has a different average width. For this project this is the perfect plate in that the data shows excellent agreement between the non-contact probe and the reference data and it shows the non-contact probe has the sensitivity to see these subtle differences (approximately 10 to 20 μm) between the channels.

Unfortunately, the reality is that bipolar plates manufactured by typical high-speed fabrication techniques, such as, injection molding compression molding, and stamping have chamfered edges and tapered sidewalls (Figure 3). The effect of this was apparent for the gage block and injection molded bipolar plate measurements where width errors of 10 um or more were common.

Using the machined plates in Figure 1 and the injection molded plates shown in Figure 3 along with reference values obtained using a more accurate dual-probe micro-feature CMM, height errors where found to be within the range of 1 to 7 um.

In addition, we demonstrated feasibility for plate parallelism measurement by conducting a simple test using the machined graphite plates where data was collected as the laser spot triangulation probe was translated across the plate overlapping the edges of the plate to collect data from the reference surface upon which the plate was fixtured. The reference plate for

FIGURE 1. Laser Spot Triangulation Probe Mounted to Z-Axis of CMM. Setup Shows Reference Gage Block, Machined Flow Field Plates from NIST Project 1, and Scanning Pictorial.

FIGURE 2. Laser Spot Triangulation Probe Comparison Data Using a Machined Flow Field Plate with Real Channel-to-Channel Differences in Width

FIGURE 3. Example Output from Laser Spot Triangulation Probe of a Injection Molded Plate
our test was a porous ceramic square vacuum chuck encased in a granite frame. The flatness of the entire surface, ceramic area and frame is less than 2 um. By applying a least-squares linear fit to the profile data that corresponds to the reference surface then removing the slope of the best-fit line from both the reference plane data and the plate surface data, the variation in parallelism between the bottom plane and plate, top plane, can be quantified. This was simplified in that we scanned only one profile line rather than numerous lines across the surface and that we used one probe and a reference plane. Application on a real production line would utilize two or more opposing probes where the differences would be analyzed.

Concurrent to this effort, we also explored photogrammetry as a potential measurement solution and we procured a “laser line” triangulation based probe similar to the individual “laser spot” probe that has thus far shown promising results. Photogrammetry was conceived as a possible solution shortly after the 2008 DOE Annual Merit Review Meeting; however our research shows that this is a “no-go” even with the enormous advancements in the resolution of digital single lens reflex cameras due to the aspect ratio between the channel depth and width.

Conclusions

• Photogrammetry is not a potential measurement solution for this application due to aspect ratio between channel depth and height.
• Phase 2 Preliminary Testing Conclusions:
  – On our intermediate probe testing platform, at a translation speed of 30 mm/s, the laser spot triangulation probe has the potential to meet the needs for this high-speed non-contact application, if limitations due to the interaction of the probe with chamfered edges and tapered sidewalls can be overcome.
  – Height errors are acceptable and for the most part sensor based only, but lateral errors are a function of the sensor and our approach that obtains position using the sampling rate of the probe in conjunction with the known velocity of the probe translation mechanism.
• Devised a new approach that synchronizes the probe data collection with the position of a precision stage with an adjustable translation velocity. This approach eliminates the need for a calibrated (known) and stable translation velocity.
• Designed, procured (awaiting delivery), and fabricated all necessary ancillary equipment (two stages and associated controllers, framing, and fixturing mechanisms) to assemble a dedicated sensor test bed to implement our revised approach (Figure 4).

Future Directions

• Assemble and test new non-contact sensor test bed.
• Test new approach for measurement of lateral dimensions.
• Investigate edge-effect.
• Using the variable translation speed of the new test bed, perform rigorous characterization of the laser spot triangulation probe accuracy as a function of scan speed up to 300 mm/s.
• Test line-based triangulation probe.
• Extend testing to other probing technologies as appropriate.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Acknowledgements

The work detailed in this report would not have been possible without the contributions of the following, all are NIST personnel and guest researchers unless otherwise noted: Dennis Everett, Bala Muralikrishnan, Wei Ren, and Ted Doiron.

FY 2010 Publications/Presentations

Objective

Evaluate the suitability of optical scatterfield metrology (OSM) as a viable measurement tool for in situ process control of catalyst coatings.

Technical Barriers

This project will address the following technical barrier from the Manufacturing R&D Fuel Cells section of the Fuel Cell 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 Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

• **Milestone 1.** Develop prototype sensors for quality control of membrane electrode assembly (MEA) manufacturing. (4Q, 2011)

• **Milestone 2.** Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)

• **Milestone 13.** Complete development of standards for metrology of proton exchange membrane (PEM) fuel cells. (4Q, 2010)

Accomplishments

• Secured 3M as a provider of catalyst-coated membrane (CCM) samples necessary to evaluate the potential sensitivity of the OSM technique to the measurement of catalyst loading. (07/2008).

• Developed an initial 12-layer three-dimensional optical model of the 3M nano-structured thin-film (NSTF) CCM in an attempt to predict the optimal configuration of the OSM instrument parameters (i.e., wavelength of the light source, illumination angle, polarization) to guide the experimental investigation efficiently.

• Demonstrated sensitivity of the OSM technique to Pt loading to a level of 0.01 mg/cm² using 3M PtMnCo NSTF (01/2010) and 3M pure Pt NSTF CCMs (06/2010).

• Secured another major manufacturer as a supplier of conventional Pt on C CCM samples for our next round of testing to further define the range of applicability of the OSM technique.

• Developed a formal collaboration plan with the National Renewable Energy Laboratory (NREL) that provides both organizations the ability to leverage each others’ capabilities in support of their own individual projects, share proprietary samples and information from industry partners using a special three-way non-disclosure agreement (NDA) executed with each interested industry partner (ongoing).

• Demonstrated our support of the NIST/NREL collaboration by providing NREL with defects fabricated using our dual beam gallium focused ion beam (FIB)/scanning electron microscope (SEM) in order to extend NREL’s membrane hole defect performance study to hole diameter sizes smaller than 150 um (3/2010).

Introduction

The need for high-speed, in situ process control measurement techniques for controlling the quality of the platinum-based catalyst layer has been identified during numerous DOE sponsored and non-DOE sponsored workshops. Current techniques for the various parameters of interest (e.g., SEM
and X-ray fluorescence [XRF] to name a few) are extremely expensive and not easily amendable to in situ application in a manufacturing production line. The Precision Engineering Division within the Manufacturing Engineering Laboratory has years of expertise with a technology identified as OSM [1], specifically its development as a process control tool for the semiconductor industry. This technique is a combination of the best attributes of traditional bright-field optical microscopy and scatterometry. More precisely, this technique takes traditional optical metrology beyond the Rayleigh criteria and focuses on the complex optical signatures of subwavelength size features, where the response can be optimized by varying the illumination angle, varying the illumination source wavelength, and application of various image analysis algorithms. Although quantitative in other applications, this technique is being used in a comparative form thus far in this application and must be correlated to measurements of the parameter of interest using the appropriate reference metrology. As such, the development for new applications requires research to optimize the OSM tool and establishing the appropriate reference metrology tool, along with the development of the appropriate analysis algorithms for both. Please refer to the stated reference for more technical details on the technique.

Prior to this project, this technique has only been applied to very discrete uniform structures, such as those typically encountered in the semiconductor industry. Because of this, the application of the OSM technique to random subwavelength structures has long been a goal but does present significant challenges. The underlying principle is that even random subwavelength structures exhibit some type of repeatable optical signature and that changes in these signatures can be correlated with the various manufacturing parameters of interest to control the quality of the product.

The overall objective of this project is to provide PEM, CCM and gas diffusion electrode manufacturers with an automated high-throughput approach for performing process control inspection of Pt loading with sensitivity equal to or better than that currently provided with XRF and other parameters of interest simultaneously. Simulations will give insight and enable manufacturers to tune their measurement equipment to the parameters of interest. For dual-side simultaneous catalyst-coating operations, this method will provide the ability to concurrently perform Pt loading measurements on both sides of a CCM independently versus XRF which is a “total” sample loading measurement.

**Approach**

To ensure accuracy of the technical details related to the fabrication and performance of catalyst layers, this project depends heavily on support from MEA manufacturers, as well as, other experts in the field. From the beginning, we have actively engaged MEA manufacturers and industry experts in an effort to identify the critical parameters of the catalyst layer and to solicit from them sample packages that vary these parameters to enable us to conduct a sensitivity study of the proposed technique.

Our initial focus over the last year or two, driven by industry input, has been to demonstrate the technique's sensitivity to catalyst loading. Then if the technique is sensitive to catalyst loading, determine how broadly applicable it is. To satisfy the second task, sensitivity studies must be conducted over the entire range of catalyst types (Pt and Pt alloys), support structures (conventional carbon-based and novel non-carbon-based supports), and substrates (membrane and both paper and woven cloth gas diffusion layers [GDL]).

The development and implementation of this technique integrates experimental work with simulation driven predictions to maximize efficiency.

**Results**

During the last year our efforts have been focused on simulation model development and experimental data collection based on 3M’s NSTF CCM, which was the first sample set we received from a major supplier. This first sample set included three NSTF CCMs with PtMnCo catalyst loadings of 0.10, 0.15, and 0.20 mg/cm². Experimentally we collected data which successfully demonstrated that the OSM technique is sensitive to catalyst loading and that the sensitivity of the technique for this specific CCM is on the order of 0.01 mg/cm². This is very comparable to the inline XRF systems available. Figure 1 shows the final reflectivity data for two different runs. The first run involves three repetitive measurements at the same location on each sample thus representing what we refer to as base repeatability. The second run involves three repetitive measurements on each sample but each measurement is at a different location. Figure 2 is additional data supporting sensitivity of the tool to catalyst loading; however in these measurements we are varying the wavelength of the illumination source. This data was collected varying different instrument parameters, illumination angle and wavelength, not only to show sensitivity to the parameter of interest but also in an attempt to determine the settings that optimize this sensitivity. These two instrument parameters are only a sampling of the variables that have been tested and that can be optimized based on the application.

To understand further the applicability of the technique we then acquired another sample set that included four 3M NSTF CCMs with pure Pt catalyst loadings of (0.05, 0.10, 0.15, and 0.20) mg/cm². Again the experimental results obtained in late May of 2010 showed sensitivity to the loading differences but more
carefully collected data sets are needed to verify the exact level of this sensitivity. Concurrent with the experimental evaluation we have worked on simulation model development which supports the experimental data in that it predicts trends, but the accuracy of the models need improvement as we are lacking the true optical properties for the materials involved. Figure 3 shows our preliminary modeling efforts.

Over the last year we have also undertaken a parallel effort where we worked with NREL to develop a collaborative agreement between the two organizations.

This agreement was described in a one-page summary that we sent to all of our industry partners in the fall of 2009. This summary explained a coordinated effort for achieving each of our project’s goals and that this is justified by the fact that the individual projects of both organizations were related but complimentary,
and such a relationship would enable us to leverage our relationship with our industry partners together to maximize efficiency through the sharing of samples and information. Finally, the summary recommended that this agreement would be facilitated by three-way NDAs among NREL, NIST, and each industry partner. Without this, both organizations would negotiate individual NDAs with each industry partner and in some instances for the same sample and information requests, in essence doubling the number to NDAs needed. Furthermore, this agreement formalizes the commitment of both organizations in leveraging each other’s capabilities in support of each organization’s individual projects without the need for funding transfers.

Because of the relationship between the NIST/NREL Collaborative Agreement, NIST reference metrology, and the OSM project we have combined this arrangement with the OSM project. To date all our industry technical partners have concurred with the proposed benefits. Several NDAs have been completed but others still remain outstanding. The following figures represent our recent efforts to demonstrate our commitment to the collaboration, in that, we provided defects fabricated using dual-beam SEM/gallium FIB in support of NREL’s desire to expand their membrane defect study to sub 150 um features (Figure 4) [2].

**Conclusions**

- Demonstrated OSM technique sensitivity to catalyst loading using two 3M NSTF CCM sample packages, one with pure Pt and the other with a PtMnCo alloy catalysts.
- Developed preliminary simulation model of 3M NSTF CCM to ultimately guide efficient experimental measurement efforts and manufacturer tool customization.
- Procured (awaiting delivery) an ellipsometer with a integrated variable environmental chamber for experimental determination of optical properties “n” and “k” for materials comprising each CCM design used for OSM sensitivity testing to support a more accurate simulation model.
- Secured a manufacturer/supplier of conventional Pt on C CCMs and a sample package for further OSM catalyst loading sensitivity testing, in an effort to more precisely define the range of applicability.
- Developed a collaborative agreement with NREL to leverage resources between organizations and industry partnerships.
- Demonstrated support of this collaborative effort by fabricating membrane defects in support of NREL defect studies.

**Future Directions**

- Use ellipsometer and additional special material sample packages to determine optical properties for 3M’s NSTF CCM.
- Refine simulation model using these optical properties and demonstrate correlation between the model and experimental results.
- Determine the level of sensitivity of the OSM technique to catalyst loading using pure Pt NSTF CCM.
- Continue experimental catalyst loading sensitivity testing using conventional Pt CCMs.
- Secure supplier(s) of catalyst-coated, paper and cloth, GDL samples.
- Develop a conceptual compact tool design suitable for manufacturing lines.
- Work with NREL and industry partners to determine the next most sensible catalyst loading parameter to study with the OSM technique.

**Disclaimer**

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

**Acknowledgements**

The work detailed in this report would not have been possible without the contributions of the following, all are NIST personnel and guest researchers unless otherwise noted: Mark Debe (3M), Mike Ulsh (NREL), Michael Stocker, Richard Silver, Andras Vladar, John Kramar, Bin Ming, Brad Damazo, Bryan Barnes, Richard Quintanilha.
### FY 2010 Publications/Presentations


### References


VI.9 High-Speed, Low-Cost Fabrication of Gas Diffusion Electrodes for Membrane Electrode Assemblies

**Objectives**
- Reduce cost in fabricating gas diffusion electrodes through the introduction of high-speed coating technology, with a focus on materials used for combined heat and power generation (CHP).
- Relate manufacturing variations to actual fuel cell performance in order to establish a cost-effective product specification.
- Develop advanced quality control methods to guide realization of these two objectives.

**Technical Barriers**
This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (Section 3.5):
- Lack of High Volume Membrane Electrode Assembly (MEA) Processes
- Low Levels of Quality Control and Inflexible Processes

**Contribution to Achievement of DOE Manufacturing R&D Milestones**
This project will contribute to achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (Section 3.5.7):
- Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)

This project addresses coating speed and uniformity of gas diffusion electrodes (GDE), a critical component for MEA fabrication. One sub-task is to develop a continuous X-ray fluorescence (XRF) analyzer that directly measures catalyst deposition level and distribution on rolled goods, ultimately guiding improvements in through-put and uniformity. This sub-task directly contributes to the forth quarter 2012 goal for in-line measurement. Another sub-task is to develop models that predict the effect of manufacturing variations in catalyst distribution and porosity in GDEs, and relate these variations as six-sigma limits for a component specification. The establishment of a model that predicts MEA performance based on manufacturing variations in GDEs contributes to improving the quality of the component as well as achieving the forth quarter 2013 DOE milestone above.

**Accomplishments**
- Developed an innovative on-line analyzer ahead of plan. For the first time have a complete “map” of precious metal catalyst level and distribution throughout the roll during coating.
- Team has established a framework for understanding ink stability issues:
  - For cathode, identified an additive that significantly improved key quality indicator by reducing the incidence of surface agglomerates on the GDE by ~80%.
- Established first critical task milestone: full length coating on carbon cloth whereby coating length increased by double.
- Identified a path to higher speed coating through reduction of coating steps by ~30%.
Introduction

The basis of this project is to create GDEs at a far lower cost than those currently available. GDEs are critical components of MEAs and represent the highest cost subcomponent of the MEA. Cost reduction will be accomplished through development of a higher throughput coating process, modeling the impact of defects due to the higher speed process, and overcoming these limitations and providing a six-sigma manufacturing specification that relates performance to defects. The main focus of the effort is creating next-generation inks through advanced additives and processing methodologies. As part of our approach, we will also develop on-line quality control methods such as determination of platinum concentration and distribution during the coating process. We will also develop correlations between manufacturing parameters and performance as well as establish models to predict the effect of manufacturing variations in MEA performance.

For this reporting period we designed, built, and validated an on-line analyzer for determination of loading and distribution of precious metal catalyst during coating. This accomplishment directly contributes to DOE’s goal of improving quality control instrumentation throughout the manufacturing process. We also developed improved ink formulations that led to lower defects during longer coating runs – a first step towards reduction in cost.

Approach

GDEs are comprised of a gas diffusion layer coated with catalyst. The gas diffusion layer is simply carbon cloth or a non-woven carbon paper that has been coated with carbon black and serves as a current collector for the catalyst. For both the carbon black and catalyst, a hydrophobic binder is added to achieve critical porosity and hydrophobicity in the final structure. Of the carbon black, catalyst, or hydrophobic binder none are highly soluble in aqueous solutions. Aqueous solutions must be used as solvents since the use of organic solvents with a highly active catalyst is too dangerous in a production environment. Also, the hydrophobic binder is shear-sensitive, meaning it becomes less stable when pumped or subjected to shear forces in the coating applicator. Thus, the challenge in this project is overcoming the inherent physical limitations in these materials through advanced formulations and processing.

Our approach to solving this challenge begins with identifying key quality GDE metrics that relate directly to ink performance, develop an understanding of the forces behind ink stability, and introduce solution measurement methods that relate ink performance to the quality metrics. With more stable ink formulations, we anticipate being able to coat longer and wider webs at higher speeds or lower numbers of application passes. This process is supplemented by two other activities that ultimately lead to lower cost GDEs. We will develop a model that will predict the impact of manufacturing variations on MEA performance, and use this model to determine the level of coating quality needed to maintain consistent current and voltage. Also, we will create on-line instruments to lead more precise coating processes.

Results

Our first objective was to develop the in-line analytical method to follow improvements in coating. For developing continuous in-line analysis of catalyst deposition, we selected a custom XRF engine designed by X-Ray Optical Systems in New York. The key to their technology is the use of micro-capillary tube optics that amplifies the fluorescence signal and thus allows a greater signal with low powered X-ray tubes. Traditional commercial XRF units need a long time to obtain a signal – roughly 60-90 seconds and would not be able to provide an accurate measurement on webs moving 8-10 cm/s. We exploited the high signal gain of the micro-capillary tube in order to facilitate very short acquisition times and thus obtain detailed distribution maps of catalyst being coated on rolls of gas diffusion layers. The following are design targets and achievements to date, and a photo of the device is shown in Figure 1.

- Safely used by production staff. Employed extensive guards and auto-shut-off switches.
- Date acquisition rate 25 ms: 10 ms achieved.
- Rail scan 10 m/s: 20 m/s achieved.
- Instrument variation +/-2.5%: <+/1% preliminary achieved.

FIGURE 1. Picture of Custom-Designed In-Line Analyzer for Precious Metal on Gas Diffusion Electrodes
• Minimum level <1 g/m² Pt: initially achieved 1.7 g/m² but believe can exceed minimum with parameter optimization.

We identified a key quality parameter for coating that relates directly to ink performance – agglomerates. Agglomerates are precipitations of catalyst, binder, or catalyst and binder that form protrusions on the gas diffusion electrode surface, interrupting the smooth coating. In the extreme case, these protrusions can pierce the membrane in the MEA. See Figure 2 for examples. As part of investigating the forces that destabilize our ink formulations, we found that the measurement of the zeta-potential of our solutions provided a measurable characteristic that is related to ink stability. For aqueous formulations, one typically needs charge to stabilize the particles and zeta-potential values between 15 and 25 mV are typically desired. For our base formulations, we obtained zeta potentials between 5 and 10 mV and when attempting to apply this ink to longer rolls of GDL developed significant agglomerations.

Using a combination of the zeta potential and developmental scale coating runs, we identified an additive that stabilized the cathode catalyst. A key to selection of this additive was to find a material that met the following selection rules: 1. stabilize ink components, 2. can be removed through higher processing temperature so no residuals remain that could interfere with catalyst performance, and 3. no significant change in porosity or hydrophobicity introduced through the use of the additive. Through this process we identified an additive that reduced cathode agglomerates by 77% over baseline formulations when scaled to the full production coating machine.

Lastly, we identified a new high energy process that facilitates creating more concentrated inks. By increasing the concentration of the catalyst and binder in the ink, we can reduce the number of application passes needed to achieve a final catalyst loading, and thus effectively “increasing speed” by actually reducing the number of coats. Although preliminary as of this writing, by using this new formulation we have reduced the number of application coats by 30% when using developmental scale coating machines.

Conclusions and Future Directions

We have developed a methodology to create more stable ink formulations, and have applied this to reduce a key quality feature – agglomerates on the electrode surface while increasing the length of GDL coated. A new instrument has been introduced for following our catalyst coating distribution and uniformity, and providing critical feedback on improvements in formulation and ink processing. A new high energy process for ink making has been identified with encouraging preliminary results. Thus, by being able to produce greater amounts of GDEs over shorter times, we can create a path to the higher volumes of MEAs targeted by the Department of Energy objectives.

Upcoming Focus:

1. Further improve additives combined with the high energy process.
2. Leverage these improvements towards either higher speed coating and/or reduction in number of passes as well as full-width coating.
3. Continue modeling and validation of the impact of manufacturing defects on performance.
4. Using the approach developed for carbon cloth gas diffusion electrodes, develop ink formulations appropriate for non-woven carbon paper gas diffusion electrodes.
VI.10 Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

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Contract Number: DE-FG36-08GO18055

Working Partners:
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• Lawrence Livermore National Laboratory (LLNL), Livermore, CA
• Pacific Northwest National Laboratory (PNNL), Richland, WA

Cost-Sharing Partner:
Boeing Research and Technology, Seattle, WA

Project Start Date: September 26, 2008
Project End Date: March 31, 2012

Project Objective

Develop new methods for manufacturing Type IV pressure vessels for hydrogen storage with the objective of lowering the overall product cost by:

- Optimizing composite usage through combining traditional filament winding (FW) and automated fiber placement (AFP) techniques,
- Exploring the usage of alternative fibers on the outer layers of the FW process,
- Investigating dry-tape technology which could drastically shorten the manufacturing time,
- Building economic and analytical models capable of evaluating FW, AFP, and tape fabrication processes including manufacturing process variables and their impact on tank mass savings, material cost savings, processing time, manufacturing energy consumption, labor and structural benefits, and
- Studying polymer material degradation under hydrogen environment.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost

This study will contribute to achieving milestone 24 of the Manufacturing R&D section of Multi-Year Research, Development and Demonstration Plan:

Develop fabrication and assembly processes for high-pressure hydrogen storage technologies that can achieve a cost of $2/kWh.

Accomplishments

- Refined the stress analysis approach to predict stresses in the transition areas between the domes and the cylinder section.
- Designed new AFP and FW patterns to create better transition between the two fibers, thus further reducing stresses.
- Improved programming of the tow-placed system to reduce the cycle time for off-part motion by about 50%.
- Designed the geometry of the liner and boss at each end of the layup mandrels as the surfaces for fiber placement, forming the tow-placed end-caps in a stand-alone operation.
- Fitted end-caps onto liner well using a heat gun and a filament-wind helical.
- Identified that there are no cost-competitive alternative fibers other than carbon fibers at this time.
- Tape fabrication processes, mechanisms, equipment schematics, and micrographs were documented for presentation to team members and DOE reviewers. Tape development was advanced by new diagnostic capabilities applied to the first generation of prototype tapes. Remedies for bubble defects found in first generation tapes were developed.

Introduction

The goal of this project is to develop an innovative manufacturing process for Type IV high-pressure hydrogen storage vessels, with the intent to significantly
lower the costs. Part of the development is to integrate
the features of high precision AFP and commercial
FW with the potential of using alternative fibers on the
outer layers of FW. As a potential, dry-tape technology
is being investigated by LLNL, which could shorten
production cycle time.

In this project period, stress analysis approach has
been refined after the second vessel failed burst test
unexpectedly. Boeing has improved programming of
the tow-placed system to reduce the cycle time for off
part motion. The first set of AFP is no longer directly
placed onto the liner, instead the end-caps are formed
on the layup mandrels that have the geometry of the
liner and boss at each end. These end-caps fitted well
on the liner with the aid of a heat gun and a FW helical.
Alternative fibers are being investigated for outer layers
of FW. Quantum and Boeing supplied manufacturing
cost information to PNNL to refine the cost model,
which has been used to assess the cost sensitivities of
this manufacturing technique compared to the baseline
FW process. LLNL continues to develop an advanced
composites manufacturing process that should be
particular well suited to the production of pressure
vessels. PNNL and LLNL will expand on their activities
in separate reports.

Approach

The approach on stress analyses has been improved
by taking the transition areas between the domes and
the cylinder section into account. The original method
analyzed the domes and the cylinder section separately,
which contributed to not realizing the failure mode of
the second vessel in the model.

Since manufacturing tow placed end-caps became
a stand-alone process, different winding sequences have
been investigated to prevent the end-caps from wrinkling
upon laying down the first FW helical.

Results

Stress Analyses

The first vessel tested in October of 2009 passed
the burst test at 23,771 psi, exceeding the requirement
of European Commission (EC) 79-2009 standard of
22,804 psi. After passing the burst test, the composite
design was refined to further reduce fiber usage on the
next vessel. The overall design of second vessel required
two layups of AFP. Instead of having fiber directly
placed onto the liner for the first AFP layup, end-caps
formed on foam tools were delivered to Quantum for
installation. The completed vessel was burst-tested in
December of 2009, but it failed at 18,666 psi, which
is below the EC 79 standard. Since the second vessel
failed unexpectedly, the approach on stress analyses was
revisited to understand why the failure was not realized
in the model.

Stress analyses on each of the first and second
vessels were based on three individual analyses on
forward dome, aft dome, and cylinder section. However,
this analysis method failed to evaluate the stresses in
the transition areas between the domes and the cylinder
section. Instead, two integrated analyses are necessary.
One is for the forward dome and the cylinder section,
and the other is for the aft dome and the cylinder
section. On the forward dome, the patterns from AFP
and FW are fed into the stress analysis model, but
the material placed in the cylinder section by AFP is
manually replaced with material of the hoops. This
simulates the real-world situation, where hoops make up
for the fiber that is missing between the domes wrapped
by AFP. The same methodology also applies for the aft
dome.

With this improved approach, stress analyses were
performed on the AFP and FW patterns from the second
vessel. The results confirmed that maximum stress was
observed at the transition areas between the domes and
the cylinder section. It is consistent with the actual burst
location, which is between the aft dome and the cylinder
section. As a result, the AFP and FW patterns have been
modified to reduce stresses at the transitions to levels
below those seen in the cylinder section of the vessel.

Third Vessel Development

The Boeing team continues to build tow-placed
layups for the latest iteration of storage vessel design.
Boeing uses the current delivery head design with
improved heating capabilities. In these recent efforts,
improvements to the programming of the system allow
for the acceleration of the off-part motion between the
end of one course and the start of another course. This
improvement reduces the cycle time for off-part motion
by about 50%.

In the build process for the current, third vessel,
layup mandrels having the geometry of the liner and
boss at each end are used as surfaces for fiber placement.
This forms the tow-placed end-caps in a stand-alone
operation. A picture of the end-caps for the most recent
vessel-design iteration is shown in Figure 1.

The first set of AFP end-caps made by Boeing
according to the modified patterns from stress analyses
was received in May for developing the third vessel.
The liner with end-caps was installed onto a winding
machine. FW patterns were laid down according to the
design. All hoop layers went onto the liner smoothly.
As soon as the first helical layer was laid down, the
end-caps wrinkled. The wrinkles were caused by air gaps
between the AFP end-caps and the liner. The tension
from the FW carbon fiber compressed the AFP end-
caps toward the cylinder section, but the end-caps were
constrained from movement in the axial direction due to FW hoop layers already placed over the edge of the AFP end-caps. This resulted in the wrinkles in the AFP end-caps. The wrinkles made these end-caps no longer useful.

On the second set of end-caps received from Boeing, it was decided to use a FW low-angle helical to capture the end-caps. The liner with end-caps was placed on a winding machine. Heat was applied to the end-caps using a heat gun. Once both end-caps started to soften and become pliable, a low-angle helical that closed around both forward and aft bosses was applied to hold the end-caps tight. Then the helical was cut off before laying down the first set of FW pattern. Once FW was finished, the vessel was put on B-stage until the surface became tack free. The vessel was then shipped back to Boeing in late June. Boeing now has the task of laying-up the next sequence of tows in this hybrid design. Once this is done, Quantum will finish the vessel with the final courses of filament wound material.

Alternative Fibers

Various alternative fibers are being investigated to further lower the cost of manufacturing fuel storage vessels by utilizing lower tensile strength fibers on the outer layers of FW due to lower stresses in comparison to the inner layers. Possible alternative fibers could include glass, basalt, Saffil, alumina, boron, and silicon carbide.

Glass and basalt fibers were investigated initially, but they have been eliminated at this stage of the research because the tensile moduli are significantly lower than the carbon fiber, which is 33.4 Msi. Quantum expects that unless the tensile modulus of the fibers on the outer layers is equal or higher than those of the inner carbon layers, the outer layers will not carry significant percentage of the pressure load. As a result, Saffil, alumina, boron, and silicon carbide fibers were further investigated. However, all these fibers have been disqualified for consideration because the fibers either do not have the required tensile modulus, are not available in continuous form, or too expensive.

Without finding an alternative fiber that is cost-effective for the application, the focus shifts back to searching for an alternative carbon fiber. The alternatives include Toray T300, Zoltek Panex35, Toho Tenax HTR40, and Cytec T-500C. After initial review, the most promising candidates are Zoltek and Toho because of their material properties and pricing.

Cost Model

PNNL developed cost models using Quantum and Boeing’s manufacturing data to compare the costs of traditional filament wound tanks with the hybrid FW+AFP tanks. Two bounding manufacturing scenarios were considered, one that optimized the composite layup without concern for machine usage and one that considered 100% machine usage. The first hybrid tank produced by Quantum and Boeing exceeded the required burst pressure and saved 11.1 kg of the 76 kg baseline (14.6%). Eliminating 11.1 kg of carbon fiber composite significantly outweighed the added manufacturing cost (for machinery and factory space) of the hybrid process. The cost model estimates that the tank cost is reduced from $23.45 to $21.75 per kWh of hydrogen based on $11/lb of carbon fiber. The gravimetric efficiency is also increased from 1.5 to 1.67 kWh/kg. Further details are provided in PNNL’s annual report.

Dry-Tape Development

Although many details of the best dry-tape processes remain proprietary, a broad spectrum of coarse economic analyses quantifies their cost advantages. Among the alternative tape fabrication processes, LLNL has been reducing two to practice. These two have been chosen, not because they will perform best (either structurally or economically), but because their development might be affordable given the limited funding available. Both alternatives LLNL is developing are capable of the speed that underlies tape fabrication economic advantages. However, those advantages degrade rapidly if any structural performance is sacrificed by the microstructure built up by fabrication. This subproject’s Phase 2 milestone will achieve full technical proof of concept by demonstrating that at least 90% of the tensile strength and 50% of the shear strength of conventional epoxy matrix composites is preserved in tape fabrication.

The first generation of tape specimens was built by pultrusion in the autumn of 2009. However, the tape specimens possessed a shortage of infused matrix in their acute-angled corners, and have occasional thin bubbles.
along the fiber axis. These microscopic defects would make that generation vulnerable to significantly reduced strength in shear. Therefore, second generation tape prototyping is underway, with new materials processing due to begin in July.

Conclusions and Future Direction

- AFP end-caps can be manufactured as a stand-alone process.
- Lower cost carbon fibers with equal tensile modulus to inner fiber and low tensile strength are still the most cost-effective alternative fibers. Down-selection will be based on price and performance.
- The third vessel has gone through the first set of AFP and FW. Boeing will be laying up the next sequence of tows. Quantum will apply the final courses of FW and perform a burst test.
- If the burst test goes well, the next composite design iteration will incorporate an alternative fiber on the outer layers of FW. Two vessels will be built for burst test and ambient cycle test.
- Boeing has started the process for the design and build of an improved head design. The new head will include features that allow fiber placement into tighter locations, such as in the polar radius. Other features will include advanced heating, cutting, and teardown capabilities.
- The cost model will be updated to reflect the improvements in tank manufacturing methods.
- PNNL will continue hydrogen degradation testing of polymer liner materials.
- Continue dry-tape development.

FY 2010 Publications/Presentations

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; the contribution of individual technology components to the overall system (i.e., from fuel production to utilization); and 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 the use of renewable fuels. Particular emphasis is given to assessing stationary fuel cell applications, fuel quality impacts on fuel cell performance, resource needs, and potential infrastructure options.

The Systems Analysis activity made several significant contributions to the Program during Fiscal Year (FY) 2010. Several analytical tools, including the Stationary Fuel Cell Power Model, the Hydrogen Demand and Resource Analysis (HyDRA) tool, and the Macro-System Model (MSM) were updated and peer reviewed to support the analytical process. Resource, infrastructure, and early market analyses were conducted to better understand supply and demand issues. In particular, biogas from waste treatment facilities and landfill systems was identified as a large resource with the HyDRA model and was determined to be predominately located near urban centers that can provide feedstock for fuel to be used in stationary fuel cells for power generation. A cost model was developed to evaluate the cost of removing impurities from these resource streams. In addition, a study was initiated to evaluate the impact of the biogas impurities on fuel cell performance and durability. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model was modified to enable criteria pollutants to be evaluated on a life-cycle basis for stationary fuel cells for combined heat and power production in comparison with other competing technologies such as natural gas microturbines, internal combustion engines, and electrical generation from natural gas and coal fired systems. Risk analyses were also conducted to help identify key research and development (R&D) gaps for fuel cell systems and areas of high risk in terms of meeting targets and timelines.

Goals

Provide system-level analysis products to support the overall Program by evaluating technologies and pathways, guiding the selection of research, development, and deployment 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 benefits of fuel cells for multiple applications such as portable, stationary, and backup power; and assess resource needs, infrastructure requirements, and potential interactions with the electric power sector.
• 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 well-to-wheels and life-cycle analyses for technologies and pathways for the overall Program by incorporating technological advances and changes.

FY 2010 Status

Systems Analysis focuses on examining the economics, benefits, risks, opportunities, and impacts of fuel cells and renewable fuels within a consistent, comprehensive analytical framework. Analysis conducted in FY 2010 included identifying early markets for fuel cells and opportunities to reduce cost through various mechanisms, such as tax credits and other legislation. The Systems Analysis sub-
program has transitioned from activities focused on key model development to the application of the models for completing critical program analyses. As evidenced by the completed and ongoing analysis activities shown in the “Accomplishments” section, the initial strategy of the Systems Analysis sub-program has been effective in providing critical analysis results that help guide the Program’s overall hydrogen and fuel cell activities.

**FY 2010 Accomplishments**

**Models**

- The MSM, a dynamic engineering transition model, was updated to include infrastructure and resource analysis for diverse resources, various regions, and a variety of 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. Infrastructure and resource analysis capabilities were made feasible by the addition of the resources model, HyDRA, and the infrastructure model, HyPRO, to the MSM.

- The Fuel Cell Power Model, developed by National Renewable Energy Laboratory (NREL) to evaluate costs from combined heat and power generation for polymer electrolyte membrane fuel cells, phosphoric acid fuel cells (PAFCs), and molten carbonate fuel cells (MCFCs), was upgraded to include business and financial analysis useful to multiple entities such as building owners, fuel cell vendors, station owners, utilities, and fleet operators. 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 the system.

**Infrastructure Analysis**

- Infrastructure analysis conducted by Oak Ridge National Laboratory with the HyTrans model, NREL with the Scenario Evaluation and Regionalization Analysis model, and Sandia National Laboratories revealed that synergies between fuel cells for stationary power generation and transportation could be realized in the early phases of market adoption of hydrogen for light-duty fuel cell vehicles. Widespread deployment of combined heat, hydrogen, and power (CHHP) could reduce the problem of hydrogen availability in the early stages of transition to fuel cell vehicles. Results of this analysis indicate that hydrogen produced from CHHP could result in smaller stations with higher capital utilization and lower hydrogen cost, supplementing hydrogen supplied from distributed natural gas–based steam methane reforming (SMR).

- Analysis conducted by NREL with the Fuel Cell Power Model indicates that hydrogen produced from a stationary fuel cell would have a lower cost than hydrogen produced from an SMR system at low volumes, as exhibited in Figure 1 (stationary fuel cells have the unique ability to produce hydrogen in addition to heat and power and to use diverse renewable fuels such as waste gas or biogas). This factor will be important during the early stages of transportation fuel cell adoption because hydrogen demand and resultant hydrogen production will be at low volumes.

- DOE participated in an infrastructure workshop sponsored by the International Partnership for Hydrogen and Fuel Cells in the Economy to examine the key drivers and gaps to early market infrastructure development for light-duty vehicles. Providing adequate fueling infrastructure for consumers is one of the key barriers to hydrogen fuel cell vehicle commercialization. The outcomes of the workshop included the following ideas:
  - Develop low-cost 100 kg/day starter stations
  - Define a “line of sight” path to business profitability
  - Create co-ops or public-private partnerships
  - Enact policies and incentives to make hydrogen more attractive to investors
  - Explore innovative ways to boost hydrogen demand by serving multiple applications
  - Promote novel business models that utilize new methods of financing
  - Leverage existing natural gas and hydrogen infrastructure to reduce costs
Environmental Analysis

- Argonne National Laboratory (ANL) enhanced the well-to-wheels analysis capabilities of the GREET model by including analysis of criteria pollutant emissions from stationary fuel cells for combined-heat-and-power (CHP) generation and CHHP generation. The analysis shows that fuel cell systems for CHP and CHHP produce significantly less carbon monoxide, particulate matter and oxides of nitrogen (NOx) emissions than conventional generation technologies. For example, Figure 2 shows that PAFCs and MCFCs emit at least 80% less NOx than other conventional generation technologies without after treatment.
• ANL has started the impact analysis of feedstock quality on stationary fuel cell performance and the costs associated with meeting the required feedstock quality specifications. The feedstocks being assessed include natural gas, landfill and anaerobic digestion biogases, and syngas from coal and biomass gasification. The key impurity analysis shows sulfur, siloxanes, heavy metals, and halides are detrimental to the fuel cell anode. Ammonia, carbon monoxide, and hydrocarbons are less damaging for higher-temperature fuel cells such as solid oxide fuel cells (SOFCs) and MCFCs. Further R&D will be needed to determine separation technologies and costs to remove these contaminants from the feedstock streams.

Resource Analysis

• Analysis by Lawrence Livermore National Laboratory of the impact of water on hydrogen production has found that it will have a minor effect—of less than $0.10/gasoline gallon equivalent. The assessment included an examination of water permitting and allocation on water cost, and found that these effects varied from region to region. Water was found to be abundant at a national level, but permitting and allocation at a regional level could be problematic in regions with high water stress such as California, Arizona, and Colorado. Expansion of industrial water demand for applications such as hydrogen production in these regions may encounter water availability limits before reaching a cost constraint.

• NREL developed a model to examine the cost of purifying biogas streams to enable them to be used in a fuel cell or in hydrogen production from steam methane reforming. Biogas—which can come from landfills, wastewater treatment plants, and farms—is an abundant energy source that is often strategically located near major urban centers; however, it contains contaminants such as ammonia, sulfur, hydrocarbons, siloxanes, and heavy metals. This model will supplement other models in the DOE portfolio for hydrogen production cost analysis, fuel cell electrical cost analysis, and greenhouse gas emission evaluation.

Programmatic Analysis

• Pacific Northwest National Laboratory analyzed the commercial benefits of the Fuel Cell Technologies (FCT) Program by tracking the commercial products and technologies developed with the support of the Program (Figure 3). The results show 198 patents were issued and 28 products were commercialized by 2010 as a result of research funded by FCT in the areas of storage, production, delivery, and fuel cells, which will be highlighted in the FY 2010 Pathways to Commercial Success Report.

• A workshop was held in FY 2010 to identify gaps to reduce costs for fuel cells for distributed CHP generation in the 200-kW to megawatt range. The gaps identified included:
  – High cost of feedstock contaminant removal
  – Need for higher power density
  – High cost of balance-of-plant components

![FIGURE 3. Cumulative Number of Commercial Technologies as a result of Energy Efficiency and Renewable Energy Funding for Hydrogen and Fuel Cells](image-url)
- Need for increased stack and cell durability
- Need to reduce platinum content of phosphoric acid fuel cells

**Budget**

The budget for the Systems Analysis activity is consistent with the goals and objectives of the sub-program and enables assessment of fuel cell applications for energy storage, stationary power generation, specialty applications, and light duty transportation. The FY 2011 budget request includes funding for resource and infrastructure analysis, as well as fuel quality evaluation, environmental analysis, overall program analysis, modeling, and systems integration. New fuel cell opportunities for energy storage and transmission will also be explored.

**FY 2011 Plans**

In FY 2011, the Systems Analysis sub-program will focus on conducting analyses to determine technology gaps for fuel cell systems and infrastructure for different applications, and utilizing fuel cells and hydrogen for energy storage and transmission. Analyses will be focused on understanding the tradeoffs and regional impacts of fuel cells with other alternative fuels and the electrical sector on a well-to-wheels basis, and the synergies of linking stationary fuel cell power generation with the electrical sector. The FY 2010 appropriation included $5.5 million for Systems Analysis; the FY 2011 request is $5 million. The budget request for FY 2011 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 Scenario Evaluation, Regionalization and Analysis (SERA) Model

Objectives

The Scenario Evaluation, Regionalization and Analysis (SERA) model\(^1\) 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 objectives of the most recent phase of the project are:

- Expanding the interoperability of SERA with the Hydrogen Demand and Resource Analysis (HyDRA) model [1]. The interoperability with HyDRA generally involves providing compatible data formats and conforming to HyDRA's data schemas.
- Developing sub-models within SERA to represent a variety of alternative infrastructure development pathways, including the utilization of stationary power combined heat and power (CHP) or combined heat, hydrogen, and power (CHHP) applications, and hydrogen production from biogas resources. These pathways are sensitive to various time metrics associated with infrastructure dynamics.
- Continuing and expanding the work on case studies using the SERA model, focusing on early markets in California and also extending the analysis to national scenarios.

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\(^1\) SERA was formerly known as the Hydrogen Deployment System Modeling Environment (HyDS-ME).

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-piped/Siloed Analytical Capability
- (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 Fuel Cell Technologies Program’s 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.
- Milestone 24. Complete the linear optimization model (HyDS) to analyze the optimum production facilities and infrastructure for hydrogen demand scenarios.

Accomplishments

Completed first-of-kind preview studies:

- Wind-hydrogen infrastructure study.
- Spatiotemporal refueling modeling analysis.
- Analysis of CHHP competition with on-site steam methane reforming (SMR).
- Constructed new spatially and temporally detailed baseline scenarios:
  - Staged rollout of fuel cell electric vehicles (FCEVs) by urban area in a manner fully consistent with published National Academy of Sciences (NAS) scenarios.
  - Analysis of FCEV rollout on national scale.

Achieved significant enhancements in SERA usability:

- Two-way interoperability with HyDRA.
- More detailed and adaptable cost models.
- Revisions to user interface.
- Improvement of database schema.
Introduction

The SERA model fills a unique and important niche in the temporal and geospatial analysis of hydrogen infrastructure build-out for production and delivery. It nicely complements other hydrogen analysis tools and is well suited to contribute to scenario analysis involving the temporally specific geospatial deployment of hydrogen production and transmission infrastructure. Its key capabilities are (i) an optimization of the 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 geographic information systems and the H2A models [2,3]. SERA is designed to answer questions such as: Which pathways will provide least-cost hydrogen for a specified demand? What network economies can be achieved by linking production facilities to multiple demand centers? How will particular technologies compete with one another?

Approach

In order to answer such questions, SERA 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.

Four methods of long-distance hydrogen transport are considered: pipeline, gaseous truck, liquid truck, and railroad. The major use of SERA 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, SERA can also weigh tradeoffs between investments in various infrastructure types, given policy constraints (greenhouse gases, etc.). Figure 1 shows the interrelationship between the input data for SERA 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 sample SERA output in the form of an optimized hydrogen infrastructure network.

Results

The software development work on enhancing SERA's interoperability with HyDRA resulted in several new technical capabilities in SERA: SERA can now retrieve map layers from HyDRA via Web feature services (WFS), can style map layers using symbology consistent with HyDRA (e.g., consistent colors and shapes for visual representations), and can retrieve regional cost data from HyDRA via WFS. Conversely, HyDRA can now ingest analysis results output from SERA: (i) hydrogen infrastructure networks, by year and (ii) delivered hydrogen costs, by year.

Additionally, we enhanced the SERA cost models by substituting current delivery cost curves with H2A...
delivery components built inside the SERA model. This allows us to use H2A standards, but achieve maximum flexibility in constructing pathways (e.g., mixed pathways) within the analyses.

We completed a preliminary study that examines the relative cost-effectiveness of supplying hydrogen refueling stations via CHHP or on-site SMR for a large urban area, under three FCEV penetration scenarios. The major conclusions of this work are: (i) CHHP-based hydrogen production for use in nearby hydrogen refueling stations typically only has cost advantages over on-site SMR hydrogen production at some of those refueling stations, particularly for the early years of FCEV penetration scenarios where hydrogen demand and station sizes are initially low; (ii) variations in SMR or CHHP facility and energy-input costs can dramatically affect the overall cost of hydrogen, but they do not affect the mix of CHHP and SMR deployment as strongly; and (iii) for these scenarios and this study region, hydrogen costs typically drop from slightly above $6/kg in early years to below $5/kg in later years.

In conjunction with the CHHP work, we implemented a spatiotemporal station placement technique that produces realistic spatial, temporal, capacity distributions for hydrogen refueling stations. This station network expansion algorithm is based upon empirical data for existing gasoline stations, simulations of how those networks have evolved over time, and the resulting station size distributions.

Other SERA efforts involved the construction of a new, highly detailed FCEV rollout scenario that matches the standard NAS scenarios [4] in terms of FCEV introduction, FCEV stock, vehicle-miles traveled, and hydrogen demand on a year-by-year basis in addition to matching the city-specific schedule in the study. Analysis of these scenarios using SERA indicates that the more accelerated demand scenarios have lower delivered costs of hydrogen, time-averaged delivered costs ranging ~$3.5/kg to ~$5/kg, and that the details of infrastructure choice are quite sensitive to feedstock costs and the infrastructure cost models.

Finally, we completed a preview study of the SERA biogas capability: this involved (i) provisionally incorporating the latest NREL biogas systems characterization into SERA, (ii) performing an illustrative analysis of infrastructure build-out highlighting the significance of biogas pathways, and (iii) developing insights for future in-depth studies involving biogas pathways. SERA uses cost estimates from the H2A biomethane systems model in conjunction with those from the H2A production model to evaluate the delivered cost of biogas-originated hydrogen. In the sample analysis that we performed (on a test case of Midwestern cities), the optimal choice of infrastructure often hinges upon the difference between biogas and natural gas prices: when the biogas price, plus the processing cost to biomethane, is less than the natural gas price, the biogas pathways have lower costs. In general, the most competitive biogas scenario is where a single large biogas plant supplies a dozen or more (typically small) on-site SMR plants.

Conclusions and Future Direction

In summary, SERA 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 SERA 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. We are also iteratively improving the detail and accuracy of the cost models in SERA in order to support more complex scenarios. In particular, we plan to examine price points between competing technologies, such as delivered “drop-in” tanks vs. on-site SMR and electrolysis production. These price points will be resolved geographically and temporally as demand increases across multiple cities in a given region. Future SERA work will also address questions about stakeholder behavior and consumer preferences will be examined (e.g., preference for station availability, fuel costs, green hydrogen): to this end, we are planning to couple SERA to a discrete-choice model for hydrogen demand.

FY 2010 Publications/Presentations


References


Objectives

- Develop models of interdependent energy infrastructure systems.
- Analyze the impacts of widespread deployment of a hydrogen fueling infrastructure.
- Analyze the impacts of stationary fuel cell systems for distributed power.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5**: Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2010)
- **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.
- Incorporated a vehicle adoption model for hydrogen-fueled vehicles, plug-in hybrid electric vehicles, and a new generation of conventional vehicles that meet the Corporate Average Fuel Economy (CAFE) regulation through the 2016 ruling.
- Incorporated a model for the impact of stationary fuel cell systems with distributed generation of electricity by combined with the provision of heat or cooling to a building, and potential co-production of hydrogen for vehicles.

Introduction

The DOE Hydrogen Program envisions the transition to hydrogen vehicles will begin by using the existing infrastructure for NG to produce hydrogen by steam-methane reforming (SMR). In addition, the transition to widespread use of hydrogen in fuel cells is expected to benefit from development of the market for stationary fuel cells (SFCs). Previously, we developed a model for the adoption of hydrogen-fueled vehicles (HFVs) and plug-in hybrid electric vehicles (PHEVs). The model showed that adoption of either of these alternative fuel vehicles (AFVs) effectively couples transportation to the markets for hydrogen, electricity, and NG.

The present work investigates the coupling of hydrogen and electricity further by adding the adoption of SFC distributed to buildings. The model is now able to examine the reduced load on the grid from distributed SFC, as well as the potential benefits of combined heat (or cooling) and power. Lastly, the application of high-temperature SFC systems allow for the potential co-production of hydrogen, for local refueling of HFVs.
Approach

We use the system dynamics approach to simulate the adoption of SFCs for a selection of buildings within the state of California, which is expected to lead the adoption of HFVs. The adoption of SFCs is specified based upon estimates of the potential for applying combined heat and power (CHP) provided by the California Energy Commission [1]. The penetration of SFCs is not modeled as a competitive adoption based on economics, so the model serves to estimate the potential impact that SFC systems can have on the electricity and fueling infrastructure.

The simulated operation of the SFC follows daily load profiles for the electricity, heating, and cooling for various buildings taken from the DOE database [2]. The hourly loads for the buildings are combined with the total electricity load for the state from California Independent System Operator data [3]. The distributed electricity provided by the SFC reduces the total state demand, which is filled by a simple dispatch model developed previously [4]; the model approximates the state electricity mix for baseload power, but assumes that all marginal electricity is provided by NG generation. Consequently, distributed electricity reduces the demand for NG generation.

The SFCs are sized for buildings and homes to operate with about a 75% capacity factor. A daily load profile for a type of building—large office, for example—is considered for each of the four seasons; the simulation timestep is a quarter of the year, so the integrated operation over a day in each season represents an average for the quarter. When the SFC can meet the building electric load, its electricity reduces the demand on the grid. When the building load exceeds the SFC capacity, the excess load is taken from the grid. Similarly, the useful heat provided by the SFC in CHP mode offsets NG demand for a combustion-driven heater. In combined cooling and power (CCP) mode, the waste heat from the SFC is used in an absorption chiller to provide cooling, thereby offsetting electricity that would have otherwise provided the air-conditioning.

The details of the SFC operation are summarized in Table 1. The model considers two types of SFCs: large, high-temperature systems and small, low-temperature proton exchange membrane fuel cells (PEMFCs). The high-temperature systems have sufficient waste heat to operate either in CHP or CCP mode, depending on which mode the building load demands for the season of year. In addition, the model allows the potential to provide combined heat and hydrogen production (CHHP mode) for fueling HFVs. For the CHHP mode, the electrical efficiency is reduced from 47% to 40%, consistent with the operational data of an example molten carbonate fuel cell system [5].

<table>
<thead>
<tr>
<th>TABLE 1. Model Assumptions for SFC Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Large Scale</strong></td>
</tr>
<tr>
<td>Capacity (GW)</td>
</tr>
<tr>
<td>Offices 7,000</td>
</tr>
<tr>
<td>Hotels 8,000</td>
</tr>
<tr>
<td>Homes 1,300,000</td>
</tr>
<tr>
<td><strong>Small Scale</strong></td>
</tr>
<tr>
<td>Capacity (GW)</td>
</tr>
<tr>
<td>Offices 7,000</td>
</tr>
<tr>
<td>Hotels 8,000</td>
</tr>
<tr>
<td>Homes 1,300,000</td>
</tr>
</tbody>
</table>

Results

The projected impacts of SFCs and vehicles on the overall CO$_2$ emissions (including all sectors) for California (CA) are shown in Figure 1. Starting from the top-most curve, the solid curve shows the continuation of existing electricity generation and vehicle travel. The business-as-legislated (BAL) curve shows the impact of two regulations: the CA Renewable Portfolio Standard (33% by 2020) and the CAFE regulation (35.5 mpg by 2016). These two existing regulatory changes will reduce CO$_2$ emissions by 18% below the unregulated emissions by mid-century.

The next simulation adds the impact of SFC to the BAL scenario to see that there is only a minor effect—about 2% further reduction in CO$_2$ emissions. The impact is small because the SFCs displace NG plants with distributed generation that is only marginally
more efficient. The large SFC systems operate with an electrical efficiency that is about 7% better than conventional generation (~40%). The PEMFC systems have approximately the same electric efficiency as the conventional NG generation. The combined benefits of heat or cooling are marginal, because on average only about one-half of the available heat is matched to the daily heating or cooling demand; the other heat is not useable, due to mismatch in the timing of the electricity load and the heating load. Figure 2 shows the fraction of the total electricity supplied to the state by the SFCs. By mid-century, the SFC systems provide 16% of CA’s electricity. The total SFC capacity is 10 GW for the state load that varies from 30 to 70 GW.

Turning now to the impact of AFVs—both PHEVs and HFVs—which replace conventional and CAFE-compliant gasoline vehicles as shown in Figure 3. The penetration of HFVs and PHEVs were adjusted previously [4] to reflect the projections by Greene et al. [6]. The performance assumptions for vehicle performance are listed in Table 3. The impact of the large number of AFVs entering the state on-road fleet is much larger than that of the SFCs, adding a further 14% reduction from the SFC scenario. Since hydrogen from SMR without sequestration brings about the same CO₂ per energy content as gasoline, the gain from HFVs is due to the greater fuel economy.

While the SFC systems do not provide a large impact on CA’s CO₂ emissions, there is the potential for distributed co-production of hydrogen for vehicles. In the AFV scenario, the hydrogen demand grows to 3 billion kg per year, of which the large-scale SFC could potentially provide 11%, or enough to fuel about 2 million vehicles per year. Early market-adoption of SFCs could potentially help support the initial HFV refueling infrastructure.

### TABLE 3. Vehicle Model Assumptions

<table>
<thead>
<tr>
<th>Model Type</th>
<th>Mileage Assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline vehicle</td>
<td>20 mpg</td>
</tr>
<tr>
<td>CAFE vehicle</td>
<td>35 mpg by 2016</td>
</tr>
<tr>
<td>PHEV</td>
<td></td>
</tr>
<tr>
<td>Gasoline mileage</td>
<td>48 mpg</td>
</tr>
<tr>
<td>Electric mileage</td>
<td>0.35 kWh/mi</td>
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<tr>
<td>Fraction electric mode</td>
<td>2/3</td>
</tr>
<tr>
<td>Electric range</td>
<td>40 miles</td>
</tr>
<tr>
<td>HFV mileage</td>
<td>70 miles/kg</td>
</tr>
<tr>
<td>Total vehicle sales rate</td>
<td>6% / yr</td>
</tr>
<tr>
<td>Total vehicle scrap rate</td>
<td>5% / yr</td>
</tr>
</tbody>
</table>

mpg – miles per gallon
Conclusions and Future Directions

The dynamic model for the CA infrastructure shows a limited impact of an optimistic penetration of stationary fuel cell systems on the overall CO2 emissions. The benefits of CHP are also limited by the matching of local building loads for electricity and heat (or cooling). However, the adoption of AFVs—primarily HFVs, but also PHEVs—brings a CO2 reduction nearly equivalent to the expected impact of existing regulations. The potential for CHHP to supply HFV in the state is significant if the SFC adoption occurs concurrently with the vehicles.

These conclusions regarding the impact of SFC with CHP are limited to the state of CA. Future work will apply the model to a region of the country where coal-fired electricity generation is dominant. Preliminary simulations suggest that the effect of SFC will be significant. Further development of the model will engage industry and utility partners to enhance the fidelity of the electricity dispatch model.

Acknowledgements

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FY 2010 Publications/Presentations


References


Objectives

- Explore the chicken-or-egg problem: co-development of the hydrogen production and delivery infrastructure and the user base which supports it.
- Understand how the system works rather than provide one forecast of system development.
  - How do different policies affect the transition?
  - How sensitive is growth to factors beyond the control of policy makers?
  - What role do consumer attitudes and behavioral characteristics play?
- Consider in a complex adaptive system the interactions between:
  - Hydrogen fuel producers and suppliers.
  - Consumers of hydrogen fuel and fuel cell vehicles (FCVs).
  - Manufacturers of FCVs.
- Extend the current agent-based model to include limited-service combined hydrogen, heat and power (CHHP) facilities as well as the regular distributed production hydrogen fueling stations (HFSs) currently modeled.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Future Market Behavior
- Stove-piped/Siloed Analytical Capability
- Inconsistent Data, Assumptions and Guidelines

Technical Targets

This project addresses the following Systems Analysis objectives:

- Develop and utilize a macro-system model of the hydrogen fuel infrastructure to support transportation systems.
- Identify and evaluate early market transformation scenarios consistent with infrastructure and hydrogen resources.

Approach

We develop a computer simulation of the transition from petroleum-based to hydrogen-based personal transportation, focused on the Los Angeles, California metropolitan area. The technique we employ is Agent-Based Modeling and Simulation (ABMS), one in which the overall system behavior emerges from the simulation of the decisions, actions, and interactions of individual players, or “agents.” Driver agents represent consumers of vehicles and fuel. They are characterized by attributes such as home location and income level, and take simulated trips around the roadway network purchasing fuel when necessary. Drivers’ vehicle purchase decisions are based on cost, the availability of fuel, their attitudes towards new technology, and interactions with other drivers. Investor agents represent the builders of the hydrogen fueling infrastructure. They assess the suitability of various sites to locate HFSs based on traffic past the site and their estimates of competition and future growth in hydrogen sales, and build HFSs accordingly. A manufacturer agent controls the supply and selling price of FCVs.

The existing model must undergo modifications and enhancements in order to be able to examine questions dealing with CHHP facilities. After implementing the necessary changes we will use the model to analyze various scenarios under the premise that owners of CHHP plants may sell limited amounts of hydrogen to consumers via hydrogen dispensing facilities (HDFs). We will explore how owners of CHHP facilities might expand the hydrogen refueling infrastructure by adding
HDFs, and how the presence of HDFs might affect the overall transition.

**Accomplishments**

The project was initiated in March 2010. At the time of the 2010 Annual Merit Review Meeting, the following model enhancements had been completed:

- Increased the granularity of the roadway network topology to allow more refueling locations and more realistic trip routing.
- Added a simple manufacturer agent to limit the supply of vehicles during the early phase of the transition.
- Based on literature estimates and discussions with an automotive market research firm, improved the calibration of driver “personalities” (attitudes towards new technology and “greenness”) to the actual distribution in the population and stated willingness to pay.
- Provided driver agents with multiple personalities to help the agents better reflect the diversity in a modeled population 1,000 times larger.
- Calibrated driver trip distances to latest National Household Travel Survey data.
- Improved investor agents’ method of estimating and projecting hydrogen sales.

**Future Directions**

- Identify candidate locations for CHHP facilities.
- Develop simplified cost structure for CHHP facilities.
- Develop algorithms for driver agents to register/purchase from HDFs based on their proximity to home/work, the agent’s mileage driven, and perhaps other factors.
- Extend driver personalities to incorporate attitudes towards FCVs influenced by the inconvenience of purchasing fuel at HDFs (e.g., lack of full-service amenities, possible registration requirement).
- Develop algorithms for driver actions in the event of a HDF running out of fuel, and the resulting costs to the driver in inconvenience.
- Conduct scenario analyses and summarize findings in a report.

**FY 2010 Publications/Presentations**

VII.4 HyTrans Model: Analyzing the Potential for Stationary Fuel Cells to Augment Hydrogen Availability in the Transition to Hydrogen Vehicles

Objectives

- Develop and maintain a computer model for simulation of the dynamic market transition from petroleum to hydrogen-powered motor vehicles and for combined heat and power (CHP).
- Identify and evaluate early market transition scenarios for the transition to hydrogen vehicles and analyze conditions that could lead to a sustainable long-term transition.
- Analyze the ultimate potential for hydrogen and fuel cell vehicles through 2050, addressing resources, hydrogen production, infrastructure, cost and benefits.
- Develop scenarios and analyze the potential for stationary combined heat-and-hydrogen power (CHHP) to increase the availability of hydrogen fuel during the early transition.

Technical Challenges

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Future Market Behavior
(B) Stove-piped/Siloed Analytical Capability

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 Fuel Cell 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 7: Complete analysis of the hydrogen infrastructure and technical target progress for the hydrogen fuel and vehicles. (2Q, 2011)
- Milestone 26: Annual model update and validation. (4Q, 2010)

Accomplishments

- Developed the first integrated market scenarios of the transition to hydrogen vehicles, measuring vehicle manufacturers’ “valley of death,” excess costs of fuel infrastructure, and establishing the sustainability of the transition if DOE technology goals are met.
- Updated HyTrans model to latest H2A models, latest Annual Energy Outlook (AEO) projections and updated vehicle technology characterizations.
- Completed analysis of potential synergies between deployment of stationary CHHP fuel cells and fuel availability during the early stages of a transition to hydrogen vehicles.

Introduction

Making a transition from petroleum-powered internal combustion engine vehicles to a hydrogen-powered system involves decisions by consumers, governments, and industry. HyTrans integrates all key components in a computer model that simulates market decision making from the present to 2050. Consumers choose among competing advanced technologies based on vehicle prices and energy costs, fuel availability and the diversity of makes and models offered. The cost and performance of advanced technology vehicles
change over time affected by cumulative experience producing vehicles, economies of scale and research and development (R&D). Energy suppliers decide what resources and conversion processes to use to produce hydrogen. Key metrics include petroleum consumption and fuel cycle greenhouse gas emissions. HyTrans was used to produce DOE’s first integrated scenarios of the transition to hydrogen vehicles [1].

In this study, the HyTrans model was used to analyze the potential for stationary fuel cells producing combined heat and electric power for buildings to serve as sources of hydrogen for motor vehicles during the early stages of a hydrogen transition. Stationary fuel cells convert a fuel such as natural gas to hydrogen, generating electricity and heat. Depending on the cycle of demand for heat and electricity, the ability to sell electricity to the grid and other factors, stationary fuel cells may also be able to produce hydrogen at relatively low cost for use by motor vehicles. Because stationary fuel cells will be co-located with large buildings and institutions, they could serve as small-scale distributed sources of hydrogen for motor vehicles thereby greatly increasing hydrogen availability in the critical stages of an early transition to hydrogen vehicles.

Approach

The analysis comprised three steps, defining scenarios of CHHP deployment, modifying and updating the HyTrans model to include hydrogen supply via CHHP, running the model and analyzing the results. The three hydrogen fuel cell vehicle market penetration scenarios of DOE’s hydrogen transition analysis [1] were used to estimate the effects of greater hydrogen availability via CHHP.

Three national scenarios of CHHP deployment were created based on a study by the California Energy Commission and the Electric Power Research Institute [5]. The scenarios were intentionally designed to be optimistic about CHHP deployment to determine whether it could potentially affect hydrogen fuel availability and hydrogen vehicle market success. The California scenarios were extrapolated to the U.S. market by scaling the California CHP penetration estimates by residential and commercial energy demand by Census Region. The Base Case reflects expected future gas and electricity prices, existing and expected emissions standards, and existing CHP cost and performance with evolutionary improvement over time. The Base Case does not, however, include the existing California Self Generation Incentive Program (SGIP).

The High-R&D + Incentives Case accelerates progress on fuel cells by three years and adds the California SGIP nationwide. The SGIP incentive for fuel cells, $2,500/kW is much higher than for other technologies and is critical to the uptake of fuel cell CHP units. The High Deployment Case accelerates technological progress for fuel cells by another two years and assumes that a larger fraction of the market is willing to consider CHP and that they will accept a longer payback period. In the reference assumptions half of potential customers require a payback in two years or less. In the High Deployment Case half will accept a three-year payback period.

The HyTrans model was then recalibrated to the 2009 AEO American Recovery and Reinvestment Act Reference Case, updated with vehicle technology characterizations from DOE’s Multi-Path Transportation Futures Study [5] as well as hydrogen production and distribution technologies from the H2A model and greenhouse gas emissions coefficients from the Greenhouse gases, Regulated Emissions and Energy use in Transportation model. Three sizes of CHHP units were represented: (1) 150 kW producing 56 kg/day, (2) 250 kW producing 93 kg/day, and (3) 1 MW producing 340 kg/day. The H2A model includes one representation of hydrogen delivery for CHHP: a short pipeline to a nearby refueling station. We added another option, collection of hydrogen from CHHP sites via tube trailer and trucking to a refueling within five miles of the CHHP site. The latter option was intended to allow greater flexibility in the quantities and timing of hydrogen production by CHHP units, as well as in the location and size of hydrogen refueling stations.

Results

The SGIP incentive has a large impact on the number of fuel cell CHP units projected for the year 2020. In the Base Case there are fewer than 2,000 fuel cell CHP units installed (Figure 1). With the SGIP nationwide almost 40,000 fuel cell CHP units are in service in 2020 in the High R&D Case, and over 60,000 in the High Deployment Case. All could potentially be CHHP units; however the actual number of CHHP units is determined by the demand for hydrogen in a given HyTrans model run. Substantial cumulative subsidies are required to achieve these levels of fuel cell deployment: $23 billion in the High R&D + Incentives Case and $43 billion in the High Deployment Case, compared with $0.5 billion in the Base Case.

Without any availability of hydrogen from CHHP, hydrogen is provided almost exclusively by distributed steam methane reforming (SMR) stations during the early transition. By 2020 there are less than 1,000 SMR stations nationwide (Figure 2). This compares with approximately 160,000 gasoline refueling stations.

In the High R&D and SGIP Case, the number of locations at which motorists can refuel with hydrogen exceeds 6,000 in 2020 and 14,000 by 2025, nearly 10% of all refueling outlets (Figure 3). The vast majority are supplied by midsize CHHP units. This reflects both the
numbers of CHHP units by size and the strong economies of scale in producing and delivering hydrogen from CHHP units. In general, hydrogen from the 250 kW units costs half as much as hydrogen from 150 kW units. Although it is still cheaper to produce hydrogen at the 1 MW units, there are far fewer of them. While the large majority of stations are supplied by CHHP in this Case, the majority of the hydrogen is supplied by larger (1,500 kg/day) distributed SMR stations.

Lack of hydrogen availability poses an extra cost for owners of fuel cell vehicles in terms of added time to access hydrogen fuel and concern about running out. The HyTrans model attempts to measure the cost of lack of availability in $/kg of hydrogen. Without the added hydrogen availability due to CHHP stations, hydrogen availability costs outside of the core regions of Los Angeles and New York remain high ($1 to $4/kg) even in 2020; availability costs in the rest of the U.S. are far higher ($4 to $9/kg). With increased hydrogen fuel availability provided by dispersed CHHP units, the cost of availability falls below $1/kg, even in the medium and low density portions of the Pacific and Northeast Census Regions (Figure 4). After 2020 availability costs are below $2/kg in all regions of the country.

Conclusions and Future Directions

Like any analysis of this kind, the results are strongly dependent on premises and assumptions. Nonetheless, the following conclusions are likely to be robust to alternative assumptions.

- Distributed production and delivery of hydrogen from CHHP units of between 250 kW and 1 MW in size could greatly reduce the costs of hydrogen fuel availability during the early stages of a transition to hydrogen.
- The fuel availability benefits of CHHP units are especially strong in areas that are not centers of hydrogen vehicle penetration.
- Insuring a sufficient number of potential sources of CHHP hydrogen will require large subsidies to fuel cell CHP installations, on the order of $20 billion to $40 billion cumulative to 2025, nationwide.
- Even with large numbers of CHHP units providing hydrogen, the greatest quantities of hydrogen are likely to be produced by distributed SMR during the first two decades or so of the transition.


FIGURE 2. Numbers of Distributed Retail Hydrogen Refueling Stations Assuming no CHHP

FIGURE 3. Number of Distributed Retail Hydrogen Refueling Stations in the High R&D and SGIP Scenario.
The highest priority areas for further analysis are: (1) developing scenarios of national CHP penetration that better represent regional factors affecting the competitiveness of fuel cell CHP, and (2) developing alternative H2A models of hydrogen delivery from CHHP installations.

**FY 2010 Publications/Presentations**


**References**


VII.5 Biogas Resources Characterization

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Project Start Date:  August 15, 2009
Project End Date:  September 30, 2010

Objectives

- Develop a cost-analysis tool for biomethane production from biogas and delivery of biomethane based on the H2A Production and H2A Delivery models, respectively.
- Collect Geographical Information System (GIS) data on select biogas resources—dairy farms, landfills, and sewage treatment plants—in California and cost data on biogas upgrading systems.
- Perform techno-economic analyses for scenarios involving production of biomethane from dairy digester biogas and delivery of the product gas to natural gas pipeline or another end-use site.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.0) of the Fuel Cells Technologies Program’s Multi-Year Research, Development and Demonstration Plan [1]:

(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 contributed to achievement of the following DOE milestones from the Systems Analysis section (4.0) of the DOE Fuel Cell Technologies Program’s 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, 2010)
- Milestone 41: Annual Analysis Conference for the hydrogen community. (4Q, 2010; 4Q, 2011)

Accomplishments

- Based on the H2A Production and H2A Delivery models, developed the H2A Biomethane, cost analysis model for biomethane production and delivery. The model determines the levelized cost of biomethane at the production site and point of delivery. It also estimates the energy consumption and emissions for the biogas upgrading system, the upstream processes, and downstream pressure-boosting compressors.
- Using GIS analysis tools, collected and evaluated geo-spatial data for biogas potential from landfills, dairy farms, and sewage treatment plants in the state of California.
- Performed a techno-economic analysis to (1) address the impact of biogas feed capacity (flow rate) on unit cost of biomethane, (2) evaluate economic feasibility of transporting the biomethane product to a natural gas pipeline, and (3) determine the critical cost components and identify opportunities for cost reduction.
- Determined that (1) the levelized cost of biomethane is greatly influenced by the wide variations in the costs of biogas and biomethane transport to a natural gas pipeline, and (2) biomethane produced from dairy-farm biogas can be economically competitive with natural gas for large-scale systems.

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Introduction

Production of biomethane (predominantly methane) from biogas presents an opportunity to reduce emissions and augment the natural gas supply. Along with these attributes, the evolving requirements of renewable portfolio standards, environmental regulations, and the available incentives are among the drivers for biomethane production and utilization. To determine the energy, economic, and environmental potential of biomethane, analysis tools, GIS data, and cost data are required, forming the premise of this project. Although biogas can be extracted from a variety of bio wastes and energy crops, stranded biogas from dairy farms, landfills, and sewage treatment plants is the primary focus here.

As a primary objective of this project, a cost-analysis model, H2A Biomethane, was developed to help perform technoeconomic analyses of scenarios involving production of biomethane from biogas and pipeline connection to the natural gas network or another demand site. Inclusion of the grid-connection feature was based on the realization that export of biomethane to the natural gas grid can expand the market for the potential biogas producers and consumers. Geo-spatial data on biogas resources (dairy farms, landfills, and sewage treatment plants) were collected for the state of California and analyzed using GIS mapping to evaluate the biogas potential in conjunction with the current natural gas consumption. Using the H2A Biomethane model, along with the GIS and cost data, “what-if” analyses were performed for scenarios focusing on biomethane production from biogas and its transport for injection into the natural pipeline.

Approach

The new analysis tool, H2A Biomethane, was developed based on the vetted H2A Production and Delivery models [2,3] that are intended to be transparent with respect to the key assumptions and procedures for calculation of the costs, energy consumption, and emissions. The methodology described in reference [4] was applied for estimating the energy requirements and emissions associated with dairy digester biogas. Reference [5] was also consulted in developing a data set for biomethane (natural gas) pipeline construction. The new model offers versatility in characterizing the upgrading process and the pipeline for transportation of the product biomethane to the natural gas grid or to another end-use site. To determine reasonable default values for the input variables/parameters of the model, cost data were collected from vendor, literature, and real-world projects involving biomethane production from biogas. Use of these sources of data helped develop validated default values with reasonable accuracy.

The preliminary techno-economic analyses conducted in this project are intended to demonstrate the capabilities of the new cost-analysis tool and to provide an insight on the cost structure for biomethane production and delivery. These analyses focus on the relative significance of the various cost components (e.g., costs of feed biogas, upgrading/cleanup process, and delivery pipeline) and explore their variation with the feed biogas capacity. Efforts are made to maintain consistency between the delivery component of this model and the H2A Delivery model in handling the pipeline extension and compression. The results of these and future analyses can lend themselves to stakeholders, including dairy farm owners, municipalities, and policymakers. This notion, coupled with the need for realistic data and practical considerations, prompted formation of a panel discussion with the stakeholders at an early stage of the project.

Results

GIS Analysis

Figure 1 presents the GIS map for the three biogas resources—dairy farms, landfills, and sewage treatment plants—in the state of California. The estimates for the total biomethane potential of these resources and the corresponding stranded gas are provided in Figure 2. At about 73% of the total potential, the aggregated...
landfills have the dominant share followed by the dairy farms at approximately 22%. However, considering that only about 50% of the biomethane potential from the landfills in that state is stranded compared to nearly 100% for the dairy farms, the dominance of the landfills lessens for future implementation. (Another potentially limiting factor for landfill gas may have to do with the lack of protocols/guidelines for permitting injection of biomethane produced from landfill gas into natural gas network.) The total biomethane potential comprises about 5% of the natural gas consumption in California.

Technoeconomic Analysis

An analysis was conducted to determine the levelized cost of biomethane production and pipeline delivery to the natural gas grid for a range of feed biogas capacity based on the following assumptions.

- Biomethane production site is about 16 km (10 miles) from the natural gas transmission line whose operating pressure is 40 bar (600 psia).
- Biogas containing 60% methane (by volume) enters the upgrading/cleanup system at the atmospheric pressure.
- Pipeline-quality biomethane leaves the upgrading system with 97% methane (by volume) at about 7 bar (105 psia) and compressed for injection into the transmission line.
- The life span for the entire system (upgrading system and extension pipeline) is 20 years.
- The investment rate of return is 10% and the inflation rate is 1.9%.
- Biogas cost is $5/GJ of the biomethane product. This cost is closer to the lower limit of the range reported in a United States Department of Agriculture report [6].

Presented in Figure 3 are the total levelized cost of biomethane and its constituents as functions of the feed biogas capacity. Considering that the biogas output capacity of the largest dairy farms rarely exceeds 400 Nm$^3$/h (based on the GIS analysis), potential local/regional clustering of the farms is the basis for the range of the feed biogas capacities covered in this analysis. Examination of these results (Figure 3) leads to the following observations.

- The total levelized cost of biomethane delivered to the natural gas grid is about $35/GJ and $11/GJ corresponding to feed biogas capacities of 250 Nm$^3$/h and 3,000 Nm$^3$/h, respectively. These results are indicative of strong dependency of the biomethane cost on the system size.

- For feed biogas capacities below 2,000 Nm$^3$/h, the pipeline transport cost is the dominant cost component. At higher capacities, the contributions of the biogas upgrading and transporting costs are about equal.

- At the assumed cost of $5/GJ, the feed biogas takes on a greater significance than the upgrading and pipeline transport constituents for biogas capacities exceeding 2,000 Nm$^3$/h.

Although all of the cost results are subject to uncertainties, the pipeline transport cost is additionally influenced by the proximity of the production site to the natural gas pipeline, a variability that is not captured in Figure 3. For example, if injection of biomethane into a distribution pipeline is permissible, a shorter extension line and less pressure-boosting compression for grid connection can ensue, resulting in a markedly lower cost.

FIGURE 2. Estimates of Total Biomethane Potentials and Stranded Amounts

FIGURE 3. Cost Analysis of Biomethane Production and Delivery
lower transport cost. Consequently, the ranking of the transport and upgrading costs may even be reversed at low biogas capacities.

The cost of biogas also has a critical role, particularly in larger systems, given its wide range stemming from the availability of various anaerobic digestion types implemented in dairy farms [6]. The total biomethane cost trend in Figure 3, coupled with the notion that the price of natural gas (residential) is approximately $9.5/GJ for the state of California and $11.7/GJ for the U.S. average [7], the biomethane production for on-site utilization (not involving transport) can be economically competitive for biogas capacities (greater than 500 Nm³/h) evaluated in Figure 2. More favorable economics can be expected when less costly biogas becomes available (e.g., biogas from covered lagoons in mild climates or from landfills). However, the cost of grid connection limits the economic competitiveness of the delivered product gas to large systems only (not accounting for any available state/federal incentives for renewables).

The results shown in Figure 3 do not include storage or any other unforeseen ancillary costs (e.g., sequestration and/or faring of the waste stream from the biogas upgrading process). Based on a report by Krich et al. [8], inclusion of a storage system for two day’s worth biomethane production can increase the cost by about $1.3 to $3 per GJ. For the case of clustered farms, the additional cost of transporting biogas (or bio waste) from the individual farms to a central location for upgrading is not addressed in this analysis either. A comprehensive and more accurate cost analysis requires details that are specific to each given project/scenario.

For cases where biomethane is produced for on- or near-site utilization and the feed biogas cost is available at low prices, the pipeline transport cost vanishes and, consequently, the upgrading cost takes on greater significance. In such scenarios, knowledge of the cost breakdown for the upgrading system can be valuable in identifying opportunities for cost reduction. Figure 4 illustrates the variation of the relative contributions of the key cost components with the feed biogas capacity. This figure suggests an increasing role of the variable costs (primarily utilities) as larger systems are considered.

Based on the emissions results of the H2A Biomethane model, the greenhouse gas emissions arising from the biogas upgrading and the upstream processes are approximately 1.84 kg/kg biomethane and -1.75 kg/kg, respectively, resulting in a net amount of 0.092 kg/kg biomethane. The emission for the biogas upgrading system is a function of the system energy efficiency and the biomethane recovery rate, which is assumed to be 99%.

The newly developed tool, along with analyses similar to the preceding, can assist the DOE Fuel Cell Technologies Program with evaluation of the economic and environmental benefits of using renewable biogas for on-site power generation with fuel cell systems. Other stakeholders, including biogas producers, can also benefit from these in the case-by-case decision making process.

Conclusions and Future Direction

- The newly developed H2A Biomethane model can lend itself to cost analysis of producing biomethane from biogas for on-site utilization or export to natural gas grid or another end-use application site. The model also allows calculation of the energy consumption and emissions for the biogas upgrading system and the upstream processes.
- Price of biogas, feed biogas capacity, distance between the production site and point of delivery, and the delivery pressure influence the levelized cost of biomethane.
- By taking advantage of the economy of scale for biogas upgrading process (biogas capacity greater than about 2,000 Nm³/h) and assuming purchase of dairy digester gas at $5/GJ, the levelized cost of biomethane production for on- or near-site utilization can be as low as $7/GJ. Therefore, biomethane produced from dairy digester biogas can be economically competitive with natural gas in certain circumstances even without applying any financial incentives.
- Achieving economy of scale for biomethane production from dairy digester biogas can be challenging because dairy farms offer relatively small feed biogas capacities (compared to landfills). Therefore, participation of near-by dairy farms in implementing a central system may be imperative if cost reductions are to be realized from the economy of scale.
Based on the predefined scope of the project, dissemination of the results at a conference or workshop is the only remaining activity. The following list outlines additional activities recommended for future work.

- Addressing oxidization and/or sequestration of the waste streams from the biogas upgrading process.
- Investigating the impact of biogas impurity level on the cost of the upgrading process.
- Performing analyses for nascent and existing installations/field studies.

**FY 2010 Publications/Presentations**


**References**


VII.6 Cost and GHG Implications of Hydrogen for Energy Storage

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Project Start Date: October 2008
Project End Date: Project continuation and direction determined annually by DOE

Objectives
- Evaluate the economic viability of hydrogen for utility-scale energy storage applications compared with other electrical energy storage technologies.
- Explore the cost and greenhouse gas (GHG) emissions impacts of the interaction between hydrogen energy storage and variable renewable electricity resources.

Technical Barriers
This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan:
(B) Stove-piped/Siloed Analytical Capability
(D) Suite of Models and Tools
(E) Unplanned Studies and Analysis

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 Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan:
- Milestone 26: Annual model update and validation. (4Q, 2010)

Accomplishments
- Analyzed the levelized cost of energy (LCOE) for hydrogen energy storage versus competing technologies, finding that hydrogen is competitive with batteries and could be a cost-effective alternative to compressed air energy storage (CAES) and pumped hydro in locations that are not suitable for these technologies.
- Analyzed a hydrogen energy storage system with 1,400 kg/day excess hydrogen, finding an LCOE of $4.69/kg, not including tanker truck transport and dispensing (which compares with about $4/kg for the production portion of an electrolysis forecourt hydrogen station).
- Analyzed a hydrogen energy storage system with 12,000 kg/day excess hydrogen, finding an LCOE of $3.33/kg, not including tanker truck transport and dispensing (which compares with about $7/kg for electrolysis at a centralized hydrogen production facility of the same size).
- Analyzed energy storage system sensitivity to electricity price, finding that sensitivity to electricity price is roughly inversely proportional to energy storage system roundtrip efficiency and that efficiency improvements to a hydrogen energy storage system, especially the fuel cell, would have a larger positive impact on LCOE than similar improvements to competing technologies.
- Performed an initial study of the amount by which hydrogen energy storage reduces the amount of wind-generated electricity that must be curtailed and reduces the LCOE of the electricity delivered.
- Preliminarily analyzed the effect of obtaining financial credits for avoided carbon emissions on the LCOE of wind-generated electricity with and without hydrogen energy storage, finding that carbon credits can reduce the wind LCOE below the grid LCOE, with the addition of hydrogen energy storage providing lower LCOE than wind without storage.

Introduction
As renewable electricity becomes a larger portion of the electricity-generation mix, new strategies will be required to accommodate fluctuations in energy generation from these sources. Energy storage has been one of the primary strategies proposed for integrating large amounts of renewable energy onto the grid. Energy storage can absorb excess electricity-generating...
capacity during times of low demand and/or high rates of generation and then reconvert the stored energy into electricity during periods of high demand and/or low renewable generation. The use of hydrogen for energy storage also creates a potential bridge between the electricity and transportation sectors: excess hydrogen generated by energy storage systems could be used to provide fuel for hydrogen-powered vehicles.

In Task 1, the LCOE of the most promising and/or mature energy storage technologies was compared with the LCOE of several hydrogen energy storage configurations. In addition, the cost of using the hydrogen energy storage system to produce excess hydrogen was evaluated. In Task 2, the use of hydrogen energy storage in conjunction with an isolated wind power plant—and its effect on electricity curtailment, credit for avoided GHG emissions, and LCOE—was explored.

**Approach**

For Task 1, a simple energy arbitrage scenario was developed for a hydrogen energy storage system consisting of a 500-MWh nominal storage capacity that is charged during off-peak hours (18 hours on weekdays and 24 hours on weekends) and discharged at a rate of 50 MW for 6 peak hours on weekdays. The system electrolyzes water to produce hydrogen, which is stored in compressed gas tanks or underground geologic formations and reconverted into electricity using a polymer electrolyte membrane fuel cell or hydrogen expansion combustion turbine. The lifecycle LCOE resulting from each hydrogen storage scenario was compared with the lifecycle LCOE resulting from use of several battery systems (nickel cadmium, sodium sulfur, and vanadium redox), pumped hydro, and CAES. The analyses were performed for the same energy arbitrage scenario, and with consistent financial and operational assumptions, using the National Renewable Energy Laboratory’s HOMER model (https://analysis.nrel.gov/homer). In addition, the cost of using the hydrogen energy storage system to produce 1,400 and 12,000 kg/day of excess hydrogen was analyzed.

For Task 2, three scenarios were modeled for an isolated wind power plant in North Dakota that transmits electricity to Chicago: 1) a base case in which electricity from a 1,000-MW wind plant with a capacity factor of about 50% is transmitted via a dedicated 750-MW capacity transmission line to the grid with no energy storage, 2) a storage-constrained case in which the wind plant is combined with a 400-MT hydrogen energy storage system at the wind plant location, and 3) a transmission-constrained case in which the wind capacity is combined with 2,600 MT of hydrogen energy storage but only 500 MW of transmission capacity is available. The LCOE and electricity curtailment resulting from these scenarios were evaluated.

**Results**

In Task 1, modeling suggested that the LCOE of hydrogen energy storage is competitive with batteries and could be a cost-effective alternative to CAES and pumped hydro in locations that are not suitable for these technologies (Figure 1). For each technology, high-cost, mid-range, and low-cost cases were analyzed, and sensitivity analyses were performed to generate a range of possible costs for each case. In Figure 1, the bottom of the bars represents the low end of the range for the low-cost cases, and the top of the bars represents the high end of the range for the high-cost cases. The numbers shown are the nominal values of the mid-range cases and can be considered an estimate for LCOE for a 3–5 year future time frame.

The range of costs for each system reflects the range found in the literature and estimates of potential cost reductions as technologies develop. The hydrogen fuel cell scenario cost range reflects the comparative immaturity of fuel cell technologies for this application. It is anticipated that costs for fuel cells will decrease as the technology matures. Cost considerations aside, hydrogen has some advantages over competing energy storage technologies. It has a very high energy density (170 kWh/m³ versus 2.4 kWh/m³ for CAES [1] and 0.7 kWh/m³ for pumped hydro [2]), which allows for the potential economic viability of aboveground storage. Also, hydrogen combustion turbines could prove to be viable for energy storage applications and could provide additional flexibility to utilities through co-firing of mixtures of natural gas and hydrogen.

The sensitivity analyses showed electricity price to be one of the most important factors influencing LCOE for each storage technology. Further analysis
showed that sensitivity to electricity price is roughly inversely proportional to the roundtrip efficiency of the energy storage technologies (Figure 2). Improvements in the efficiency of hydrogen storage system equipment, especially the fuel cell, would have a larger positive impact on LCOE than similar improvements for competing technologies.

Using the hydrogen energy storage system to produce 1,400 kg/day of excess hydrogen reduces the overall LCOE for this scenario by about 6% compared with the purely energy arbitrage scenario, and the excess hydrogen is produced for $4.69/kg. Excess hydrogen produced in this way is still not competitive with hydrogen produced in a dedicated, distributed electrolysis process with the same daily output of hydrogen ($4.00/kg). However, producing 12,000 kg/day of excess hydrogen to feed into a hydrogen pipeline results in a cost of $3.33/kg, substantially less expensive than the $6.86/kg for a dedicated, centralized 12,000-kg/day hydrogen electrolysis facility.

In Task 2, the preliminary analysis suggested that combining hydrogen energy storage with electricity from an isolated wind power plant reduces the amount of wind-generated electricity that must be curtailed and reduces the LCOE (Table 1). This preliminary analysis also suggested that combining wind power with hydrogen energy storage enhances the reduction in LCOE resulting from instituting a credit for avoided carbon emissions (Table 1).

**Conclusions and Future Direction**

The modeling analyses performed in Fiscal Year (FY) 2009 and FY 2010 suggested that hydrogen energy storage is economically competitive with batteries and could be a cost-effective alternative to CAES and pumped hydro in locations that are not suitable for these technologies. Excess hydrogen could be produced for the transportation market. In addition, preliminary analyses suggested that using hydrogen energy storage in conjunction with an isolated wind power plant could reduce electricity curtailment and LCOE for the wind plant. Additional work is needed to elucidate the impact of hydrogen storage on GHG emissions and credits for avoided emissions, especially in comparison to CAES. Future work may include the following:

- Further explore the costs and benefits of dual-use hydrogen energy storage systems in which hydrogen is used for electricity storage and fuel for vehicles.
- Develop a methodology for optimizing the size of the storage system components and transmission to minimize costs for an isolated wind or solar installation.
- Analyze an isolated solar installation with hydrogen energy storage.
- Compare GHG emissions/carbon tax implications for hydrogen energy storage and CAES.

**FY 2010 Publications/Presentations**


**References**


VII.7 Hydrogen and Water: Engineering, Economics and Environment

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Phone: (202) 586-7932
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Start Date: Fiscal Year (FY) 2007
Project End Date: Project continuation and direction determined annually by DOE

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

(A) Future Market Behavior
(D) Feedstock Issues
(E) Unplanned Analyses

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 Fuel Cell 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 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

- Concluded that under foreseeable price regimes, water management is unlikely to add more than $0.05 to the cost of a kilogram of hydrogen via analysis of water withdrawal and consumption for hydrogen process and cooling water.
- Determined most economic cooling and water treatment technologies under variable water purchase and disposal price regimes.
- Created a national map of water stress by watershed through collaborations with the National Energy Technology Laboratory (NETL) and Sandia National Laboratories.
- Identified potential hydrogen markets with high risk factors (beyond water price) for water impacts.

Introduction

Water is a critical feedstock in the production of hydrogen. Major changes in the energy infrastructure (as envisioned in a transformation to a hydrogen economy) will necessarily result in changes to the water infrastructure.

Water is used as a chemical feedstock for hydrogen production and as a coolant for the production process. 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**

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.

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 follow the hydrogen roll-out scenarios envisioned by Greene and Leiby [1] to determine the impact of hydrogen market penetration on various watersheds. In collaboration with Sandia National Laboratories and NETL, we determine the level of water stress in each of the potential hydrogen markets, as well as the competing industrial water demand. We also analyze water purchase and discharge prices at the regional level to identify economic impacts of water on hydrogen at the regional level.

**Results**

As of this progress report, the final report for the hydrogen/water analysis is undergoing final revisions. An economic optimization of technologies for water management related to hydrogen production has been completed, and a regional analysis of water stresses and impacts on hydrogen production has been conducted.

Table 1 conveys the results of the techno-economic analysis. Multiple water treatment and cooling were analyzed. The three that were generally resulted in the lowest cost of hydrogen are arrayed on the right hand side of the table. For various combinations of water purchase and discharge prices (and assuming that other costs, such as labor and electricity, in the H2A model remained constant) the resulting hydrogen prices are shown in the center. As purchase and discharge prices rise, the least-cost water-management technologies shift. Because water purchase and discharge prices may be uncorrelated (Figure 1), the least-cost water option may not simply be the lowest withdrawal option.

Figure 2 shows the results of the water stress analysis that was performed for the entire nation at the watershed level. The blue “pinpoints” represent metropolitan areas highlighted in previous analyses as likely to have significant hydrogen vehicle penetration within the next 15 years. Table 2 lists these areas and provides quantitative metrics of risk to hydrogen rollout. Water stress, in this analysis, is defined as the total water

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<th>Water Purchase Price ($/gal)</th>
<th>$0.0001</th>
<th>$0.001</th>
<th>$0.01</th>
<th>$0.10</th>
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**Table 1.** The price of central steam methane reformed hydrogen, in $/kg-H₂, as calculated by H2A spreadsheets modified to account for water purchase and discharge prices and the varying capital and operating costs of different cooling and water treatment systems. The cells colored red indicate the lowest hydrogen price from among the three water-technology options.
withdrawal within a watershed divided by the total annual flow into that watershed (including precipitation, groundwater influx and runoff from other watersheds). A water stress greater than unity does not necessarily indicate unsustainable water usage because a significant fraction of all withdrawn water is discharged within the watershed from which it was withdrawn. However, the most highly stressed areas are, without a doubt, using water beyond their local means, either from “fossil” water resources (aquifers that are being depleted) or from water imports. High water-stress areas likely to be impacted by more severe water policies in the near-term.

**Conclusions and Future Directions**

- Water is an important issue for hydrogen stakeholders to monitor because the areas anticipated to have the earliest hydrogen rollout (particularly the Los Angeles area) are some of the most highly water-stressed. Hydrogen producers in these areas may be faced with limited ability to procure a water permit.
- Although permitting may be an issue, water is inexpensive and abundant on a national scale. Under all reasonable water-price scenarios, the total cost of water to hydrogen producers (including the capital cost of treatment and cooling systems) is unlikely to exceed $0.05/kg-H₂
- Hydrogen will not be adopted “in a vacuum.” Hydrogen will displace other fuels, each of which has its own water footprint. Therefore, the net impact of hydrogen on water resources will be somewhat lower than this engineering/economic analysis shows.

**FIGURE 1.** Water discharge (sewer) prices plotted against water purchase prices for 34 different municipalities. There is wide variability in water prices and little correlation between purchase and discharge prices.

**FIGURE 2.** A Google Earth™ map of the United States showing 329 watersheds. The watersheds are color-coded by the levated withdrawals (ground plus surface water) divided by the total water influx (precipitation plus stream inflow). Red regions are more highly stressed. The metropolitan areas expected to see early hydrogen rollout are labeled.
TABLE 2. Metropolitan areas likely to roll out hydrogen with their relevant watersheds. Water stress is calculated as the sum of total water supply (ground and surface) in all relevant watersheds divided by the sum of total water withdrawal in those same watersheds. Water used for hydrogen was calculated by using the number of predicted 1,500 kg/day stations [2] in each metro area and multiplying by a water intensive SMR-based hydrogen production technology (8.5 gallons withdrawal per kg hydrogen). The percent of supply used for hydrogen is calculated by dividing the water used for hydrogen by the total surface and groundwater supplies in the relevant watersheds. The percent increase in industrial water use is calculated by dividing the amount of water used for hydrogen by the watershed(s)-wide industrial use of water. Zero-discharge and dry cooling technologies are capable of reducing these figures by a factor of 4.

<table>
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<tr>
<th>Metro Area</th>
<th>Watersheds</th>
<th>Water Stress</th>
<th>Water used for Hydrogen (MGal/day)</th>
<th>% of supply used for hydrogen</th>
<th>% increase in industrial water usage</th>
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FY 2010 Publications/Presentations


References


VII.8 Analysis of Business Cases with the Fuel Cell Power Model

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Subcontractors:
IDC Energy Insights, Farmington, MA

Project Start Date: September, 2009
Project End Date: September 2010

Objectives

The objective of this project is to revise the H2A Fuel Cell Power model to suit the analytic needs of business and financial decision makers and model end-users. To meet this objective, a Business Tab will be developed within the Fuel Cell Power excel model. It is not expected that the Business Tab will replace in-house financial models used to assess investment options, but it will extend the capability to do financial and business analysis using the model. This will prove especially valuable for tri-generation systems due to multiple stakeholders and energy product revenue streams. Understanding and fulfilling this objective will require significant stakeholder feedback on the decisions making process in question and tab design criteria.

Technical Barriers

This project addresses the following technical barriers from the 4.5 section of the Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan (MYPB):

- (B) Stove-piped/Siloed Analytical Capability
- (D) Suite of Models and Tools
- (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 MYPP:

- Milestone 8. Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness.

Accomplishments

- Reviewed H2A model structure to identify possible extensions.
- Outlined a theoretical tab format and “to-do” list of potential revisions.
- Collected feedback from internal NREL Business Review Team, including staff from the Strategic Energy Analysis, Deployment and Commercialization, and Federal Energy Management centers.
- Presented the FC Power model and proposed Business Tab design features to the California Hydrogen Business Council (CHBC), the Hydrogen Utility Group (HUG), and the California Fuel Cell Partnership (CaFCP), and collected feedback from each group on analytic capability priorities.
- Received feedback from industry representatives through an online questionnaire developed and administered in collaboration with IDC Energy Insights.
- Revised Business Case tab design accordingly.

Introduction

Stationary fuel cell systems configured to provide heat and power to building can also be configured to provide hydrogen as a third energy product. As depicted in Figure 1, these distributed energy systems would displace power provided by the electricity grid, heat provided by burning natural gas and hydrogen produced from a pathway such as conversion of natural gas via steam methane reforming onsite at a fueling station. Installation of a tri-generation combined, heat, hydrogen and power (CHHP) fuel cell system would involve a large number of stakeholders, including building owners and operators, natural gas and electric utilities, project financiers, fleet managers, fuel cell vendors, fueling station owners and operators, and (potentially) third party developers. The successful initiation of this type of
The project will depend upon rapid identification of benefits to each of the involved stakeholders. The Fuel Cell Power model (FCPower), developed by the National Renewable Energy Laboratory for the Department of Energy, is an analytic tool that can facilitate this process by providing a first-cut estimate of project costs and benefits [1]. The FCPower model is a publicly available, financial model, programmed in Excel™, that can be tailored to a particular building application by importing site-specific information such as hourly building energy demands, feedstock costs, fuel cell system costs and operating characteristics, and various financial assumptions.

The goal of this project is to design a Business Tab within the FCPower model that caters to the analytic needs of a business decision maker. The Business Tab consolidates all the key questions and analytic capabilities pertinent to a business end user in one location within the model. The FCPower model is based upon the discounted cash flow framework of the DOE H2A Models, which were originally designed for a technical rather than business end-user [2]. With addition of the Business Tab, it is anticipated that an interested stakeholder, such as a building owner/operator, would rely upon technical personal to set up and calibrate the model to represent a proposed fuel cell project, and then the model would be passed on to a financial analyst within the same organization to explore strategic business “what-if” questions and financial metrics. Versions of the FCPower model tailored to a specific combined heat and power (CHP) or CHHP building project can also be circulated among multiple project stakeholders to communicate and reach agreement on basic project assumptions. Designing a Business Tab for a new end user required collection of information on the decision making processes most likely to be involved in this early project screening phase. The following sections describe the process undertaken to collect this input from key stakeholders as well as some of the resulting design criteria.

**Approach**

The approach to designing the Business Tab involved collecting input from experts internal and external to NREL. Internal input was received from a Business Review Team consisting of NREL staff in the Strategic Energy Analysis, Deployment and Commercialization, and Federal Energy Management centers. Key external stakeholders included staff from the CaFCP, the HUG and the CHBC. Short multi-choice forms were circulated at these meetings to gauge priority or emphasis placed upon different financial metrics (see examples). Additional input was provided from external stakeholders on an ad hoc basis through hydrogen and fuel cell meetings and conferences. Based upon preliminary suggestions and design criteria provided by these internal and external experts, a questionnaire was developed and administered in collaboration with IDC Energy Insights (www.idc-ei.com) and administered to 100 stakeholders from pertinent organizations, including utilities, accounting
or financial, hospitals, hotels, big box stores, car dealers, hotels, convention centers, government facilities, transportation and warehousing, etc. Sections of the questionnaire inquired into the decision making process of the particular organization, and asked focused questions on the types of financial metrics typically relied upon to reach decisions about large capital investments. A typical list of potential metrics is shown below.

a. Net Present Value (NPV)
b. Internal Rate of Return (IRR)
c. Payback Period
d. Total Capital Cost
e. Maintenance Cost/Savings
f. Energy Cost/Savings
g. Revenue Opportunity
h. Vendor Brand Name Recognition
i. Vendor Financial Stability
j. Efficiency/energy improvements for Corporate Social Responsibility or Sustainability Goals
k–m. Other (please specify)

These and other proposed enhancements to the FCPOWER model are based upon a review of the model capabilities and possible extensions to the discounted cash flow calculations. In most cases only minor modifications are required to enable these capabilities due to the detailed existing H2A financial framework. In addition to identifying priority decision metrics, specific analytic capabilities were discussed, such as the capability to specify hydrogen, heat or electricity price and subsequently calculating IRR (a new capability not included in the original H2A models).

Results

Feedback received through the process described above was compiled, organized by type, prioritized, and associated with specific Tab designs and analytic capabilities. Examples of some of these suggestions are listed in the following, including Big Picture suggestions and Detailed Suggestions.

Big Picture Suggestions

• Make costs and benefits prominent. To keep stakeholders engaged in the project as additional information is collected and analyzed, a clear line of sight is needed to keep potential benefits prominent. This prominence provides motivation to endure transaction costs during the formative screening stage of the project.
• Provide access to technological information. Stakeholders can often be at a disadvantage due to an information imbalance among multiple parties, especially with adoption of new technologies. Providing links to information resources can help even out this imbalance and build confidence for key decision makers.

Detailed Suggestions

• Provide one-sheet printout for executive reading.
• Enable IRR as output and as function of various “what if” assumptions.
• Allow solving for hurdle rates, as stakeholders will know their own hurdle rates.
• Facilitate spot checking of basic financial assumptions.
• Include significant flexibility on treatment of tax credits.
• Allow exploration of alternative future feedstock prices (e.g., natural gas).
• Include a visual display of how hourly and peak demand would be offset.

The general structure of the Business Case Tab, developed in response to these and other suggestions, is indicated in Figure 2. The sections of the worksheet shown are accessible by scrolling down the worksheet. Upon opening the Business Tab, an end user will first see the key results and variables associated with the costs and benefits of the stationary fuel cell CHP or CHHP installation. Scrolling down to the next section, an end user would find a number of commonly used “what if” financial questions. These have been identified as typical inquiries of a business-oriented end user through the outreach activities described previously. Users will also find a section with links to external resources providing additional information on the core technology, fuel cells, in order to familiarize them with the technology and therefore reduce any information imbalances among stakeholders. Subsequent sections include results and input cells associated with taxes and incentives, a detailed balance sheet and cash flows, system performance, utility and feedstock assumptions, and additional advanced or less-common analytic capabilities.

Conclusions and Future Direction

A first-cut analysis of the costs and benefits of installing a stationary fuel cell system in CHP or CHHP configuration at a building can provide key decision makers with project screening criteria. The FCPOWER model, based upon the detailed H2A discounted cash flow framework, is cable of providing these criteria after being calibrated to a particular facility installation. However, the H2A models were originally designed with a technical end user in mind. A Business Tab has therefore been developed to make the FCPOWER model
more useful for a business-oriented end user. Extensive input was collected, both internal and external to NREL, to determine design criteria and priority analysis capabilities for the Business Tab. Having collected and categorized these criteria and design suggestions, the Business Tab will be included in the next release of the FCPower model. If deemed appropriate, similar tabs will be integrated into future versions of some H2A production and delivery models, especially those focused on infrastructure components subject to financial scrutiny by multiple stakeholders, such as onsite steam methane reforming or electrolysis systems.

References

VII.9 Fuel Quality in Fuel Cell Systems

Objectives

- Study the impact of impurities on fuel cell systems.
- Identify the key impurities of concern.
- Recommend research and development (R&D) strategies to mitigate the effect of the impurities.

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(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 achieving the following DOE Systems Analysis milestones from the Systems Analysis section of the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- Milestone 8: Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014) The study described here analyzes the quality of resources/feedstock, their conversion to reformate, and subsequent purification to identify the technology readiness and ability to sustain the operation of reformate-based fuel cell systems.

Accomplishments

A database has been set up to document the impurities encountered in stationary fuel cell systems by reviewing the literature and other public domain information:

- The impurities encountered in these systems have been identified.
- The effect of the impurities on the fuel processor components and their management options are being studied.
- The tolerance of the various fuel cells to the impurities is being documented.

Introduction

Fuel cell systems are being deployed in stationary applications for the generation of electricity, heat, and hydrogen. These systems comprise a variety of fuel cells ranging from the low temperature polymer electrolyte fuel cell (PEFC) to the high temperature solid oxide fuel cell (SOFC). Depending on the application and location, these systems are being designed for, or operate on reformate or syngas produced from various fuels that include natural gas, biogas, coal gas, etc. All of these fuels contain species that can potentially damage or pose a hazard for the fuel cell anode or other unit operations and processes that precede the fuel cell. These effects include loss in performance or durability and require additional components to reduce, if not eliminate, the impurity concentrations to tolerable levels. These impurity management options increase the complexity of the process and add to the capital and operating costs (regeneration, replacement and disposal of spent material, maintenance, etc.)

This project reviews the various impurities encountered in fuel cell systems with the objective of identifying which components (e.g., reformer, heat exchanger, fuel cell, etc.) in the system are affected, the extent of the deleterious effect, the impurity management options being practiced in the field and their effectiveness. For example, the presence of sulfur can lead to poisoning of the reforming catalyst which then results in coke formation and rapid failure of the reformer. To avoid this scenario the plant manager will install a sulfur-removal process. The decision on the desulfurization process (e.g., hydrodesulfurization or ambient sorbent bed and its size, etc.) will be made by considering the tradeoffs between the cost and complication of the process against the loss in productivity (hydrogen yield, power output) and other
considerations (e.g., deactivation rate, cost of disposing the spent sorbent, frequency of maintenance, etc.).

**Approach**

- Information relating to impurities and their impact on fuel cell systems are being collected from the literature and through personal communication with fuel cell developers. Data from the literature and from other public domain sources are being incorporated into a database, which classifies the information in terms of type of application, the type of impurity species encountered and their effect on the system, the technologies that are used for their removal or abatement, and the level at which a fuel cell can tolerate the impurity.
- The data will be analyzed to identify the impurities with respect to their pervasiveness, the difficulty of removal, and cost burdens. Ideally, it will be preferable to translate these factors in terms of cost impact, since this will allow a comparison across different systems and applications.

**Results**

A database has been set up to document and study the effect of fuel quality on fuel cell systems. Table 1 shows data from a demonstration project at the Penrose Power Station in Sun Valley, CA [1], where landfill gas was cleaned, reformed and then fed into a phosphoric acid fuel cell (PAFC) to generate 137 kW of electric power.

**TABLE 1. Data from a Landfill Gas Fueled Fuel Cell Demonstration at Penrose Power Station, CA**

<table>
<thead>
<tr>
<th>Category</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Application</td>
<td>Commercial Demonstration</td>
</tr>
<tr>
<td>Type of Fuel Cell</td>
<td>PAFC</td>
</tr>
<tr>
<td>Output</td>
<td>137 kW</td>
</tr>
<tr>
<td>Feedstock</td>
<td>Landfill Gas</td>
</tr>
<tr>
<td>Impurities</td>
<td>Sulfur, Halides, Siloxanes, Non-Methane Organic Carbons (NMOC)</td>
</tr>
<tr>
<td>Feedstock Purification</td>
<td>1. Claus Reaction on Carbon</td>
</tr>
<tr>
<td></td>
<td>2. Refrigerated Condensation</td>
</tr>
<tr>
<td></td>
<td>3. Desiccant</td>
</tr>
<tr>
<td></td>
<td>4. Activated Carbon</td>
</tr>
<tr>
<td>Feedstock Conversion</td>
<td>Reformer</td>
</tr>
<tr>
<td></td>
<td>Water-Gas Shift Reactor</td>
</tr>
<tr>
<td>Reformate/Syngas Purification</td>
<td>Not Available</td>
</tr>
<tr>
<td>Concentration entering Fuel Cell</td>
<td>Sulfur as $\text{H}_2\text{S} \sim 0.4 \text{ ppm}$</td>
</tr>
<tr>
<td></td>
<td>Halide as $\text{HCl} \sim 0.01 \text{ ppm}$</td>
</tr>
<tr>
<td></td>
<td>Siloxane $\sim 0.08\text{ mg/dcm}$</td>
</tr>
<tr>
<td></td>
<td>NMOC $\sim 14\text{ ppm}$</td>
</tr>
<tr>
<td>Effect on Fuel Cell</td>
<td>Not Available</td>
</tr>
<tr>
<td>Impurity Tolerance</td>
<td>Sulfur 3 ppm</td>
</tr>
<tr>
<td></td>
<td>Halide 3 ppm</td>
</tr>
</tbody>
</table>

Landfill gas contains sulfur, halides, siloxanes, and hydrocarbons. For the Penrose plant, a number of clean-up units were installed to reduce the impurity concentrations to acceptable levels, which were reported to be 3 ppm for sulfur and halides. In order to understand the impact of the impurities and compare them against other applications, it is desirable to know what the clean-up process adds to the cost of the electric power that is generated.

A closer look at landfill gas [1-6] shows (Table 2) that the impurity species that are present at low concentrations can be classified into paraffins, sulfur, cyclics, aromatics, halides, and organic silicon. Hydrogen sulfide is the predominant sulfur species with concentrations that can approach 400 ppm. The organic silicon species include a large number of species each of which can be as high as 15 mg/Nm$^3$.

**TABLE 2. Typical Species Present in Landfill Gas**

<table>
<thead>
<tr>
<th>Major Species</th>
<th>%</th>
<th>Aromatics ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4$</td>
<td>41-54</td>
<td>Isopropyltoluene</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>32-35</td>
<td>Benzene</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>0.7-0.9</td>
<td>Toluene</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>11-13</td>
<td>Xylene (and isomers)</td>
</tr>
<tr>
<td>Paraffins</td>
<td>ppm</td>
<td>Styrene</td>
</tr>
<tr>
<td>Ethane</td>
<td>&lt; 220</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Butane</td>
<td>&lt; 100</td>
<td>Trimethylbenzene</td>
</tr>
<tr>
<td>Pentane</td>
<td>&lt; 970</td>
<td>Halides ppm</td>
</tr>
<tr>
<td>Hexanes</td>
<td>&lt; 390</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ppm</td>
<td>Dichloroethane</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>&lt; 430</td>
<td>Dichloroethane</td>
</tr>
<tr>
<td>Methyl Mercaptan</td>
<td>&lt; 3</td>
<td>Cis-1,2 Dichloroethane</td>
</tr>
<tr>
<td>Ethyl Mercaptan</td>
<td>&lt; 0.5</td>
<td>Methylene Chloride</td>
</tr>
<tr>
<td>Dimethyl Sulfide</td>
<td>&lt; 8</td>
<td>Dichlorofluoromethane</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>&lt; 0.5</td>
<td>Trichloroethene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vinyl Chloride</td>
</tr>
<tr>
<td>Cyclics</td>
<td>ppm</td>
<td>Organic Silicon mg/Nm$^3$</td>
</tr>
<tr>
<td>Pinene</td>
<td>&lt; 14</td>
<td>(D3, D4*, D5, L2, L4)</td>
</tr>
<tr>
<td>Limonene</td>
<td>&lt; 35</td>
<td>Trimethylsilanol</td>
</tr>
</tbody>
</table>

The presence of siloxanes in landfill gas pose challenges for fuel processing since these species react at higher temperatures to produce silica which then deposits on the surfaces of catalysts and heat exchangers. Siloxanes can be removed with sorbents such as silica gel, bentonite, etc. However, the gravimetric capacity of these sorbents tends to be low and is adversely affected by the presence of other species. For example, silica gel’s capacity for siloxane uptake [6] drops from 10%
for dry gas to less than 1% when the relative humidity is increased to 50%. Similarly, the presence of volatile organic compounds prevents the adsorption of siloxanes on carbon.

Sulfur is present in almost all the feedstocks used for power generation and plagues the fuel cell industry because of their ability to poison heterogeneous and electrochemical catalysts. Some sulfur species can be removed with sorbents such as activated carbon, while others require more reaction based processes such as the Claus process or hydrodesulfurization. The latter reaction produces H$_2$S and COS, which then have to be reacted with other reagents such as ZnO or other sorbents. These processes are complex because of the effects of temperature, competition of sorption sites with H$_2$O, kinetics, and low gravimetric capacities of the sorbents. Table 3 shows some of the media that are used for the removal of H$_2$S [7,8].

**TABLE 3. Media Used for H$_2$S Removal**

<table>
<thead>
<tr>
<th>Medium</th>
<th>Regeneration</th>
<th>Capacity (kg H$_2$S/kg Fe$_2$O$_3$)</th>
<th>$$/kg of H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Sponge (Iron Oxide)</td>
<td>2-3 X</td>
<td>2.5</td>
<td>0.35-1.35</td>
</tr>
<tr>
<td>Sulfa Treat$^a$ (Iron Oxide)</td>
<td>No</td>
<td>0.5-0.7</td>
<td>4.85-5.00</td>
</tr>
<tr>
<td>Sulfur Rite$^b$ (Iron Oxide)</td>
<td>No</td>
<td></td>
<td>7.95-8.50</td>
</tr>
<tr>
<td>Media G2$^c$ (Iron Oxide)</td>
<td>15 X</td>
<td>0.5</td>
<td>2.90-3.00</td>
</tr>
<tr>
<td>Impregnated Activated Carbon</td>
<td>Yes</td>
<td>0.12 g-S/g-C</td>
<td>1.75-2.00</td>
</tr>
</tbody>
</table>

Other methods that are employed for the removal of impurities from the reformate stream include phase change to condense out species such as metal vapors from coal syngas, separation membranes, etc. The most comprehensive method for hydrogen enrichment is the pressure swing adsorption which can produce very high purity hydrogen and is very effective for the removal of sulfur and ammonia. Unfortunately, these units require pressurization of the gas stream which is energy intensive, and the operation of the multiple beds tends to be complex.

The data available in the literature on the effect of impurities on fuel cell systems covers a range of systems and conditions [9-13]. Although comparison on a common basis is difficult, some trends and contributing factors are evident. For example, the higher temperature fuel cells show greater tolerance to impurities – the SOFC can tolerate orders of magnitude higher concentrations of ammonia and sulfur than the low temperature PEFCs. Even for a particular type of fuel cell, the performance loss is affected by the nature and concentration of the impurity, the current density, the composition of the fuel, the exposure time, etc.

As an example, introduction of 2 ppm H$_2$S into a natural gas reformed syngas causes the voltage in a button-size SOFC cell to drop sharply by 10%. Increasing the H$_2$S concentration to 5 ppm doubles the performance loss to 20% [15]. The database being assimilated in this project includes similar data on a host of impurities tested at various conditions in fuel cells with varying anode compositions. Analysis of performance data, however, can be much more coherent when the tests are coordinated to address specific questions on similar hardware under consistent conditions.

**Conclusions and Future Directions**

- A database is being set up to document the impurity levels and their management in stationary fuel cell applications:
  - The data are being classified on the basis of the unit operations and processes of the system.
- The key impurities in the feedstock fuel and the fuel gas to the anode have been identified:
  - The concentrations of these impurities are being documented.
- Sulfur and siloxanes have detrimental effects on fuel cells and components that precede them.
- The higher temperature fuel cells demonstrate higher tolerance to impurities such as sulfur, carbon monoxide, and sulfur.
- The database will be analyzed to identify trends and key technical challenges faced by the stationary fuel cell industry. This will be followed by recommendations on R&D needs.

**FY 2010 Publications/Presentations**


**References**


VII.10 Macro System Model

Objectives

- Develop a macro-system model (MSM):
  - Aimed at performing rapid cross-cutting analysis.
  - Utilizing and linking other models.
  - Improving consistency between models.
- Support decisions regarding programmatic investments through analyses and sensitivity runs.
- Support estimates of program outputs and outcomes.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell 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 System Analysis section of the Fuel Cell 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 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 1.8c).
- Linked with geospatial model HyDRA to add the spatial dimension to the MSM.
- Integrated MSM with the temporal pathway evolution assessment tool HyPro.

Introduction

At the DOE Hydrogen Program’s behest, we are developing an MSM 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 because 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 a common platform for data exchange necessary to update integrated models when the component models have been updated.

The MSM is being built on a framework inspired by an example of the federated object model (FOM). FOMs also link together models and are exemplified by the Department of Defense high level architecture [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 [2], HDSAM V2.0 [3], and GREET V1.8c [4]. Thus, Figure 1 [5] shows the levelized cost of the hydrogen pathways. The levelized cost of hydrogen is calculated directly in the H2A model for the distributed hydrogen production cases because the H2A distributed hydrogen production model includes the forecourt station capital and operating costs. For central production cases, the levelized cost of hydrogen is the sum of levelized production cost calculated in H2A, levelized delivery cost calculated in HDSAM, and the cost of excess production due to losses in delivery. For distributed production, the costs of compression, storage, and dispensing (CSD) are about $1.88/kg and are included in the production cost. For central production, the CSD costs are included in the delivery cost and depend upon the delivery technology (gas in pipelines vs. liquid from trucks). Note that the delivery costs are $2-$3/kg hydrogen; delivery costs may need to be reduced to make central production technologies competitive with distributed production technologies.

Connecting hydrogen production and other costs with associated emissions is one of the advantages that the MSM provides by linking together different models. Figure 2 shows the levelized hydrogen fuel cost per mile and the well-to-wheels (WTW) greenhouse gas (GHG) emissions for each of the seven pathways assessed based on U.S. average fuel costs and fuel cycle energy requirements. For comparison, it also shows the projected 2009 market price per mile (in 2005 dollars) and GHG emissions for gasoline-, diesel-, and E85-fueled vehicles. The levelized fuel cost was put onto a per-mile basis. The projected fuel cost per mile for most of the hydrogen pathways (based on projected, mature fuel cell electric vehicle markets) is similar to that for gasoline in a traditional vehicle and corn ethanol as E85 fuel in a flexible-fuel internal combustion engine (ICE) vehicle. The fuel costs per mile for gasoline in a hybrid electric vehicle (HEV) and diesel in a conventional diesel ICE vehicle are lower. The dotted green cloud in the figure represents the stochastic analysis results obtained based on input distributions for the forecourt steam methane reforming (SMR) production option [6]. The dispersion of the data points well surpasses the differences between the central (with pipeline delivery)
and distributed SMR production options. This relates to both the per-mile cost of hydrogen and the WTW GHG emissions. Similarly, the blue cloud shows the stochastic analysis result for the central biomass case. For the latter, as seen in the figure, the data point distribution is less significant when compared with the differences incurred by switching from pipeline to liquid truck delivery.

As key MSM inputs are sometimes region-specific, it is important to add the geospatial dimension into the range of the MSM features. Bilateral links with the online geospatial tool HyDRA [7] have been developed that allow the MSM user to easily apply regional electricity and natural gas (NG) feedstock data as MSM inputs and, conversely, update the HyDRA database and maps with the latest MSM version outputs. As an example, Figure 3 shows the results obtained for a selected (from HyDRA interface) region. For every county in the region, HyDRA supplies the MSM with the electricity grid mix and price data, and the MSM calculates hydrogen production (via electrolysis) costs and associated WTW GHG emissions. (The interaction between the models is implemented via internet.) As a result, regions with both lower hydrogen production cost and lower WTW GHG emissions can be easily selected.

The transition to high-market-penetration levels for hydrogen fuel cell vehicles will likely involve several hydrogen production/delivery/dispensing pathways. To facilitate this analysis and to involve the temporal dimension, the temporal pathway evolution assessment tool HyPro [8] is integrated with the MSM. As a result, HyPro inputs are updated via MSM (Figure 4) with latest current H2A Production and HDSAM models, and the MSM facilitates probing into the effect of any of the HyARC, HDSAM, or H2A Production model parameters on the potential evolution of hydrogen production/delivery/dispensing pathways.

**Conclusions and Future Directions**

- By linking production/delivery/dispensing models, the MSM is a tool for rapid cross-cutting comparative analysis of various production/delivery pathways.
- The U.S. region-specific data are readily available as MSM inputs via live MSM/HyDRA links.
As a result of linking HyPro with MSM, pathway evolution is examined in a manner consistent with latest versions of H2A and HDSAM.

Future directions:

- Include vehicle production and maintenance in the MSM analysis.
- Add combined heat and power as a production option.
- Expand delivery and distribution options to include the 700-bar storage, cryo-compressed and tube trailer delivery.
- Continue updating the MSM links to new model versions as they are released.

FY 2010 Publications/Presentations


References


Objectives

- Conduct fuel-cycle analysis of stationary fuel cell (FC) systems (to help development of hydrogen production and FC technologies).
- Engage in discussions and dissemination of energy and environmental benefits of FC systems and applications.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell 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 Analysis

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 Fuel Cell 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

- Conducted energy use and greenhouse gas (GHG) emissions analysis of FC systems for combined heat and power (CHP) and combined heat, hydrogen, and power (CHHP) generation, which showed that CHP and CHHP FCs offer significant reduction in energy use and GHG emissions compared to distributed combustion generation technologies.
- Conducted criteria pollutants emissions analysis of FC systems for CHP and CHHP generation, which showed that CHP and CHHP FCs offer reductions in criteria pollutant emissions compared to distributed combustion generation technologies.
  - FC systems for CHP and CHHP provide significantly less carbon monoxide (CO), particulate matter (PM), and oxides of nitrogen (NOx) emissions than conventional combustion generation technologies.
  - Utilization of byproduct heat is critical to the fuel-cycle emission performance of FC systems for distributed power generation.
  - CHHP FC systems provide better utilization of byproduct heat compared to CHP FC systems when heat is utilized for producing additional amounts of hydrogen.

Introduction

The pathway to the application of FCs in hydrogen vehicles will be assisted by the introduction of FCs in markets with fewer technical challenges than automobiles. Distributed power generation and forklifts are near-term markets in which FCs can be successful. One of the issues associated with transforming the market of FCs to these early markets is their potential fuel-cycle energy use and emissions benefits – this issue is important because many sectors of the U.S. economy are becoming increasingly subject to reduction of energy use and emissions of GHGs and air pollutants. An earlier study by ANL examined the fuel-cycle energy use and GHG emissions of FCs for forklift propulsion systems and distributed power generation. In addition to polymer electrolyte membrane (PEM), FC technologies suitable for distributed power generation include phosphoric acid FCs (PAFCs) and molten carbonate FCs (MCFCs). 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 for
the refueling of FC forklifts in a nearby facility or for the generation of supplemental electricity to satisfy a facility's electric load during peak demand periods. The availability of a hydrogen co-product may also overcome one of the barriers to introducing hydrogen FC vehicles (FCVs) to some early FCV market places by facilitating a distributed source of hydrogen while effectively employing the primary energy source and the initial capital investment of the FC to serve a facility's demand for electric and heat energy.

This analysis evaluates the fuel-cycle criteria pollutant emissions, in addition to GHG emissions, associated with the application of PAFCs and MCFCs to CHP and CHHP generation. It also evaluates the fuel-cycle GHG and criteria pollutant emissions of other combustion technologies for CHP, such as internal combustion engines (ICEs) and microturbines (MTs). These FC and combustion technologies are compared against the conventional technologies that supply buildings with electricity and heat, such as the local grid generation mix and the combustion technologies typically used to meet the facility's heating demand. Three facility types, representing a hospital, a large office building, and a warehouse located in two different climatic regions (Chicago and Los Angeles), were evaluated for their carbon footprint and criteria pollutants emissions. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model has been expanded to address the fuel-cycle GHG emissions and criteria pollutant emissions associated with the application of FCs to CHP and CHHP generation.

Approach

Fuel-cycle analysis of various power-generation technologies in this study calculates the energy use and emission occurrences per unit of consumed energy at end-use. These occurrences include the initial recovery, processing, and transportation of the primary fuels, as well as the generation of heat, hydrogen, and electricity. The energy use and emissions primarily depend on the energy conversion efficiency of each process in the fuel cycle pathway. Efficiency and emissions data for the distributed generation technologies of interest to this analysis are extracted from testing data reported by U.S. Environmental Protection Agency, as well as data provided by California Air Resource Board and industry sources. For CHP and CHHP FC systems, the efficiency data are extracted from the H2A power model developed by National Renewable Energy Laboratory, which simulates the hourly FC performance based on actual (load-following) performance data. These efficiencies, as shown in Table 1, are generally lower than those obtained from steady-state testing at peak performance or rated power due to performance degradation as a result of typical duty cycles and unsteady operation in the field.

The reported thermal efficiencies in Table 1 assume that the entire amount of recoverable waste-heat is utilized.

Two different approaches for fuel-cycle analysis of CHP and CHHP applications have been considered in this analysis: a total demand approach and a displacement approach. The total demand approach compares the impact of various technologies in satisfying a facility's demand for electricity, hydrogen and heat. It accounts for the energy use and emissions associated with the on-site generation of power, heat, and hydrogen, as well as the energy use and emissions associated with the generation of supplemental heat, hydrogen, and grid power. The system boundary for this approach includes the FC and the supplemental systems that satisfy the building's excess electricity and heat demands. The energy use and emissions for this approach are evaluated per one million Btu (mmBtu) of combined electric, heat, and hydrogen demand. The displacement approach compares different technologies for the on-site generation of electricity and hydrogen, and calculates credits for the heat byproduct. The system boundary for this approach only includes the distributed generator system and assumes full utilization of any heat byproduct. The energy use and emissions for this approach are evaluated per one million Btu of net electricity and hydrogen generation. The credit of by-product heat is calculated from the displacement of equivalent amount of heat from a typical standalone heating system. The displaced heat is assumed to be produced from a natural gas (NG)-fired heater with 90% efficiency. A major difference between the two fuel cycle approaches is the percentage utilization of the heat byproduct. In the displacement approach, the entire amount of heat available from the generators is assumed to displace conventional heat production from NG-fired burners, although a significant amount of heat could be rejected by the facility because generators often produce more heat than required by the instantaneous demands, and the facility is assumed not to have a heat storage tank. Thus, while the effect of heat utilization (HU) is properly captured in the total demand approach, the displacement approach assumes 100% utilization of heat byproduct. The fuel-cycle results presented below are based on the displacement approach.

Results

The fuel-cycle results for various distributed generation technologies were examined based on estimates of efficiency and emission factors shown in Table 1. Figures 1-5 show the fuel-cycle GHG and criteria pollutant emissions associated with different generation technologies using the displacement approach. The relative benefits of the CHP and CHHP systems compared to other generation technologies 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 and GHG emissions compared to CHP fuel cell systems due to the better utilization of byproduct heat in making hydrogen (Figure 1). Criteria pollutant emissions are comparable for CHP and CHHP FC systems, but are significantly less than those for all other generation systems (Figures 2-5). The amount of displaced heat for the different generators is critical to their overall performance. This is apparent in Figure 2 for CO emissions where the displaced heat results in negative emissions for FC systems (i.e., a net credit). The credit for CHHP FCs is less compared to CHP FCs due to the utilization of the coproduced heat to make hydrogen, and thus less heat byproduct is produced and displaced. FC systems produce an order of magnitude less NOx compared to combustion generation technologies as shown in Figure 3. They also produce significantly less PM compared to other distributed generation technologies and grid generation mix in U.S. and California (Figure 4). All distributed generation technologies powered by NG produce much less oxides of sulfur (SOx) compared to the grid generation mix in the U.S. and California, mainly due to the much low sulfur content of NG (Figure 5).

<table>
<thead>
<tr>
<th>Technology</th>
<th>Type</th>
<th>Efficiency</th>
<th>Emission Factors (grams/mmBTU of fuel input)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Electric</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>PAFC</td>
<td>CHHP</td>
<td>29%</td>
<td>18%</td>
</tr>
<tr>
<td></td>
<td>CHP</td>
<td>38%</td>
<td>0%</td>
</tr>
<tr>
<td>MCFC</td>
<td>CHHP</td>
<td>39%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>CHP</td>
<td>46%</td>
<td>0%</td>
</tr>
<tr>
<td>NG ICE with aftertreatment</td>
<td>CHP</td>
<td>36%</td>
<td>0%</td>
</tr>
<tr>
<td>NG MT</td>
<td>CHP</td>
<td>28%</td>
<td>0%</td>
</tr>
</tbody>
</table>

TABLE 1. Energy Efficiency and Emission Factors for Distributed Power Generation Technologies

FIGURE 1. Fuel Cycle GHG Emissions of Different Generation Systems
FIGURE 2. Fuel Cycle CO Emissions of Different Generation Systems

FIGURE 3. Fuel Cycle NOx Emissions of Different Generation Systems
FIGURE 4. Fuel Cycle PM Emissions of Different Generation Systems

FIGURE 5. Fuel Cycle SOx Emissions of Different Generation Systems
Conclusions and Future Directions

Conclusions

FC systems for distributed power generation in CHP or CHHP achieve significant reductions in criteria pollutant emissions:

- FC systems for CHP and CHHP provide significantly less CO, PM, and NOx emissions compared to conventional generation technologies.
- Utilization of byproduct heat is critical to the fuel-cycle emission performance of FC systems for distributed power generation.
- CHHP FC systems provide better utilization of byproduct heat compared to CHP FC systems.

Future Work

- Complete fuel-cycle analysis of FC CHHP systems for criteria pollutants as well as energy use and GHGs.

FY 2010 Publications/Presentations

Objectives

- Perform analysis of topics of interest to the Fuel Cell Technologies (FCT) Program related to projected CO₂ benefits of fuel cell applications.
- Provide additional analytical support to the FCT Program to respond to departmental data requests and other needs.

Technical Barriers

(A) Future Market Behavior
(C) Inconsistent Data and Assumptions
(E) Unplanned Studies and Analysis

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to the achievement of the following DOE milestones from the Systems Analysis section of the FCT Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 22: Completed the modification of the MARKAL model to include hydrogen analysis. (4Q, 2007)

Accomplishments

- Examined the impact of changes in various Program cost assumptions for fuel cell costs, cost of onboard storage, hydrogen distribution costs and carbon prices on market penetration of fuel cell vehicles and carbon emissions. The analysis was presented to the FCT Program.

- Analyzed the benefits of biomass-to-hydrogen in deep CO₂ emission reduction scenarios. This analysis demonstrated that the use of biomass-to-hydrogen with carbon capture and sequestration (CCS) can greatly reduce the cost of meeting deep carbon emission reduction goals. A paper has been written based on the results and will be submitted to a journal for publication.

Introduction

The goal of this analysis is to explore the role that hydrogen technologies can play in reducing carbon emissions. Our analysis for the last two fiscal years include a sensitivity analysis of fuel cell vehicle market penetration to changes in production, distribution and vehicle costs and CO₂ prices, as well as analysis to examine the benefits of biomass-to-hydrogen in deep CO₂ emission reduction scenarios.

Approach

MARKAL Sensitivity Analysis

Our primary analytical tool is the 10 Region U.S. MARKAL model developed by BNL. The model was calibrated to the Energy Information Administration's (EIA's) 2009 Annual Energy Outlook. The first analysis under this project is the sensitivity analysis that we performed in Fiscal Year (FY) 2009 using our 10 Region U.S. MARKAL model. Our goal was to examine the impact of changes in various Program cost assumptions.

The cost assumptions we looked at included: hydrogen distribution cost where we looked at the program goal of $1.00 per kg, as well as $1.50 and $2.00. The next cost sensitivity was the cost of the fuel cell for vehicle applications where we tested the Program goal of $30 per kW, as well as costs of $40, $50 and $60 per kW. We also looked at the cost of on-board storage and the impacts of a ten year delay in the commercialization of fuel cell vehicles. Finally, we tested the impact of a range of carbon prices from $0 to $100 per tonne of CO₂, to see the impact of carbon prices on fuel cell vehicle market penetration, the desired hydrogen feedstocks and total CO₂ emissions.

Role of Biomass-to-Hydrogen in Deep CO₂ Emission Reduction Scenarios

The second analysis under this project is an analysis of the benefits of biomass to hydrogen in deep CO₂ emission reduction scenarios. This analysis also used
the 10 region U.S. MARKAL model. For this analysis, we have two sets of technology scenarios. The first set is based primarily on the EIA assumptions, with the exception of light-duty vehicles where we have included the research and development (R&D) improvements from the Vehicle Technologies Program research in light weighting, hybridization and battery technologies. We then have a second technology scenario where we include the FCT Program’s R&D goals for hydrogen production, distribution and stationary and mobile fuel cells. We used the CO₂ cap from the Waxman-Markey bill that was passed by the House of Representatives in 2009. We only modeled provisions directly related to the CO₂ cap and trade provisions. Other provisions, such as national renewable portfolio and appliance standards were not modeled. Since we wanted to explore the impacts of hydrogen technologies under more stringent carbon caps, we decided to look at what might happen if the domestic or international offsets were excluded from the legislation.

Results

MARKAL Sensitivity Analysis

The key results for the sensitivity analysis relate to impacts of carbon prices on the MARKAL model’s choice of hydrogen production technologies and the impacts of increased fuel cell and onboard storage costs on fuel cell vehicle market penetration. As shown in Table 1, without a carbon price, the model primarily chooses to use central coal and distributed gas reforming to produce hydrogen. However, with increased prices of carbon, the model rapidly switches to using more biomass with CCS.

With respect to the impacts of alternative costs of vehicle fuel cells and on board storage, increasing the cost of either component will reduce overall market penetration of fuel cell vehicles. However, the impacts of changing the cost of onboard storage has a relatively minor effect, while increasing the cost of the fuel cell to $50 or more per kW has a dramatic impact on fuel cell vehicle market share (Figure 1).

Role of Biomass-to-Hydrogen in Deep CO₂ Emission Reduction Scenarios

The Waxman-Markey cap and trade provision is a market-based program for reducing greenhouse gas emissions. The ultimate goal is to reduce emissions by 83% below 2005 levels by 2050. However, small utilities are exempt from the regulation and covered entities can secure permits by purchasing domestic and international carbon offsets. Overall, up to 2 giga-tonnes of CO₂ offsets can be used annually. Also, banking and trading of permits is permitted. The net effect of the allowing offsets and exempting small utilities is that the effective CO₂ emissions cap is much higher than advertised. Since we wanted to explore the impacts of hydrogen
technologies under more stringent carbon caps, we decided to look at what might happen if the domestic or international offsets were excluded from the legislation.

A total of eight cases were run. They are:

- Reference Case: Ref. Case
- Reference with Carbon Cap: Ref. w/CC
- Reference with Carbon Cap Without International Offsets: Ref. w/CC w/o IO
- Reference with Carbon Cap Without Any Offsets: Ref. w/CC w/o AO
- FCT Program: FCTP Case
- FCT Program with Carbon Cap: FCTP w/CC
- FCT Program with Carbon Cap Without International Offsets: FCTP w/CC w/o IO
- FCT Program with Carbon Cap Without Any Offsets: FCTP w/CC w/o AO

Comparing the Reference Case with the FCT Program Case without a carbon policy, there is a 37% reduction in direct transportation sector emissions. However, this is partially offset by an increase in industrial sector emissions, where we account for the direct emissions from producing hydrogen. Overall, there is a 10% reduction in carbon emissions relative to the reference case (Figure 2).

When we add the Waxman-Markey CO₂ cap, we see a significant difference between the reference and hydrogen technology scenarios. With the FCT Program assumptions, there is a dramatic reduction in transportation and industrial emissions due to efficient fuel cell vehicles and the “negative” carbon emissions from biomass-to-hydrogen with CCS. Figure 3 shows that the 2050 carbon emissions from the power generation sector are higher than with the reference technology scenario. With the increased savings in the industrial and transportation emissions other sectors can emit more and still comply with the overall CO₂ cap. In this case, the model finds that the biomass-to-hydrogen technology has much lower marginal cost than some of the power sector technologies that were chosen in the Reference with Carbon Cap case.

Looking at 2050 carbon emissions by sector for the two technology scenarios and under the different carbon caps, Figure 4 shows a significant reduction in transportation and industrial carbon emissions for the advanced hydrogen cases on the right side of the chart, than for the reference case technology cases on the left.
You can also see total carbon emissions are lower for the FCT cases due to a reduced use of offsets and banking of carbon credits.

With the introduction of the Waxman-Markey cap (with offsets), there is a significant increase in use of biomass in both cases. With the FCTP assumptions, we get a significant increase in the overall consumption of biomass, due to the use of biomass to hydrogen with CCS. However, under the more stringent carbon caps where we don’t allow international or any offsets, the reference technology set biomass consumption catches up with the advanced hydrogen technology cases. The primary difference is that under the reference technology set, the model relies on biomass-to-liquids with CCS, where the FCT Program cases use both biomass-to-liquids and biomass-to-hydrogen with CCS (Figure 5).

**Conclusions and Future Directions**

- The use of biomass-to-hydrogen with CCS can greatly reduce the cost of meeting deep carbon emission reduction goals.
- Biomass-to-liquids with CCS generates “negative” CO₂ emissions, however, the hydrogen pathway generates deeper reductions per ton of biomass used.
- Under the two most stringent CO₂ caps, both biomass-to-liquids with CCS and hydrogen with CCS are needed.
- While the transport sector may be a more difficult sector to achieve deep CO₂ emission reductions, with a successful R&D program, deep CO₂ emission reductions can be achieved with a significant reduction in cost of meeting the CO₂ cap.
FY 2010 Publications/Presentations


VII.13 Pathways to Commercial Success: Technologies and Products Supported by the FCT Program

Objectives

This objective of this project is to provide a retrospective assessment of Fuel Cell Technologies (FCT) Program benefits by tracking commercial successes of FCT-developed technologies (and technologies developed by FCT 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 projects 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 Fuel Cell 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 Fuel Cell Technologies Program Multi-Year Research, 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 FCT Program and its predecessor programs.
- Updated the FCT technology tracking database containing information on commercial and emerging technologies.

Introduction

The FCT 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, 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 FCT-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 FCT Program (or funding from EERE predecessor programs) or from grants under programs such as Small Business Innovation Research and Small Business Technology Transfer.

Data gathered about the technologies were then entered into a FCT 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 FCT Program personnel to review.

**Results**

The patent search and analysis, identified 198 patents: 99 fuel cell patents, 74 production/delivery patents, and 25 storage patents. Figure 1 shows the patents awarded in each year, starting with pre-2000 patent awards through 2010. As the figure shows, 2006 had significantly more patents than the other individual years. The storage patent awards are spread out over the entire period, with a peak of four awards in 2004, while fuel cell and production/delivery patents peaked in 2006 with 12 patents in each category.

Three types of organizations received the patents: national laboratories (100 patents), private companies (76 patents), and universities (22 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 68% of the awards in the storage area. While the universities received fewer total patent awards, they had 59% 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, six patents are used in commercial products and 36 are part of research now taking place on emerging technologies identified on the technology tracking list compiled. In addition, 84 awarded patents are still being used in research that is more than three years from a commercial product. Of the 198 patents reviewed, 36% are no longer being used in research. In the production/delivery area, 73% of the patents are still actively being pursued through use in continuing research, emerging technologies, or commercially available products. The storage and fuel cell areas also have a majority of their patents being actively pursued.

In the second effort PNNL identified 28 commercial technologies that have entered the market including five using patents identified in the first effort. Figure 3 shows the cumulative number of commercial technologies entering the market. Of the 28 technologies, 27 are still commercially available. Years 2000–2006 showed a steady addition of technologies entering the market of one to three per year. In 2007, and 2008, five and seven technologies entered the market respectively. For 2009 and 2010 the rate of technologies entering the market returned to one to three per year. This effort also identified 52 emerging technologies. Figure 4 shows the distribution of the emerging technologies in the FCT research areas. The number of fuel cell technologies is more then half of the total number of emerging technologies.

A total of 52 emerging and 28 commercial technology descriptions are being prepared and will be included in the updated 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.

**FY 2010 Publications/Presentations**

VII. Systems Analysis

FIGURE 1. Number of Patents Awarded Over Time

<table>
<thead>
<tr>
<th>Year</th>
<th>Storage</th>
<th>Production/Delivery</th>
<th>Fuel Cell</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre 2000</td>
<td>3</td>
<td>7</td>
<td>14</td>
<td>24</td>
</tr>
<tr>
<td>2000</td>
<td>1</td>
<td>5</td>
<td>10</td>
<td>16</td>
</tr>
<tr>
<td>2001</td>
<td>3</td>
<td>7</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>2002</td>
<td>2</td>
<td>7</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>2003</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>2004</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>2005</td>
<td>2</td>
<td>12</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>2006</td>
<td>3</td>
<td>9</td>
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<td>2009</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>2010*</td>
<td>25</td>
<td>74</td>
<td>99</td>
<td>198</td>
</tr>
</tbody>
</table>

FIGURE 2. Status of Awarded Patents

<table>
<thead>
<tr>
<th>Category</th>
<th>Storage</th>
<th>Production/Delivery</th>
<th>Fuel Cell</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used in Commercial Product</td>
<td>0</td>
<td>1</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Part of Emerging Technology</td>
<td>6</td>
<td>18</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>Still Used in Research and/or Seeking to License</td>
<td>11</td>
<td>35</td>
<td>38</td>
<td>84</td>
</tr>
<tr>
<td>No Longer Being Pursued</td>
<td>8</td>
<td>20</td>
<td>44</td>
<td>72</td>
</tr>
</tbody>
</table>

Total

Storage: 0 + 6 + 11 + 8 = 25
Production/Delivery: 1 + 18 + 35 + 20 = 74
Fuel Cell: 5 + 12 + 38 + 44 = 99
Total: 24 + 16 + 21 + 15 + 16 + 12 + 12 + 26 + 18 + 8 + 18 + 12 = 198
VII.14 Fuel Cell Power Model: Evaluation of CHP and CHHP Applications

Objectives

- Accurately model performance of stationary fuel cells in combined heat and power (CHP) and combined heat, hydrogen, and power (CHHP) applications.
- Combine detailed performance information with a comprehensive discounted cash flow methodology to evaluate lifecycle costs.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Stove-piped/Siloed Analytical Capability
(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 milestones from the Systems Analysis section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 26: Annual model update and validation. (4Q, 2010)

Accomplishments

- Published Version 1.2 of the Fuel Cell Power Model.
- Provided presentations, webinars, and one-on-one guidance to train Fuel Cell Power Model users.
- Used the Fuel Cell Power Model in support of a wide range of actual and proposed fuel cell installations as well as theoretical research projects.
- Analyzed the effect of additional fuel for CHHP system hydrogen overproduction, finding that using additional fuel to boost hydrogen production reduces hydrogen cost.
- Compared fuel cell CHHP and steam methane reforming (SMR) hydrogen production strategies, finding that hydrogen production from CHHP is less expensive than from SMR for small-scale systems.
- Modeled a case study of a system combining dairy farm digester gas and fuel cell CHP, finding a payback time of about 7 years with an 8.5% internal rate of return (IRR) and emissions savings of about 750 g CO₂eq/kWh electricity generated.

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 (GHG) 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. This need resulted in creation of the Fuel Cell Power Model. Because the Fuel Cell Power Model is based on the H2A platform, it can be used for cross-cutting analysis in conjunction with other DOE tools, including the H2A production and delivery models, H2A Delivery Scenario Analysis Model (HDSAM), Macro System Model (MSM), Hydrogen Demand and Resource Analysis (HyDRA), and Scenario Evaluation, Regionalization and Analysis (SERA).
The Fuel Cell Power Model analyzes the technical and economic aspects of high-temperature fuel cell–based tri-generation systems in CHP and CHHP applications. 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, for the phosphoric acid fuel cell system, demand priority (i.e., whether the system follows electricity or heat demand) and can accept default 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 IRR. It also determines the amount and type of energy input and output and the associated GHG emissions. Version 1.2 of the Fuel Cell Power Model was completed in Fiscal Year (FY) 2010. Training was provided to Fuel Cell Power Model users, and the model was used to analyze a variety of CHP and CHHP applications.

Approach

The potential advantages of a fuel cell–based tri-generation system depend on numerous variables, including the type of building/application 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 Fuel Cell Power Model analyzes energy supply and demand for each hour over the course of a year. Case studies demonstrate the model’s functionality and value for modeling various applications and tri-generation regimes. The enhancements to Version 1.2 of the model enable financial decision-makers to evaluate the business case for a CHP or CHHP installation using a variety of financial metrics.

Results

Version 1.2 of the Fuel Cell Power Model was completed, which included the following enhancements:

- A single simple-to-use home for business case analyses, including calculating: cost without IRR, simple payback period, solutions for different variables (e.g., IRR, net present value), total lifecycle cost, benefit-to-cost ratio, and savings-to-investment ratio.
- Enhanced presentation of financial output from the model.
- More accurate evaluation of the “baseline” system (building energy costs prior to installation of the fuel cell system).
- Enhanced differentiation between technical operating and cost parameters and financial parameters, providing financial analysts with a more streamlined user interface dedicated to financial analysis.

Training and support was provided to Fuel Cell Power Model users, including presentations, webinars, and one-on-one guidance. Market transformation analyses were completed for several commercial and government entities. In addition, a variety of organizations used the Fuel Cell Power Model to support a wide range of actual and proposed fuel cell installations as well as theoretical research projects, including the following:

- National Renewable Energy Laboratory campus
- NASA Ames Research Center
- Los Alamitos Military base
- U.S. Postal Service Distribution Facility, San Francisco
- Materials and Systems Research, Inc.
- Sandia National Laboratories/Lawrence Livermore National Laboratory campus
- Three stores in a large grocery chain
- Five large food-processing facilities
- DOE generic scenario studies
- Spatial model development for deployment in conjunction with SERA
- Biogas case studies

Among the DOE studies conducted using the Fuel Cell Power Model was an analysis of the effect of additional fuel for CHHP system hydrogen.
overproduction; the study found that using additional fuel to boost hydrogen production reduces hydrogen cost. Another study compared fuel cell CHHP and SMR hydrogen production strategies, finding that hydrogen production from CHHP is less expensive than from SMR for small-scale systems (Figure 2).

A case study was developed for a system combining dairy farm digester gas and fuel cell CHP (Figure 3).

Input data included capital costs, operation and maintenance costs, expected life, and performance of the digester, gas cleanup, and fuel cell components; applicable government incentives; on-site energy demands; and energy costs. Using these data, the Fuel Cell Power Model showed a payback time of about 7 years with an 8.5% IRR. It also showed a GHG emissions reduction of about 750 g CO₂eq/kWh electricity generated, primarily owing to less GHG-intensive manure management and displacement of grid electricity (Figure 4).

Conclusions and Future Directions

In FY 2010, Fuel Cell Power Model efforts focused on three areas: improving the model’s analytical capabilities (including the completion of Version 1.2), training and supporting the model’s user community, and performing analyses using the model. Future work may include the following:

- Enhance the Fuel Cell Power Model in response to needs identified through its user community.
- Enhance the model’s business case analysis capabilities using experience from the business community.
- Develop additional case studies, with data from actual fuel cell installations for comparison.
VII. Systems Analysis

- Use the Fuel Cell Power Model to evaluate early hydrogen transition scenarios and the potential effects on electricity systems and GHG emissions.
- Add analysis capabilities for solid oxide fuel cells and residential-sized systems to the Fuel Cell Power Model.
- Integrate the Fuel Cell Power Model with DOE’s MSM and SERA.

FY 2010 Publications/Presentations


VII.15 Geo-Spatial Analysis of Hydrogen Infrastructure

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E-mail: olga.sozinova@nrel.gov

Contract Number: DE-AC36-08GO28308
Project Start Date: May 28, 2009
Project End Date: November 30, 2010

Objectives

- Develop a tool to allow users to compare hydrogen production pathways and policy options within a single common framework.
- Identify low-cost hydrogen production pathways at demand centers across the U.S.
- Perform scenario analysis to characterize the effect of factors such as the price of carbon, hydrogen demand, and feedstock costs on hydrogen price, resource utilization, and carbon dioxide (CO₂) emissions.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Fuel Cell 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 contributes to achievement of the following DOE Systems Analysis milestones from the Systems Analysis section of the Fuel Cell 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). The Hydrogen Logistics Model enables geographic analysis of hydrogen supply, demand, delivery and selling price.

- **Milestone 11**: Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness (2Q 2015). The Hydrogen Logistics Model helps quantify the impact of hydrogen production pathways and carbon policy on greenhouse gas emissions from hydrogen production.

Accomplishments

- Developed a user-interactive tool to allow scenario analysis comparison between hydrogen production pathways and policy options within a single common framework.

- Identified the least-cost hydrogen production pathways at demand centers across the United States under a variety of demand, carbon tax, and resource price scenarios. Results indicate that coal, natural gas, and biomass-based production pathways dominate the supply over a robust set of input assumptions.

- Estimated hydrogen cost contributions, carbon mitigation cost, and resource utilization under several different scenarios. The average delivered cost of hydrogen was estimated to range from $4.60/kg to $5.45/kg depending on the level of demand, availability of carbon capture, and the cost of CO₂.

Introduction

A number of hydrogen production, delivery, and storage options are being investigated that could eventually meet the demands of future hydrogen vehicles. Hydrogen production options include natural gas steam methane reforming, coal gasification, high-temperature nuclear electrolysis or thermochemical water splitting, and renewable options (e.g., biomass gasification, solar- and wind-based water electrolysis, solar thermochemical water splitting). The cost and availability of these resources varies widely based on the geographic location of demand and the size of the production facilities.
To help understand the economics of different hydrogen production pathways, TIAX developed a tool to estimate the price of delivered hydrogen to major demand centers across the U.S., as well as the associated resource utilization that is required to meet this demand. Hydrogen price and resource utilization were estimated by determining the location-specific combination of resources that minimizes the cost of delivering hydrogen. The present effort extends prior work [1] by incorporating additional conventional supply resources, carbon capture and sequestration (CC&S), and improving the compatibility between the Hydrogen Logistics Model inputs and outputs and other hydrogen crosscutting analysis models recently developed or currently under development for the DOE Hydrogen Program.

### Approach

A hydrogen production and infrastructure modeling tool (the Hydrogen Logistics Model) was developed to investigate the resource constraints and fuel cost of a future hydrogen fueling infrastructure in the U.S. The Hydrogen Logistics Model is an interactive tool that uses geographic information system (GIS) data to optimally deploy hydrogen production resources. The inputs to the Logistics Model include location, quantity, and cost information for hydrogen production feedstocks, and the location and size of demand centers. Data was gathered from a variety of publically available sources, notably the National Renewable Energy Laboratory’s (NREL’s) GIS database [2], the DOE’s Energy Information Administration [3], and H2A Production case studies [4]. A linear optimization algorithm uses these inputs to select the combination of hydrogen production resources that minimizes the average price for hydrogen at individual demand centers across the U.S. To account for the geographical variation in hydrogen resource feedstock supply and projected hydrogen demand, the model deconstructs the U.S. into a grid of discrete nodes, each with an associated resource supply and hydrogen demand. Using these inputs, the model projects the resources, infrastructure, and delivered price of hydrogen to each demand center. Ten different hydrogen production pathways were evaluated: coal gasification, natural gas, nuclear electrolysis, nuclear thermochemical hydrogen, biomass gasification, wind electrolysis, solar thermochemical, concentrating solar powered electrolysis, solar photovoltaic powered electrolysis, and landfill gas (LFG).

The Hydrogen Logistics Model was used to analyze a base case plus several sensitivity scenarios that vary factors such as demand, the price of CO₂, technology availability, and cost assumptions.

### Results

The results of scenario analysis performed using the Hydrogen Logistics Model indicate that if CC&S is available, hydrogen is produced primarily from fossil-based production pathways – even with carbon taxes as high as $100 per ton – although biomass and LFG also make an important contribution. If CC&S is not available, biomass becomes the dominant production pathway. Other resources – notably wind, nuclear, or solar thermochemical hydrogen – become widely adopted only when CC&S is unavailable and using favorable cost assumptions. The average delivered price of hydrogen was estimated to vary from $4.60 per kg under a high demand scenario with no carbon tax to $5.40 per kg under a high demand scenario with $100 per ton carbon tax and no CC&S available.

In the base case scenario, which assumes a $25 per ton carbon tax and that CC&S is utilized and does not include LFG, hydrogen is produced primarily from fossil resources (~80% of supply), with biomass accounting for the remaining 20% at an average delivered price of approximately $4.90/kg H₂. A summary of these base case results is shown in Table 1.

The dominant contributor to the price of hydrogen is the delivery cost, which averages $3.25/kg H₂ (nearly 70% of the selling price), and does not vary appreciably with the production pathway (Figure 1). Analysis of the variable (per-mile) and fixed delivery costs showed a large price impact, but relatively minor shifts in resource utilization. Carbon mitigation costs (carbon taxes plus the cost of CC&S) account for less than 5% of the selling price in the base case, but reduce emissions by 93% compared to a scenario with no carbon constraints. An illustrative map of the geographical distribution of the delivered price of hydrogen to demand centers is

### Table 1. Summary of Base Case Scenario Results

<table>
<thead>
<tr>
<th>Type</th>
<th>Production (TPD)</th>
<th>Percent</th>
<th>Avg. Cost ($/kg)</th>
<th># Plants</th>
<th>Avg. Plant Size (TPD)</th>
<th>Avg. Delivery Dist (mi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>8,040</td>
<td>20%</td>
<td>$5.05</td>
<td>28</td>
<td>320</td>
<td>100</td>
</tr>
<tr>
<td>Coal</td>
<td>20,000</td>
<td>50%</td>
<td>$4.88</td>
<td>10</td>
<td>2,020</td>
<td>80</td>
</tr>
<tr>
<td>NG</td>
<td>11,800</td>
<td>30%</td>
<td>$4.86</td>
<td>13</td>
<td>915</td>
<td>70</td>
</tr>
<tr>
<td>Total</td>
<td>39,800</td>
<td>100%</td>
<td>$4.91</td>
<td>51</td>
<td>805</td>
<td>80</td>
</tr>
</tbody>
</table>

TPD = tons per day; NG = natural gas; Avg. = average
VII. Systems Analysis

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DOE Hydrogen Program

Kromer – TIAX, LLC

As shown in Figure 2; alternative maps showing details such as the location and type of production plants and the delivery infrastructure may also be generated. As shown, hydrogen prices range from a low of $4.50 to a high of $5.95 per kg; a primary determinant of this price variation is the population density.

In addition to the base case, sensitivity scenarios that vary hydrogen demand (low, medium, and high); size of CO2 tax ($0, $25, and $100 per ton); availability of CC&S technology; and the cost and availability for individual production pathways (favorable wind, favorable nuclear, favorable solar thermochemical, and including landfill gas) were evaluated. Figure 3 shows the resource utilization and average hydrogen selling price using four different sets of carbon constraints at three different levels of demand. This set of scenarios uses the same cost assumptions as those used in the base case. As shown, only coal, natural gas, and biomass resources are utilized, although the distribution between the three varies across the scenarios. In particular, increasing the cost of carbon causes a shift from coal to natural gas and biomass, while increasing demand tends to favor fossil resources over biomass. These scenarios do not include LFG-to-hydrogen pathway, which was included as a sensitivity scenario. If it is included, its market share ranges from 30% at low demand to 4% at high demand with a modest downward effect on the price of hydrogen.

Other hydrogen production pathways – wind electrolysis, nuclear electrolysis, nuclear thermochemical, and solar thermochemical – are adopted only when more favorable cost assumptions are included in combination with high carbon taxes ($100 per ton) and assuming that carbon capture is not available. Figure 4 shows the effect of these more favorable cost assumptions at three different demand levels.

Additional calculations were performed to estimate the CO2 emissions impact and CO2 mitigation cost (in dollars per ton of CO2 avoided). These calculations show that if CC&S is available, CO2 emissions can be reduced by upwards of 95% at a cost of $15 to $20 per ton of CO2 avoided compared to a case with no carbon constraints. If CC&S is not available, CO2 emissions reductions range from 80 to 100% with costs ranging from $20 to $50 per ton. The cost and efficacy of CO2 mitigation is strongly influenced by demand if CC&S is not available, and weakly influenced if it is. These results suggest that at low demand, CO2 emissions can be avoided at relatively low cost across a robust set of scenario, but that the feasibility and widespread deployment CC&S is a critical element to low-cost and efficacious CO2 mitigation at high demand.

Conclusions and Future Directions

TIAX developed the Hydrogen Logistics Model to allow comparison between hydrogen production
pathways and to perform scenario analysis on future hydrogen fueling infrastructure. Key conclusions from this scenario analysis include:

- If carbon capture and sequestration is available or if the price of carbon is low, hydrogen is produced primarily from fossil-based production pathways, although biomass and LFG also make an important contribution, accounting for up to 30% of supply.
- LFG and biomass are the most economic non-fossil production pathways, and are adopted under a robust set of input assumptions. Other low carbon pathways are only adopted when favorable cost assumptions are included in combination with high carbon taxes.
- The average delivered price of hydrogen ranges from $4.60/kg to $5.45/kg. The efficacy of carbon capture and the level of demand are the key factors influencing this price variation.
- Using base case assumptions, the average delivered price of hydrogen is $4.90. This price varies geographically from $4.50 to $5.95 per kg. The dominant contribution to the hydrogen price is the delivery cost; population density is the primary determinant of the geographic variation in the price of hydrogen.
- The cost and efficacy of CO₂ mitigation is strongly influenced by demand if CC&S is not available and weakly influenced by demand if it is. Carbon mitigation costs range from $15 to $25 per ton of CO₂ avoided if carbon capture is available, but rise to as high as $50 per ton under high demand scenarios without carbon capture. From a policy perspective, this suggests that at low demand, CO₂ emissions can be avoided at relatively low cost, regardless of the costs and availability of technologies such as CC&S, nuclear-to-hydrogen, or low cost wind. However, the feasibility and widespread deployment CC&S is a critical element to low-cost and efficacious CO₂ mitigation as demand rises.

The current project has been completed. However, several additional areas for further work are proposed:

- Include distributed production pathways in the analysis: allows comparison of centralized and distributed production within the same framework.
- Further integrate inputs and outputs with existing Hydrogen Program tools (HyDRA, Macro-System Model, etc) or GIS tools (e.g., ArcGIS).
- Use a design-of-experiments approach to model hydrogen infrastructure transition and evolution over time.
- Introduce additional policy constraints – e.g., renewable portfolio standards, low carbon fuel mandates, production tax credits.
- Model competition with alternative end-uses (e.g., electricity).
- Characterize high sensitivity parameters using Monte Carlo analysis.

**FY 2010 Publications/Presentations**


**References**

VII.16 HyDRA: Hydrogen Demand and Resource Analysis Tool

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.
- Support interoperability between HyDRA and similar applications in other domains of energy infrastructure research.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell 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/Integration Milestones

This project will contribute to achievement of the following DOE milestones from the System Analysis and System 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 (System Integration): MSM analysis test cases. (4Q, 2006; 3Q, 2009; 4Q, 2010)

Accomplishments

- Completed the Macro System Model (MSM) dynamic integration that can, at the user’s request, produce six data layers based on user specified parameters and load them into HyDRA for visualization and querying.
- Initial interoperability between HyDRA and the Scenario Evaluation, Regionalization and Analysis (SERA) model was achieved in Fiscal Year (FY) 2010:
  - External datasets from multiple locations are available within the HyDRA interface.
  - Worked with SERA leadership to finalize the initial data input and delivery needs for SERA which will be supported by HyDRA.
- The strategy will also support interoperability between HyDRA and other systems, models, and analysis applications including the Bioenergy Knowledge Discovery Framework (BKDF).
- Interaction with the BKDF:
  - Enhancements on the BKDF project resulted in several data services being made available to HyDRA in the fourth quarter of FY 2010.
- Increased the number of spatial data layers related to hydrogen resource, infrastructure, and demand to over 90 layers. These datasets are comprised of background data, model input data, and results spatial analyses and modeling efforts.
- A diverse group of 257 users from 62 countries accessed the HyDRA application over 2,000 times in FY 2010.
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 analysis results from multiple domains of research to be explored and compared from within a single interface.

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 maps that can be queried to access the numbers behind the visualization. It is available at http://maps.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 can create their own spatial datasets and provide them to the HyDRA application to create a completely customizable and dynamic analysis tool.

The capability to explore and query spatial data layers is a core capability of the HyDRA application. There are currently more than 90 datasets available in the system including resource cost and availability, hydrogen production potential, hydrogen production cost, resource consumption, hydrogen demand, infrastructure, and results from integration with other hydrogen models. The ability to access externally hosted datasets and also to run the MSM model from within the HyDRA application will provide access to a significant number of additional datasets. Additionally, dynamic data acquisition services will provide up-to-date versions of data that change over time.

Results

The major HyDRA efforts that we completed this year involve the integration of HyDRA with the MSM, developments to support interoperability between HyDRA and SERA, and preliminary development of spatial analysis and complex querying within HyDRA.

The development of the HyDRA/MSM integration allows for an MSM job to be initiated from an MSM tab in the HyDRA interface. Users can submit a job to the MSM for any state and specify various parameters within their request. Users are limited to running jobs on a state basis due to the time each MSM run requires. MSM jobs take over five minutes per county to run, so larger states that include a sensitivity analysis on electricity cost can take several days. As a result the MSM jobs are submitted in a batch format so that users can send their MSM jobs from HyDRA and then continue using the application while the jobs run in the background. Status information is available in the MSM tab within the HyDRA application.

At this time the forecourt electrolysis MSM scenario can be run from within HyDRA. The interface provides a form for the entry of the required parameters and sends these to the MSM along with the electricity cost and grid mix for every county in the state. The MSM generates a resultant hydrogen cost, greenhouse gas emissions, total energy usage, fossil energy usage and petroleum energy usage for every county in the state. These data are accessible to the user through an interface in the HyDRA application along with the specific parameters entered by the user in the request (Figures 1). Additionally, a preliminary design was completed to support querying of HyDRA data by the MSM.

The NREL HyDRA team built a Web service (a specific uniform resource locator [URL] that allows computers to exchange data) that includes user authentication to allow MSM to access data contained in the HyDRA database such as the electricity and natural gas rates for specific counties (Figure 2). A Web
service specification was created that will allow the MSM team and the HyDRA team to develop in parallel which. This integration was completed early in the third quarter of FY 2010.

The effort to support interoperability between HyDRA and SERA is being implemented in such a way as to support interoperability between HyDRA and a number of other applications as well (Figure 3). This development effort allows users to specify external datasets that can be dynamically loaded into the HyDRA interface and also to load some HyDRA data directly within other applications. A prototype of this capability is shown in Figure 4 by displaying live weather data, which is an external data source, over the MSM greenhouse gas emissions.

As new datasets are ingested into HyDRA which support analysis and modeling efforts, such as the SERA model, HyDRA will become a venue for results of analysis and modeling applications. Users are able to load these results directly into HyDRA along with the existing HyDRA data layers and external data from applications such as the BKDF.

Conclusions and Future Directions

HyDRA provides a single point of reference for spatial data related to hydrogen. Improvements to the user interface and functionality provides an intuitive user experience. Additionally, the enhanced interoperability of HyDRA simplifies the direct use of this data in analysis and modeling and places HyDRA at the center of many other applications and research efforts. In the future HyDRA will:

- Develop a process for automatically updating SERA input data in the HyDRA application on a regular basis.
- Develop an interface to explore, visualize and display complex temporal and multivariate datasets.
- Provide an interface to dynamically create, print, and export images of maps and charts.
- Allow users to customize map classification and dynamically manipulate charting variables.
- Formalize data interoperability relationships and data exchanges between other spatial data analysis and visualization applications in other domains of research.
- Continue to 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.
- Continue to 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 2010 Publications/Presentations


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 toward technology readiness. Technology Validation tests, demonstrates, and validates hydrogen fuel cell technologies and infrastructure and uses the results to provide feedback to the Program’s research and development (R&D) activities.

**Goal**

Validate—under real-world operating conditions—the status, relative to Program targets, of integrated hydrogen and fuel cell technologies that will be used in both the transition and early market periods for transportation, infrastructure, and electric power generation.

**Objectives**

- **2014:** Validate a stationary fuel cell system that co-produces hydrogen and electricity at 40% efficiency, with 40,000-hour durability.
- **2015:** Validate fuel cell vehicles achieving 5,000-hour durability (service life of vehicle) and a 300-mile driving range between fueling.

**FY 2010 Technology Status**

In 2010, the National Learning Demonstration—a government-industry cost shared project initiated in 2004 with four automobile and energy company teams—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 five years has been analyzed. Thus far, more than 2.8 million miles have been traveled by the fuel cell vehicles in the project and 130,000 kg of hydrogen has been either produced or dispensed, with some of this hydrogen being used in vehicles not in the Learning Demonstration. Demonstrated fuel cell durability has exceeded 2,500 hours, and the vehicle driving range has exceeded the goal of 250 miles. Fuel cell system efficiency data at about 25% net power is 53–59% which is close to the DOE target of 60%.

In June 2009, the National Renewable Energy Laboratory (NREL) and Savannah River National Laboratory (SRNL) verified that Toyota’s FCHV-adv fuel cell vehicle can achieve a driving range of 430 miles without refueling (Figure 1). The report and related video on range estimates for the Toyota FCHV-adv have been issued.¹

**FY 2010 Accomplishments**

National Learning Demonstration

- Learning Demonstration projects by Ford and Chevron were completed in Fiscal Year (FY) 2010, and DOE expects final reports soon.
- Generation-2 vehicles continued to be operated by customers, and data was provided to the Hydrogen Secure Data Center at NREL (Figure 2).
- Figure 3 shows all of the major key performance metrics that have been reported in the National Hydrogen Learning Demonstration.

FIGURE 1. In June 2009, NREL and SRNL Verified Toyota FCVH-adv Driving Range of >400 Miles (without refueling)

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Average Trip Distance (miles)</th>
<th>H₂ Consumed (kg)</th>
<th>Remaining Usable H₂ (kg)</th>
<th>Calculated Remaining Range (miles)</th>
<th>Total Range (miles)</th>
<th>Average Total Range (miles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>331.50</td>
<td>4.8255</td>
<td>1.4854</td>
<td>102.04</td>
<td>433.55</td>
<td>431</td>
</tr>
<tr>
<td>#2</td>
<td>331.45</td>
<td>4.8751</td>
<td>1.4328</td>
<td>97.41</td>
<td>428.87</td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 2. Learning Demonstration Project Teams and their Two Generations of Vehicles
Fuel Cell Bus Evaluation

- Data has been collected on nine fuel cell buses at five sites. Overall, the buses have traveled more than 395,000 miles. Fuel economy results of the fuel cell buses were 39% to 141% better than diesel and compressed natural gas buses.

Hawaii Hydrogen Power Parks

- Selection of a contractor has been made, all agreements have been executed, and the hydrogen station is due to be delivered to Hawaii in FY 2010.
- The selected system is from PowerTech which produces 12 kg of hydrogen per day and allows rapid-fill to 350 bar with flexibility to expand output.
- At the Volcanoes National Park site, hydrogen is to be produced through electrolysis powered by renewable electricity from Hawaii Electric Light Company.
- Specifications for the shuttle buses were developed by the Hawaii Volcanoes National Park and the Hawaii Center for Advanced Transportation Technologies.
- The PowerTech fueling station will be deployed at the Marine Corps base in Hawaii to support General Motors Equinox fuel cell vehicles until vehicles at Volcanoes National Park are ready for deployment.

Energy Station at Fountain Valley

- Air Products and FuelCell Energy shipped the fuel cell system to Fountain Valley, California, and completed the installation at the Orange County Sanitation District. Initial operation will use natural gas, in order to obtain baseline information to compare with the system’s operation prior to shipment.

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**Vehicle Performance Metrics**

<table>
<thead>
<tr>
<th></th>
<th>Gen 1 Vehicle</th>
<th>Gen 2 Vehicle</th>
<th>2009 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel Cell Stack Durability</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max Team Projected Hours to 10% Voltage Degradation</td>
<td>1,807 hours</td>
<td>2,521 hours</td>
<td></td>
</tr>
<tr>
<td>Average Fuel Cell Durability Projection</td>
<td>821 hours</td>
<td>1,062 hours</td>
<td></td>
</tr>
<tr>
<td>Max Hours of Operation by a Single FC Stack to Date</td>
<td>2,375 hours</td>
<td>1,261 hours</td>
<td></td>
</tr>
<tr>
<td><strong>Driving Range</strong></td>
<td>103-190 miles</td>
<td>196-254 miles</td>
<td>250 miles</td>
</tr>
<tr>
<td><strong>Fuel Economy (Window Sticker)</strong></td>
<td>42 – 57 mi/kg</td>
<td>43 – 58 mi/kg</td>
<td>no target</td>
</tr>
<tr>
<td><strong>Fuel Cell Efficiency at 1/4 Power</strong></td>
<td>51 - 58%</td>
<td>53 - 59%</td>
<td>60%</td>
</tr>
<tr>
<td><strong>Fuel Cell Efficiency at Full Power</strong></td>
<td>30 - 54%</td>
<td>42 - 53%</td>
<td>50%</td>
</tr>
</tbody>
</table>

**Infrastructure Performance Metrics**

<table>
<thead>
<tr>
<th></th>
<th>On-site natural gas reform</th>
<th>On-site Electrolysis</th>
<th>2009 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂ Cost at Station (early market)</strong></td>
<td>$7.70 - $10.30</td>
<td>$10.00 - $12.90</td>
<td>$3/gge</td>
</tr>
<tr>
<td>Average H₂ Fueling Rate</td>
<td>0.77 kg/min</td>
<td>1.0 kg/min</td>
<td></td>
</tr>
</tbody>
</table>

*Outside of this project, DOE independent panels concluded at 500 replicate stations/year: Distributed natural gas reform at 1500 kg/day: $2.75-$3.50/kg (2006) Distributed electrolysis at 1500 kg/day: $4.90-$5.70 (2009)

FC – fuel cell; gge – gasoline gallon equivalent

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**FIGURE 3.** Summary of Key Performance Metrics for the Learning Demonstration
The funding portfolio for Technology Validation addresses the need to validate integrated hydrogen and fuel cell technologies for transportation, infrastructure, and electric power generation in a systems context, under real-world operating conditions. In FY 2010, $13 million in funding was appropriated for the Technology Validation sub-program. The President’s FY 2011 request includes $11 million for Technology Validation activities.

FIGURE 4. Concept for the Energy Station at Fountain Valley, California

Budget

The funding portfolio for Technology Validation addresses the need to validate integrated hydrogen and fuel cell technologies for transportation, infrastructure, and electric power generation in a systems context, under real-world operating conditions. In FY 2010, $13 million in funding was appropriated for the Technology Validation sub-program. The President’s FY 2011 request includes $11 million for Technology Validation activities.
FY 2011 Plans

In FY 2011 the final two National Learning Demonstration projects (General Motors and Mercedes-Benz North America) will conclude and final reports will be prepared.

The Program’s validation activities also encompass fuel cell buses. The Technology Validation sub-program collaborates with the Department of Transportation to validate fuel cell and hydrogen technologies in transit bus demonstrations conducted by the Federal Transit Administration, and to harmonize data collection efforts with other fuel cell buses demonstrations worldwide.

In FY 2011, the power park at Volcanoes National Park will begin operation, supplying electricity to the visitors’ center and hydrogen fuel to the plug-in hybrid fuel cell shuttle buses.

The Hydrogen Energy Station at Fountain Valley will be fully operational in FY 2011 and data will be collected on electric power and heat generation, hydrogen production, and vehicle refueling.

Within its Market Transformation activities, the Program has collaborated with the Department of Defense (DOD) Defense Logistics Agency (DLA) on the demonstration of fuel cell forklifts. As the main provider of fuel and supplies for the DOD 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 operation and performance data of the forklifts.

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Objectives

- By 2008, validate that hydrogen vehicles have a 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/gallons of gasoline equivalent (gge) (untaxed) delivered and safe and convenient refueling by drivers (with training).
- Assist DOE in demonstrating the use of fuel cell electric vehicles (FCEVs) 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 technical progress.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Fuel Cell Technologies (FCT) Program’s 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

Throughout the duration of this project, researchers are gathering data and providing technical analysis that is contributing to achieving the following DOE technology validation milestones from the FCT Program’s Multi-Year Research, Development, and Demonstration Plan:

- **Milestone 2:** Demonstrate FCEVs that achieve 50% higher fuel economy than gasoline vehicles (Q3, FY 2005). This milestone was achieved.
- **Milestone 3:** Decision for purchase of additional vehicles based on projected vehicle performance and durability and hydrogen cost criteria (Q4, FY 2006). This milestone was 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). This milestone was achieved.
- **Milestone 5:** Validate vehicle refueling time of 5 minutes or less for a 5 kg tank [1kg/min] (Q4, FY 2006). At the time of the milestone, we had analyzed over 2,000 vehicle refueling events and had 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 3.5 years later, data from over 25,000 refueling events showed improved results with an average rate of 0.77 kg/min with 22% of refueling events exceeding 1 kg/min. This milestone was 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). Currently, the data show that communication fills can refuel at a higher rate (up to 1.8 kg/min) and have an average fill rate 30% higher than non-communication fills (0.86 kg/min vs. 0.66 kg/min). This milestone was achieved.
• Accomplishments
  • Received and processed data from a total of 436,000 individual vehicle trips, amounting to over 98 GB of on-road data, since inception of the project.
  • Created and published 80 CDPs (the ninth and largest set of public results) representing results from analyzing almost five years of Learning Demonstration data.
  • Documented and archived each quarter's analysis results in the Fleet Analysis Toolkit (FAT) graphical user interface.
  • Milestone 8: Fuel cell vehicles demonstrate the ability to achieve a 250-mile range without impacting passenger cargo compartment (Q4, FY 2008). This milestone was achieved in 2008 using data from the Learning Demonstration results, with range between 196–254 miles. In June 2009, an on-road driving range evaluation was performed in collaboration with Toyota and Savannah River National Laboratory. The results indicated a 431-mile on-road range was possible in southern California using Toyota’s FCHV-adv fuel cell vehicle. This milestone was achieved.
  • Milestone 10: Validate FCEVs 2,000-hour fuel cell durability using fuel cell degradation data (Q4, FY 2009). On-road fuel cell voltage data from second-generation fuel cell systems were analyzed and published in the Fall 2009 CDP results. Results indicate that the highest projected team average to 10% voltage degradation for second-generation systems was 2,521 hours, with a four-team average of 1,020 hours. The Spring 2010 results only slightly increased the average (to 1,062 hours) and the highest team remained the same at 2,521 hours. This milestone was achieved.
  • Milestone 23: Total of 10 stations constructed with advanced sensor systems and operating procedures (Q1, FY 2008). This milestone was achieved.
  • Milestone 24: Validate a hydrogen cost of $3.00/gge (based on volume production) (Q4, FY 2009). Cost estimates from the Learning Demonstration energy company partners were used as input to an H2A analysis to project the hydrogen cost for 1,500 kg/day early market fueling stations. Results indicate that on-site natural gas reforming would lead to a range of $8-$10/kg and on-site electrolysis would lead to $10-$13/kg hydrogen cost. While these results do not meet the $3/gge cost target, two external independent panels concluded that distributed natural gas reforming could lead to $2.75-$3.50/kg [1] and distributed electrolysis could lead to $4.90-$5.70 [2]. This milestone was achieved outside of the Learning Demonstration project.

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 FCEVs and hydrogen refueling infrastructure under real-world conditions using multiple sites, varying climates, and a variety of sources for hydrogen. Specific targets for 2009 were hydrogen vehicles with a range greater than 250 miles, 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 project duration, particularly between the first- and second-generation fuel cell vehicles. 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 FCT R&D activities more quickly toward cost-effective, reliable hydrogen FCEVs and supporting refueling infrastructure.

Approach

Our approach to accomplishing the project’s objectives is structured around a highly collaborative relationship with each of the industry teams, including Chevron/Hyundai-Kia, Daimler/BP, Ford/BP, General Motors/Shell, and Air Products (through the DOE California Hydrogen Infrastructure Project). 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 teams. Our primary objectives are to feed the current technical challenges and opportunities back into the DOE FCT 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 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 most significant results. Additional CDPs are being conceived as additional results and results of interest are identified, and as we receive requests from DOE, industry, and the codes and standards community. 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 to obtain feedback on our methodologies.

Results

The results in Fiscal Year (FY) 2010 came from analyzing an additional year of data (January – December 2009), creating a total of 80 new or updated CDPs, and presenting these results at many technical conferences. To accomplish this, we continued to improve and revise our in-house analysis tool, FAT. Since there are 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 conferences in the last year as two distinct sets of results (labeled “Fall 2009” and “Spring 2010”). Since all 80 of the results are now available on the Web site, this report will just include some of the highlights over the last year. Figure 1 shows the cumulative number of vehicles that have been deployed by quarter and hydrogen storage system type. A total of 144 vehicles were deployed through March, with 127 of those vehicles retired from the project and 17 still on the road. By fall 2010, there should be roughly 40 vehicles on the road with a cumulative 160 vehicles deployed since project inception.

- **Real-World Vehicle Driving Range:** In FY 2008, the driving range of the project’s FCEVs was evaluated based on fuel economy from dynamometer testing and on-board hydrogen storage amounts and compared to the 250-mile target. Since that time, significant on-road data have been obtained from second- and first-generation vehicles. This allowed us to evaluate the distribution of real-world driving ranges of all the vehicles in the project. The data show (Figure 2) that there has been a 45% improvement in the median real-world driving range.
range of second-generation vehicles (81 miles) as compared to first-generation (56 miles), based on distances driven between over 25,000 refueling events. Obviously the vehicles are capable of two to three times greater range than this, but the median distance travelled between refuelings is one way to measure the improvement in the vehicles’ capability and the way in which they are actually being driven. The Toyota on-road FCHV-adv range evaluation (discussed in the milestone section) was an additional way to see how far FCEVs could be driven in everyday typical use in southern California through a one-day test with two vehicles.

**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 when 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 conditions. This enabled us to track the gradual degradation of the stacks with time and do a linear fit through each team’s data. The methodology was subsequently improved to include a two-segment linear fit and also use a weighting algorithm to come up with a more robust fleet average.

In the past three and a half years since the first fuel cell durability evaluation, many more hours have been accumulated on the fuel cell stacks. The maximum number of hours a first-generation stack has accumulated without repair is 2,375, which is the longest stack durability from a light-duty vehicle FCEV in normal use published to date. Now that the data submissions are complete on first-generation stacks, we can make some conclusions. The initial power degradation is steeper in the first 200 hour hours and flattens out after that (see Figure 3 for the maximum fuel cell power loss as a function of operating hours, with an overall red trend line added). We also needed around 1,000 hours of data accumulated to determine the slope of the more gradual degradation. Finally, with significant drops in power observed at 1,900–2,000 hours, it appears as though this is a solid upper bound on first-generation stack durability. For second-generation fuel cell stacks, the range of maximum hours accumulated from the four teams is now ~800 to over 1,200 hours, with the range of team average hours accumulated of ~300 to 1,100 hours. Relative to projected durability, the Spring 2010 results indicate that the highest average projected team time to 10% voltage degradation for second-generation systems was 2,521 hours, with a multi-team average projection of 1,062 hours.
Therefore, the 2,000-hour target for durability has been validated.

- **Factors Affecting Fuel Cell Durability – Voltage Transients:** In the Spring 2010 results, there were several new results that quantified fuel cell voltage transients from multiple different angles. NREL used a 3-step process where we 1) defined a voltage transient cycle by a drop in voltage, followed by a rise, and finally a steady-state period; 2) identified the voltage transient cycles during all data we had accumulated; and 3) categorized and collected transient cycle details for subsequent analysis. One of the highlights from this analysis was that we observed a significant reduction in the voltage transients for second-generation systems from the first-generation systems (a factor of four reduction in voltage cycles per mile for one team). This comes from a combination of hybridization and control strategy improvements, and should help to improve overall durability. In the coming year, NREL will evaluate whether or not an effect on durability from voltage cycling can be determined based on an expanded multivariate analysis.

- **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 one-quarter-power is 60%. Data from the four Learning Demonstration teams showed a range of first-generation net system efficiencies from 51% to 58%, which is very close to the target. Results are now available for the second-generation systems, which revealed slightly improved efficiency at one-quarter-power of 53% to 59%. These results are significant because they show that the system efficiency has not been sacrificed in order to achieve improved durability and freeze capability. In addition to the efficiency at one-quarter-power, we have updated CDP 8 to include the range of system efficiency as a function of power, sweeping from 5% power up to 100% power, as shown in Figure 4.

- **Summary of Performance against Major Project Targets:** Since there are so many results for the two generations of vehicles in this project, we have summarized the key performance numbers and compared them to DOE targets in Table 1. The table shows that this project has exceeded the expectations established in 2003 by DOE, with all of the key targets being achieved except for on-site hydrogen production cost, which would have been difficult to

TABLE 1. Learning Demonstration Key Performance Metrics Summary.

<table>
<thead>
<tr>
<th>Vehicle Performance Metrics</th>
<th>Gen 1 Vehicle</th>
<th>Gen 2 Vehicle</th>
<th>2009 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel Cell Stack Durability</strong></td>
<td></td>
<td></td>
<td>2,000 hours</td>
</tr>
<tr>
<td>Max Team Projected Hours to</td>
<td>1,807 hours</td>
<td>2,521 hours</td>
<td></td>
</tr>
<tr>
<td>10% Voltage Degradation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Fuel Cell Durability</td>
<td>821 hours</td>
<td>1,062 hours</td>
<td></td>
</tr>
<tr>
<td>Projection</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max Hours of Operation by a Single FC Stack to Date</td>
<td>2,375 hours</td>
<td>1,261 hours</td>
<td></td>
</tr>
<tr>
<td><strong>Driving Range</strong></td>
<td>103-190 miles</td>
<td>196-254 miles</td>
<td>250 miles</td>
</tr>
<tr>
<td><strong>Fuel Economy (Window Sticker)</strong></td>
<td>42 – 57 mi/kg</td>
<td>43 – 58 mi/kg</td>
<td>no target</td>
</tr>
<tr>
<td><strong>Fuel Cell Efficiency at ¼ Power</strong></td>
<td>51 - 58%</td>
<td>53 - 59%</td>
<td>60%</td>
</tr>
<tr>
<td><strong>Fuel Cell Efficiency at Full Power</strong></td>
<td>30 - 54%</td>
<td>42 - 53%</td>
<td>50%</td>
</tr>
<tr>
<td><strong>Infrastructure Performance Metrics</strong></td>
<td></td>
<td></td>
<td>2009 Target</td>
</tr>
<tr>
<td><strong>H₂ Cost at Station (early market)</strong></td>
<td>$7.70 - $10.30</td>
<td>$10.00 - $12.90</td>
<td>$3/gge</td>
</tr>
<tr>
<td>Average H₂ Fueling Rate</td>
<td>0.77 kg/min</td>
<td>1.0 kg/min</td>
<td></td>
</tr>
</tbody>
</table>

1 Gross stack power minus fuel cell system auxiliaries, per DRAFT SAE J2615. Excludes power electronics and electric drive.
2 Ratio of DC output energy to the lower heating value of the input fuel (hydrogen).
3 Individual test data linearly interpolated at 5,10,15,25,50,75, and 100% of max net power. Values at high power linearly extrapolated due to steady state dynamometer cooling limitations.

*Outside of this project, DOE independent panels concluded at 500 replicate stations/year: Distributed natural gas reforming at 1500 kg/day: $2.75-$3.50/kg (2006)
Distributed electrolysis at 1500 kg/day: $4.90-$5.70 (2009)
demonstrate through this project. Additional data accumulated and analyzed in 2010–2012 will assess the latest generation of FCEV technology, which includes improvements over the second-generation systems included in the results to date. It will also include data analysis from many new hydrogen stations being commissioned in California, all of which will have 700-bar fueling capability.

Conclusions and Future Direction

- Completed the first five years of the seven-year project with 144 vehicles deployed in fleet operation, 23 project refueling stations constructed, and no major safety barriers encountered.
- Analyzed data from 436,000 individual vehicle trips covering 2.5 million miles traveled and 130,000 kg hydrogen produced or dispensed.
- Verified that high fuel cell system efficiency was maintained from Gen 1 to Gen 2 systems, with Gen 2 efficiency at quarter-power ranging from 53 to 59%, close to the 60% DOE target.
- Published 80 CDPs to date and made them directly accessible to the public from an NREL Web site.
- Expanded fuel cell system degradation analysis to include detailed transient voltage study and metrics.
- We will create new and update CDPs based on data collected through June 2010 (Fall 2010 CDPs) and present results for publication at 2010 Fuel Cell Seminar.
- We will support original equipment manufacturers, energy companies, and state organizations in California in coordinating early infrastructure plans.
- We will gather and analyze data from a relatively large hydrogen station in Burbank, California, along with many new stations that are being opened in California in the next year.
- NREL will continue to identify opportunities to feed findings from the project back into Vehicle Technologies and Fuel Cell Technologies programs and industry R&D activities to maintain the project as a “learning demonstration.”
- We will continue to gather data from FCEVs and hydrogen stations through 2011, and publish the Spring 2011 and Fall 2011 CDPs and potentially one final set of results in Spring 2012.
- As the last deliverable from this project, we will write a final comprehensive summary report for publication.

FY 2010 Publications/Presentations


References


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

Start Date: January 15, 2004  
Projected End Date: December 31, 2009

Objectives

Validate performance targets:
• Fuel cell stack durability: >2,000 hours  
• Vehicle range: >250 miles  
• Hydrogen cost: <$3.00/gasoline gallon equivalent (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 reformulation of natural gas  
• High pressure steam reformulation of natural gas  
• Electrolysis of water

Technical Barriers

This project addressed the following technical barriers from the Technology Validation section of the Fuel Cell 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

Contribution to Achievement of DOE Technology Validation Milestones

This project contributed to achievement of the following DOE milestones from the Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation Project of the Fuel Cell 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 entered the project  
• One additional vehicle was added to the project  
• Five infrastructure stations provided safe operation for the duration of the project  
• Two maintenance facilities provided safe vehicle operation  
• Safe and convenient refueling by drivers was demonstrated
VIII. Technology Validation

- Cold weather vehicles testing completed
- Survey of fuel cell vehicle (FCV) drivers conducted

Introduction

As a result of President Bush’s Initiative, the DOE detailed a strategy to develop a hydrogen economy that emphasized 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 was an important first step towards achieving the above strategy because the selected consortia developed a complete system solution(s) that addressed all elements of infrastructure and vehicle development.

The goals were accomplished by developing hydrogen infrastructures and hydrogen-powered vehicles at selected U.S. locations. This Technology Validation project provided an opportunity to participate in a cost-shared demonstration of hydrogen infrastructure and vehicle technologies.

Approach

CTV and its project team of HMC, HATCI, UTC and the site hosts operated a fully integrated fueling and fleet operation consisting of 32 FCVs, (including two different generations) while 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 was collected in a manner that allowed ‘consumer’ (including station operators, fuelers, drivers and maintenance workers) feedback to be recognized and incorporated into lessons learned.

Learning’s from the early phases of this project were incorporated into later phases in a way that allowed 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 . . . “, vehicles were operated 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 1). Hyundai addressed the barrier of “Lack of facilities for maintaining hydrogen vehicles” by operating three maintenance facilities including the training of operators to maintain the vehicles (Figure 2). Training was also conducted for first responders at all stations. Refresher training was offered each year to local first responders to support the training of new responders to the communities around the hydrogen stations. In addition, hypothetical fire response drills were held at the stations (Figure 3).

In support of DOE’s objective “By 2009, . . . safe and convenient refueling by drivers (with training),” Chevron trained drivers to conduct fueling of the FCVs. Drivers performed hundreds of safe refueling events at several infrastructure stations 24/7 (Figure 4).
Chevron operated 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 was provided to NREL and is stored at the Hydrogen Secure Data Facility in Golden, Colorado. A hydrogen energy station operated at HATCI in Chino, California. This station demonstrated the on-site auto-thermal reformation of natural gas. The Chino site served 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 operated at ACT in Oakland California. This station was only partially funded by the DOE project but the data from the station was shared with NREL. This station demonstrated the use of on-site low-pressure and high-pressure steam methane reforming.

A hydrogen energy station was installed at the Progress Energy site in Orlando, Florida. This station was not funded by DOE but CTV reported the station data to NREL. A hydrogen energy station operated at the SCE site in Rosemead, California. This site demonstrated on-site production of hydrogen using electrolysis. A cold-weather hydrogen energy station operated at the Selfridge Air National Guard site in Selfridge, Michigan.

Conclusions and Future Directions

Thirty-two vehicles were entered into the project. One additional vehicle was added to the project. Four vehicles remain in operation at HATCI in Chino, California. The other vehicles have been retired. Five hydrogen infrastructure stations have completed operation for the project.

FY 2010 Publications/Presentations

Objectives

- Record, collect and report data from fuel cell vehicles (FCVs) and the hydrogen fueling operations to validate DOE targets:

<table>
<thead>
<tr>
<th>Performance Measure</th>
<th>2009</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Cell Stack Durability</td>
<td>2000</td>
<td>5000</td>
</tr>
<tr>
<td>Vehicle Range</td>
<td>250</td>
<td>300</td>
</tr>
<tr>
<td>Hydrogen Cost at Station</td>
<td>$3/gge</td>
<td>$2-3/gge</td>
</tr>
</tbody>
</table>

- Demonstrate the safe installation of hydrogen fueling stations and fuel cell service facilities as well as the safe operation of all FCVs.
- Continuously update safety manuals and provide training.
- Participate in various working groups to ensure continuous progress towards establishing codes and standards essential for FCV commercialization.
- Raise public awareness of hydrogen technology and demonstration projects.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Fuel Cell 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 7**: Validate vehicle refueling time of 5 minutes or less for a 5 kg of hydrogen (1 kg/min) at 5,000 psi through the use of advanced communication technology. (4Q2007)
- **Milestone 8**: Fuel cell vehicles demonstrate the ability to achieve 250 mile range without impacting passenger cargo compartment. (4Q2008)
- **Milestone 10**: Validate FCVs 2,000 hour fuel cell durability using fuel cell degradation data. (4Q2009)
- **Milestone 12**: Validate cold start capability at -20°C. (2Q2011)

Accomplishments

- Externally operated Gen II vehicles for the sixth consecutive year although the vehicles were designed for a 2-year operation.
- Submitted over 100 DVDs of raw data to the National Renewable Energy Laboratory (NREL).
- Finalized internal operation and testing of Gen II pre-production vehicles.
- Preparing for Gen II deployment with external customers and dealership.
- Improved equipment reliability and maintained operation of the DTE refueling station.
Participated in various working groups to ensure continuous progress with regards to codes and standards.

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 Mercedes Team, together with its partners, have been testing the technology by operating and fueling hydrogen FCVs under real world conditions in varying climate, terrain and driving conditions. Vehicle infrastructure data has been collected to monitor the progress toward the hydrogen vehicle and infrastructure performance targets of $2.00–3.00/gasoline gallon equivalent (gge) hydrogen production cost and 2,000-hour fuel cell durability. Furthermore, progress has been made to validate cold-start capability at -20°C. 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 Mercedes 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 similar operations as Gen I vehicles to compare technology maturity during the project 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 FCVs against the DOE technology validation milestones. The energy partners have installed an infrastructure to provide hydrogen to the Mercedes 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 Mercedes 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, and emergency responders training.

Results

Gen I FCVs

Although the Gen I FCV fleet was designed for a 2-year operation, A-Class FCVs have outperformed engineering expectations as the vehicles have been in full operation for over six consecutive years. Since the inception of this demonstration project, customers have fuelled and driven the vehicles in a variety regions providing a complete range of climate and traffic conditions from congested city driving to open road highways (see Figure 1) to rural roads. All Gen I vehicles have been equipped with extensive data acquisition and reporting capability, allowing the Mercedes Team to generate over 100 DVDs of vehicle raw data for submission to NREL.

Gen II Technical Accomplishments

As the Gen I FCVs have been driven for over six years, the Mercedes Team is gradually transitioning the operation from Gen I A-Class FCVs to Gen II B-Class FCVs. Gen II FCVs have been tested and internally operated in a wide range of terrains, driving conditions and climates including diverse temperature, humidity and ambient air pressure. For example, the B-Class FCVs were operated under real-life winter conditions at double-digit, below-zero temperatures where cold-start capability was subjected to thorough scrutiny and FCVs repeatedly started with frozen fuel cell systems (see Figure 2). B-Class FCVs were also
driven in deserts during the harsh summer months when temperatures may reach up to 122°F (Figure 3). To expedite mileage accumulation and expeditiously provide DOE with on-road data, Gen II vehicles were operated by test operators on routes specifically selected to simulate real-world conditions. These durability tests demonstrated the reliable vehicle configuration and uncompromising performance of the Mercedes Gen II FCV. To complement on-road testing, the Mercedes Team performed dynamometer tests showing that Gen II vehicles exceed the 2009 DOE range targets and attain best-in-class fuel economy.

Not only has the Mercedes Team finalized the assembly and manufacturing of all B-Class FCVs designated for external operations through an assembly process similar to traditional vehicles, but authorized Mercedes-Benz dealership are being selected for Gen II fuel cell market in southern California. These dealers will act as the handover point, and make the transaction to customers. These dealers will also provide all customer interfaces for service and maintenance activities, as well as the turn-in point at lease end. The Mercedes Team is in the process of selecting initial customers from a compiled list of inquiries received via normal channels, previous partners in the A-Class FCV project and specific fuel cell related inquiries.

Codes and Standards

The Mercedes Team participated in various working groups to support and assist in the development of codes and standards necessary to commercialize FCVs. Of particular note is Society of Automotive Engineers (SAE) J2601, “Fueling Protocols for Gaseous Hydrogen Surface Vehicles,” the first worldwide published guideline that established a fueling baseline for hydrogen FCVs. It is anticipated that future stations funded by the California Air Resources Board (CARB) and the California Energy Commission (CEC) will adhere to J2601. The SAE Fueling Interface Group has also made strides with J2600, “Compressed Hydrogen Surface Vehicle Fueling Connection Devices” and is currently determining whether the guideline should follow the proposed H70 geometry from the corresponding International Organization for Standardization (ISO) document. A revised draft of J2719, “Information Report on the Development of Hydrogen Quality Guideline for Fuel Cell Vehicles” is expected by June of 2010 in which the report will incorporate the proposed changes from corresponding ISO documents. The SAE Safety Working Group has made continued efforts to update J2578, “Recommended Practice for General Fuel Cell Vehicle Safety” and J2579, “Technical Information Report for Fuel Systems in fuel Cell and Other H2 Vehicles.”

The Mercedes Team began its initial involvement with Canadian Standards Association (CSA) America 4.3 (“Temperature Compensation systems”) and ISO Working Group 5 in which the members are actively involved in Draft International Standard 17268, “Gaseous Hydrogen Land Vehicle Refueling Connection Devices.”

NextEnergy

NextEnergy continued to work on the National Fire Protection Association 2 Standard, intended to provide clarity to the infrastructure design process and to streamline permitting. NextEnergy is a voting member of the technical committee which has been instrumental in developing this extraction code for the industry. Being a voting member continues indefinitely but NextEnergy believes that it is vital to continue participation through the initial release and the first modification cycle of the document.

NextEnergy Center also held a 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, CSA America, Compressed Gas Association, International Code Council, and the ISO.

Safety and Health

The process of fully commissioning the Burbank Station was completed. As a part of this process, a number of test fills were performed by the Mercedes Team to ensure that all of the safety and communication systems were fully operational. Additionally, fueling training was provided to employees of Mercedes, California Fuel Cell Partnership and City of Burbank.

Despite the novelty of 70 MPa fueling, the Mercedes Team determined that the technology was mature.
enough to remove the personal protective equipment requirements at the City of Burbank Station for both 35 MPa and 70 MPa fueling.

The Incident Management Plan is receiving a major overhaul, as it is revised to fit the 2010 customer model. While the Plan is still in development, select dealers will play an active role in some safety relevant communications. In addition, the Safety Plan was updated to reflect the new company structure.

Outreach and Media

Mercedes-Benz FCVs were on display at several national shows over the course of 2009 and 2010. The year began with a presence at the Detroit Auto Show where the Concept BlueZero with its battery and fuel cell electric drive models was presented along with video material about the next generation B-Class F-Cell. The F-Cell was incorporated into the Mercedes-Benz exhibit at the Washington Auto Show in Washington, D.C. in February. The following month in Columbia, South Carolina, the Mercedes Team organized a presence at the National Hydrogen Association meeting where the 700 bar A-Class F-Cell was part of a ride-n-drive and the F600 cutaway model attracted participants in the exhibition hall. Finally, at the Los Angeles Auto Show in December, the B-Class F-Cell was presented for the first time in North America as part of a sustainability platform at the Mercedes-Benz exhibit booth.

The largest FCV-specific outreach event was the Hydrogen Road Tour in which seven auto manufacturers including Daimler participated. The convoy drove over 1,400 miles in nine days starting near the Mexican border in Chula Vista, CA and ending in Vancouver, Canada with a ride-n-drive finale at the Hydrogen and Fuel Cells 2009 Conference. The Team participated with two 700 bar A-Class FCVs. The A-Class F-Cells performed well and capably held their own vis-à-vis the newer FCV models of the other manufacturers.

Fueling Stations and Co-Production Facilities

DTE Hydrogen Technology Park

DTE Energy completed the installation of the replacement electrolyzer/dispenser, and as a result, the site equipment has run the best of any year thus far. DTE Energy has had a number of tours of the DTE Energy Hydrogen Technology Park both from industry, educational institutions and the general public (Figure 4). On Thanksgiving Day, the Park was shown on local television featuring solar, hydrogen and green economy. Not only was remote data collection added to collect dispenser data at the site, but modifications were also made to the dispenser to support fast-fill communications with 700 bar vehicles. Final technical report for the Technology Validation portion of the project has been finished with Lawrence Technological University graduate students and has been sent to the State of Michigan.

Preparing for Fueling Infrastructure

As FCVs transition from a demonstration phase to commercialization, the development of well-established hydrogen fueling station network is critical and, as a result, the Mercedes Team has been actively collaborating with other auto manufacturers, government officials and energy partners to build a hydrogen fueling infrastructure:

- Supported CARB/CEC by recommending station specifications, site locations and supplier qualification guidelines.
- Provided commitment letters to appropriate suppliers requesting government funding and meeting Mercedes-Benz Research & Development North America requirements.
- Worked with the California Fuel Cell Partnership to develop an action plan detailing strategy for deploying hydrogen fuelling stations and FCVs.
- Collaborated with other auto manufacturers to determine and coordinate locations of future fueling stations.

Summary and Future Directions

Summary

- Improved equipment reliability and maintained operation of the DTE hydrogen fueling station.
- Continued mileage accumulation of Gen I vehicles.
- Finalized internal operation and testing of Gen II pre-production vehicles.
- Preparing for Gen II deployment with external customers and dealerships.
• Participated in various working groups to ensure continuous progress with regards to codes and standards.
• Continued data collection, analysis and reporting.

Future Work

• Prepare for Gen II demonstrations.
• Maintain and finalize smooth operation of Gen I FCVs with on-going service, maintenance and customer support.
• Begin customer operations of production-level Gen II vehicles.
• Maintain the high quality of technical vehicle and infrastructure data reporting to NREL.
• Enlist support of corporate communications for a more expansive national outreach in addition to ongoing community and industry related events.

Lessons Learned

Deploying FCVs and placing a hydrogen fueling station is a unique experience that breaks new ground. Based on the experiences and lessons learned, the following conclusions and recommendations are made:

• Extensive real world experience provided by DOE’s Demonstration and Validation Project has shown that vehicles are ready for the commercialization phase.
• Customers need public, customer-friendly fueling stations with no access agreements.
• Older, strategically located hydrogen fueling stations need to be updated with 700 bar fast-fill fueling standards, such as “SAE J2601 (A70), to enable safe, fast and effective fueling for all vehicles.
• Auto manufacturer, energy company and government agency coordination is important for optimal selection of sites.
• Continued DOE funding and political support is essential.
Objectives

General Motors and energy partner Shell Hydrogen, LLC, will deploy a system of hydrogen fuel cell electric vehicles (FCEVs) integrated with a hydrogen refueling infrastructure to operate under real world conditions. With this deployment General Motors and Shell Hydrogen will:

- Demonstrate progressive generations of fuel cell system technology.
- Demonstrate multiple approaches to $\text{H}_2$ generation and delivery for vehicle refueling.
- Collect and report operating data.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Fuel Cell 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 Fuel Cell 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**: Six stations and two maintenance facilities constructed with advanced sensor systems and operating procedures. (4Q, 2006)

Accomplishments

General Motors has accomplished the following project milestones:

- Deployed 60 vehicles demonstrating two generations of GM’s proprietary fuel cell technology in various terrains, driving conditions, and climates (see Figure 1).

- 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.
VIII. Technology Validation

Established retail and retail-like hydrogen stations for public fueling:
- Six fueling stations in operation spreading across the eastern and western regions.
- 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.
- Hydrogen 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.

Shell Hydrogen opened new stations in the New York City metropolitan area at the John F. Kennedy International Airport and in Bronx during 2009. They also commissioned a station in Culver City, California (Los Angeles). These stations utilize hydrogen compressed gas delivered by truck and dispense hydrogen at 700 bar utilizing equipment supplied by several companies.

Gathered comprehensive feedback on all elements of customer experience and vehicle performance to guide future FCEV and infrastructure development.

Collected vehicle and station data using automated logbook entry and automated wireless data transfer from vehicles to a data server.

Conducted and verified extensive cold weather performance testing; additionally, vehicles were deployed in the north east U.S. through several winters and performed as customers expected (see Figure 2).

GM continues to operate and maintain 10 baseline Phase 2 (Gen2) FCEVs through 2011 or until failure.

Ten additional Phase 2 FCEVs equipped with technology developed during the initial part of Phase 2 were added in 2010 in order to extend learnings. These “Technology Insertion” vehicles were deployed and are accumulating miles (see Figure 3).

Three fuel cell systems were instrumented with the same hardware as the Technology Insertion vehicles and are running accelerated durability tests on test stands.

Introduction

Over the five-year period to date, the project has made significant progress in support of the long-term goals of DOE’s Technical Validation sub-program. GM has deployed eight Phase 1 FCEVs and 42 of its commercially-developed Phase 2 FCEVs and has maintained them through the use of two primary maintenance and training hubs and two additional satellite locations.

For the rest of the project, GM will continue to operate and maintain 10 baseline Phase 2 FCEVs. These baseline Phase 2 FCEVs will continue to operate through 2011 or until failure. The purpose is to demonstrate long stack durability with extended vehicle operating hours (see Figure 4). In addition, 10 new Phase 2 FCEVs have been equipped with the most recent materials and controls technology in order to demonstrate the progress made in the project to date.
These “Technology Insertion” vehicles are currently deployed and are accumulating miles and generating data for submission to DOE according to the National Renewable Energy Laboratory (NREL) data reporting templates.

In order to accelerate the learnings on the most recent technology stack design, three fuel cell systems were instrumented with the same hardware as the Technology Insertion vehicles and are running accelerated durability cycles on test stands. These fuel cell systems operate under a stressful, accelerated protocol in order to capture early learnings.

Shell Hydrogen will no longer participate in the rest of this project. GM will continue to utilize the Shell Hydrogen stations and other hydrogen refueling stations outside of the project to provide fuel for the demonstration vehicles.

**Approach**

- Demonstrate FCEVs:
  - Deploy FCEVs in various terrains, driving conditions, and climates including cold weather.
  - Demonstrate two generations of fuel cell technology.
- Insert Technology with recent advances to test Phase 2 learnings.
- Establish retail-like hydrogen stations for public fueling:
  - Install and operate total of six fueling stations on east and west coasts.
  - Explore hydrogen generation/delivery options such as electrolysis.
- Set up maintenance and service operations in support of FCEVs:
  - Train personnel in maintenance, fueling, technical support, safety.
- Generate and report data required:
  - Capture vehicle on-road and dynamometer test data.
  - Capture hydrogen infrastructure production/fueling data.
- Evaluate vehicle performance against targets:
  - Vehicle range, stack durability, cold-weather performance.

**Results**

Phase 2 FCEVs were launched in the fourth quarter of 2007 in the eastern and western regions. All 42 Phase 2 vehicles were deployed by the end of the third quarter of 2008. Thirty-two vehicles completed their deployment at the end of the third quarter of 2009, and 10 baseline Phase 2 vehicles will continue to report data through the third quarter of 2011 or until failure in order to support stack durability estimates. All 10 Technology Insertion vehicles were deployed by the end of the second quarter of 2010.

Beginning-of-life chassis dynamometer testing was conducted for a “Technology Insertion” vehicle in June 2010.

Accelerated fuel cell system durability testing will continue through 2010.

GM continues to submit infrastructure data templates for Ardsley, NY, Clean Energy LAX, CA and Culver City, CA. The 10 baseline and the 10 “Technology Insertion” vehicles continue to utilize many stations for refueling including Monroe County, NY, Honeoye Falls, NY, West Point, NY, Ft. Belvoir, VA and Burbank, CA.

The hydrogen orientation program for emergency first responders continues to be delivered on request in cities where GM’s DOE vehicles operate totaling over 1,500 people trained.

NextEnergy Center chaired task groups made up of a consortium of industry experts on hydrogen to provide feedback on the National Fire Protection Agency (NFPA) hydrogen codes. Task Groups completed their review of the latest NFPA revision. NextEnergy Center has successfully transferred hydrogen permitting database tools to new Web site. They coordinated with DOE and its partners to transfer the databases’ layout and functionality to DOE ownership, for public benefit.

**Conclusions and Future Directions**

- FCEVs fully meet all functional needs for day-to-day use by individual customers.
- FCEVs are fully functional in sub-freezing cold weather conditions.
- Fuel cell stack durability rapidly increased and is expected to meet or exceed the DOE target of 2,000 hours during the completion of this project.
- GM is taking a significant step by introducing elements of our next generation fuel cell stack and system into a small group of Equinox FCEVs for continued Gen2 operation/demonstration during 2010 and 2011. GM believes that the learnings from the demo project so far have helped enable materials and operating controls within the fuel cell system that will clearly demonstrate the ability of the Gen2 vehicles to meet and exceed the demo project stack durability goal of 2,000 hours.
- Furthermore, GM looks forward to a continued relationship and collaboration with NREL in the areas of fuel cell stack and FCEV data analysis methods. GM believes that this work is helping establish a strong foundation for future work
throughout the fuel cell industry to develop universally accepted metrics for assessing the performance of fuel cells and FCEV.

- GM will continue to provide data for baseline and Technology Insertion vehicles that are deployed and operating.
- Provide lab data from accelerated durability testing to enhance understanding of fuel cell durability.

**FY 2010 Publications/Presentations**

2. An onsite review meeting with NREL, DOE, and GM personnel is planned for August 2010.
VIII.5 Validation of an Integrated Hydrogen Energy Station

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 Hydrogen 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
(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 Fuel Cell 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 shop validation test of hydrogen energy station at FuelCell Energy’s facility in Danbury, CT, including >7,000 hours of integrated operation, producing 2 to 4 kilograms per hour of hydrogen (total in excess of 2,350 kilograms of hydrogen) and >200 kW-net alternating current (AC) power, and performing a 7-day continuous operation test. Fuel used was pipeline natural gas.
- Operated Hydrogen Energy Station on simulated digester gas by addition of carbon dioxide to the methane supply. System performance matched predictions for power and hydrogen production. Verified ability to switch between anaerobic digester gas and natural gas.
- Developed operating map (cycle time vs. feed rate) for hydrogen pressure swing adsorption (PSA) system.
- Tested and validated programming for automated integration and de-integration of PSA system from fuel cell and anode exhaust gas processing skid.
- Ordered new fuel cell stack for 3-year demonstration program at Orange County Sanitation District (OCSD), with funding also
provided by CA Air Resources Board and South Coast Air Quality Management District.

- Began packaging hydrogen energy station for shipment to OCSD.
- Extended DOE cooperative agreement to 31 March 2011, with additional funding toward procurement of fuel cell stack for operation at OCSD.

**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 DFC® power plant (electricity only) 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 efficiently recovered from the dilute anode effluent gases. The recovery and purification of hydrogen from the anode presents several challenges:

- The anode off-gas is a low-pressure, high-temperature gas stream that contains ~10% hydrogen by volume.
- The anode exhaust stream must be heat integrated with the fuel cell to ensure high overall system efficiency.
- 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 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 was fabricated and shop tested. Prior to shipping to the field, the entire system was installed at FuelCell Energy’s facility in Danbury, CT for complete system check-out and validation. In Phase 4, the system will be operated on municipal waste water derived biogas at OCSD, Fountain Valley, California, under a 3-year project. DOE will receive 6 months of data from the initial operating phase 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 resultant 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 direct current voltage, which is then converted to AC by an inverter in the electrical balance of plant. The system produces 480 VAC, 60 Hz, and a nominal 300 kW without hydrogen co-production. Excess carbon dioxide and
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 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 hydrogen-ready DFC®300 is provided in Figure 2, and a photograph of the anode exhaust processing and hydrogen purification system is provided in Figure 3. This testing had several key objectives, including the demonstration of variable production of both electricity and hydrogen, optimization of the process control system and overall controls philosophy, and testing and development (if needed) of systems that respond to upset conditions.

Figure 4 shows the main results of the shop validation test of the hydrogen energy station. During initial testing in March/April 2009, the system was operated in hydrogen coproduction mode for the first time; in order to better understand the dynamics and interaction of the fuel cell with the PSA system, limitations were placed on the rate of change in key control parameters surrounding the extraction and processing of anode exhaust gas from the DFC®300. Programming was then added to the control system to further automate the Hydrogen Energy Station to allow for unattended operation, and the process was restarted in July 2009. The operation and control of the system, including automated integration and de-integration of the PSA from the balance of plant, was excellent.

The feed gas to the fuel cell was then modified by the addition of sufficient carbon dioxide to simulate the anticipated concentration in anaerobic digester gas. The system performed well, and the map for cycle time as a
function of feed gas flowrate was developed. The design hydrogen production rate (2 to 4 kilograms per hour) and purity (less than 0.2 parts per million by volume (ppmv) carbon monoxide and less than 2 ppmv carbon dioxide) were achieved at all operating conditions tested during the Danbury phase of the project.

Conclusions and Future Direction

- The shop validation test for the hydrogen energy station was completed during the reporting period. Excellent results were achieved that met or exceeded the expected performance of the unit.
- The hydrogen energy station is being shipped to OCSD. Following installation and commissioning, operation will begin on natural gas to compare performance with the results of the shop validation test. Digester gas from the wastewater treatment facility will then be introduced to the system to demonstrate the production of renewable electricity and hydrogen. 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).
- The current DOE project includes operation of the Hydrogen Energy Station for up to 6 months.

FY 2010 Publications/Presentations

VIII.6 California Hydrogen Infrastructure Project

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Contract Number: DE-FC36-05GO85026  

Subcontractor and Working Partner:  
• University of California, Irvine (UCI), Irvine, CA  
• National Fuel Cell Research Center (NFCRC), Irvine, CA  

Project Start Date: August 1, 2005  
Project End Date: December 31, 2010  

Objectives

• Demonstrate a cost-effective infrastructure model in California for possible nationwide implementation:  
  – 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:  
(C) Hydrogen Refueling Infrastructure  

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 Fuel Cell 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.  
• Began construction of hydrogen pipeline fueling station (350 and 700 bar dispensing) in Torrance, CA.  
• Began 6-month deployment of 350 bar mobile station (HF-150) in Placerville, CA.  
• Submitted permit application for renewable hydrogen fueling station (350 and 700 bar dispensing) in Fountain Valley, CA.

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’ eRAM 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 online 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 six cars per day. When starting with full storage, four to five cars can be filled in succession. The station continues to see increasing use over time, with average station throughout having doubled over the past 12 months. A photograph of the dispensing system is provided in Figure 1.

The world’s first fueling station supplied by a hydrogen pipeline began construction in February 2010 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 under development by Shell Hydrogen. A 4 kg/hr compressor skid and a total of 100 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. Two dual dispensers for both 350 and 700 bar hydrogen are 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. A photograph of the dispenser area is provided in Figure 2. Station commissioning is expected to begin in August 2010.

The HF-150 (shown in Figure 3) 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 dispense approximately 80 to 90 kg before needing to be refilled. In March 2010, Air Products began a 6-month deployment of an HF-150 mobile fueler at the District Office of the U.S. Forest Service in Placerville, CA.

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 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). The hydrogen dispenser will be co-located with an existing compressed natural gas fueling island; Figure 4 shows a photograph of the existing dispenser and the proposed location for the hydrogen fueling equipment. A modification to the Cooperative Agreement was executed on 30 September 2009 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. Construction of the fueling station will begin pending final approval by the City of Fountain Valley of the construction permit application. Station commissioning is expected to commence in September 2010.

Conclusions and Future Directions

Planned future work includes:

- UCI Fueling Station – Continue operation of gaseous dispensers.
- Torrance Pipeline Fueling Station – Commission both 350 and 700 bar systems.
- Fountain Valley Renewable Station – Acquire necessary permits, install and commission both 350 and 700 bar systems.
- Hydrogen Fueler (HF-150) – Complete second deployment in northern California.
- Infrastructure data acquisition, analysis and delivery – report data to DOE.

FY 2010 Publications/Presentations

1. A presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (June 2010).
VIII.7 Technology Validation: Fuel Cell Bus Evaluations

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John Garbak  
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Subcontractor:  
Kevin Chandler, Battelle, Columbus, OH

Start Date: March 2001  
Projected End Date: Projected continuation and direction determined annually by DOE

Objectives

- Determine the status of fuel cell bus (FCB) technologies in transit applications by evaluating them in real-world service.
- Coordinate with the Department of Transportation’s Federal Transit Administration (FTA) on the data collection for the National Fuel Cell Bus Program and with 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 Fuel Cell Technologies Program’s Multi-Year Research, Development, and Demonstration Plan:

(A) Lack of Fuel Cell Vehicle Performance and Durability Data  
(C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data  
(D) Maintenance and Training Facilities

Contribution to Achievement of DOE Technology Validation Milestones

Milestone 18: Validate fuel cell durability of 3,500 hours, 300+ mile range and fuel cell stack power density of 1.5kW/L. (4Qtr 2012) Two of the five current-generation FCBs evaluated in this project have achieved more than 6,000 hours on the fuel cell system with no major repairs. One of these systems has logged more than 7,000 hours in service. 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.

Accomplishments

- Completed collection and analysis of current-generation 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 at three transit agencies.

Introduction

Transit agencies continue to aid the FCB industry in developing and optimizing advanced transportation technologies. These in-service demonstrations are necessary to validate the performance of the current generation of fuel cell systems and to determine issues that require further development. Using fuel cells in a transit application can help accelerate the learning curve for the technology because of the high mileage accumulation in short periods of time. During the last year, major progress has been made in improving fuel cell durability; however, more work is needed to improve reliability, increase durability to meet the needs of transit agencies, lower capital and operating costs, and transition maintenance to transit staff.

Approach

NREL uses a standard 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 include aggregate data products that protect each manufacturer’s specific data. To date, NREL has collected this type of data from two fuel cell manufacturers. Aggregate results will be published if and when enough data are available to protect each company’s identity and source data.

Results

During Fiscal Year 2010, NREL collected data on current-generation FCB demonstrations at three transit agencies in the United States: SunLine Transit Agency in Thousand Palms, California; Connecticut Transit (CTTRANSIT) in Hartford, Connecticut; and AC Transit in Oakland, California. The first two of these evaluations were funded by DOE, and the third evaluation was covered by funding from FTA. Under DOE funding, NREL also began collecting data on next-generation FCBs at three agencies: City of Burbank, California; AC Transit; and SunLine. NREL published results from the current-generation FCBs. A summary of selected results is included in this report, followed by an overview of the next-generation FCBs being evaluated.

The current-generation FCBs in service at AC Transit, CTTRANSIT, and SunLine are all of the same basic design: Van Hool 40-foot buses with ISE Corp. hybrid-electric drives and UTC Power fuel cell power systems. During the early demonstration period, the manufacturer partners used the performance data to validate the systems and further develop the product and components. Beginning in November 2007, UTC Power replaced the fuel cell power systems in each of the five buses with newer versions that were developed incorporating many of the lessons learned from the previous operation of these fuel cell buses. NREL collected operational and performance data on these FCBs and conventional baseline buses at each agency. Table 1 provides a summary of results from the operation at each agency after the new fuel cells were installed. Data from the baseline buses are included in the table.

<table>
<thead>
<tr>
<th>Table 1. Summary Data Results</th>
</tr>
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<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Vehicle data</td>
</tr>
<tr>
<td>AC Transit</td>
</tr>
<tr>
<td>CTTRANSIT</td>
</tr>
<tr>
<td>SunLine</td>
</tr>
<tr>
<td>FCB</td>
</tr>
<tr>
<td>Number of buses</td>
</tr>
<tr>
<td>Date period</td>
</tr>
<tr>
<td>AC Transit</td>
</tr>
<tr>
<td>CTTRANSIT</td>
</tr>
<tr>
<td>SunLine</td>
</tr>
<tr>
<td>Dec 07 - Jan 10</td>
</tr>
<tr>
<td>Number of months</td>
</tr>
<tr>
<td>Total fleet miles</td>
</tr>
<tr>
<td>Average miles per month</td>
</tr>
<tr>
<td>Fuel economy (mi/kg)</td>
</tr>
<tr>
<td>Fuel economy (mi/diesel eq. gal)</td>
</tr>
<tr>
<td>Average speed (mph)</td>
</tr>
<tr>
<td>Availability</td>
</tr>
</tbody>
</table>

Figure 1 shows the fuel economy of the buses at each location in miles per diesel gallon equivalent. (Note that the baseline buses at SunLine are compressed natural gas [CNG] buses – SunLine does not operate diesel buses.) The FCBs at the three locations showed fuel economy improvement ranging from 48% to 123% when compared to diesel and compressed natural gas baseline buses. This figure also illustrates the variability of the results from fleet to fleet. The results are affected by several factors,
including duty-cycle characteristics (average number of stops, average speed, and idle time). Also, the diesel buses at AC Transit do not have air conditioning but the fuel cell buses do. The CTTRANSIT diesel buses operate at twice the average speed of the FCB operating on the Star Shuttle Route, which causes significantly lower fuel economy for the FCB compared to the fuel economies at the other two agencies.

One measure of reliability for the transit industry is miles between roadcall (MBRC). A roadcall is the failure of an in-service bus that causes the bus to be replaced on route or causes a significant delay in schedule. NREL typically reports MBRC for the entire bus and for the propulsion system separately to show the reliability of the FCBs. Over time, these FCBs have been shown to have propulsion system MBRCs that are much lower than MBRCs for the baseline buses. This is not necessarily due to the fuel cell power system, but instead has mostly been because of traction battery issues. To illustrate the improvement in reliability of the fuel cell power system in the buses, Figure 2 tracks the combined monthly fuel cell system MBRC since the buses went into service. The shading in the middle of the chart marks the time during which all five FCBs had the newer version fuel cell systems installed. The average fuel cell system MBRC shows an upward trend and has increased by 21% with the newer version system. In fact, two of these fuel cell systems accumulated significant hours without any major repairs (one is over 7,000 hours and a second is over 6,000 hours).

Another measure of reliability for the transit industry is availability—the percentage of days a bus is planned for service compared to the percentage of days the bus is actually available. When a bus is unavailable, NREL reports the cause by one of several categories. To show the improvement in fuel cell system reliability over time, Figure 3 tracks the percentage of time by month that the buses are unavailable because of the fuel cell system. As in Figure 2, the shaded area denotes the period of time when the newer version fuel cells were installed. The chart shows a marked improvement for the new fuel cell systems.

NREL began collecting data on several next-generation FCBs at the following three transit agencies:

- City of Burbank – one battery dominant, plug-in hybrid FCB developed by Proterra using Hydrogenics fuel cells and lithium titanate batteries.
- SunLine – one New Flyer 40-ft FCB with an ISE hybrid system, Ballard fuel cells, and lithium ion batteries.
- AC Transit – 12 next-generation Van Hool FCBs with a hybrid system integrated by Van Hool and UTC Power fuel cell power system.

NREL also began data collection on another Proterra FCB in Columbia, South Carolina, under the FTA project.

Conclusions and Future Direction

Over the last two years, first-generation fuel cell propulsion systems in buses have shown progress, although they are still considered prototypes in the early stages of technological development. Manufacturers have learned from the results of these first-generation demonstrations and have incorporated design improvements into next-generation fuel cell systems that are now beginning field demonstrations. There are still challenges to overcome, and more data are needed on these new systems just being introduced. Remaining challenges include:

- Lowering costs of purchasing, operating, and maintaining buses and infrastructure.
- Increasing durability/reliability of the fuel cell systems and other components to match transit needs.
- Transferring all maintenance to transit personnel.
Future work by NREL 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
  - SunLine
  - 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 electric vehicle demonstrations.
- Coordinating with FTA to ensure harmonized data-collection efforts for the National Fuel Cell Bus Program.
- Coordinating with national and international FCB demonstration sites.

**FY 2010 Publications/Presentations**

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 December 2013.
- 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 fuel vehicle test bed for the NPS.
- Attract new partners and applications for the Big Island hydrogen infrastructure.
- Conduct outreach to local authorities and the general public regarding hydrogen infrastructure.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(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

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to the following Technology Validation milestones from the Multi-Year Research, Development and Demonstration Plan:

- 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.

Accomplishments

- Signed an implementation agreement with the State of Hawaii (DOE funds via State Energy Office) contracting HNEI 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. Compressor, storage and dispenser sized to support increased production capacity.
- Issued a request for proposal for the supply of “turn-key” fueling station.
- Applied for and received a special research and development energy supply agreement from the Hawaiian Electric Light Company through the State of Hawaii Public Utilities Commission.
- Obtained KMC approval and support as the site of the fueling station.
Hawaii Volcanoes National Park superintendent approved Categorical Exclusion for siting and operation of the fueling station.

Completed background sounds survey at the KMC site.

Assisted HAVO to develop an aggressive acoustic specification for the fueling station. Extensive acoustic data analysis by NPS Natural Sounds Program department. Acoustic level specification not to exceed 35 dba at 75 meters based on proximity of closest sleeping quarters;

Assisted HAVO to secure bus funding ($1 million) from the Federal Transit Administration via the Department of Interior. These buses to serve as the primary vehicles for the Power Park project.

Assisted HAVO to secure $600,000 in cost share funding from the Hawaii Hydrogen Investment Capital Special Fund (Hydrogen Fund) to support the HAVO bus conversion funding.

Issued a contract to Powertech for the supply of a “turn-key” fueling station due for completion by the end of July 2010 and delivery by the end of August 2010.

Developed a fueling station site plan layout.

Introduction

The Hawaii Hydrogen Power Park (Power Park) was established to support the DOE Hydrogen Program Technology Validation sub-program. Funded by the DOE through the Department of Business, Economic Development and Tourism’s Strategic Industries Division, in its role as the Hawaii State Energy Office, with the University of Hawaii’s HNEI as the implementing partner, the Power Park conducts engineering and economic validation of pre-commercial hydrogen technologies. The Power Park is supporting the testing and validation of hydrogen fueling system technologies on the big island of Hawaii including production utilizing renewable energy, compression, storage, delivery, and dispensing to hydrogen vehicles. In parallel, HAVO is planning to acquire initially two battery-dominant fuel cell plug-in hybrid electric vehicle shuttle buses. The source of HAVO funds is from the Department of Transportation through the NPS Alternative Transportation in the Parks and Public Lands Program. It is intended to support HAVO's hydrogen fueling requirements with the infrastructure developed in the Power Park.

Approach

- Procure a turn-key H\textsubscript{2} fueling station designed for ease of installation:
  - Modular design and installation plan to greatly reduce installation timeline, cost, and risk.
  - Conduct a factory acceptance trial prior to shipping the system.
  - Supplier to provide detailed infrastructure template with precisely located module connection points. These are precisely replicated on the site prior to shipping.
  - System modules craned into place and connected to utilities. Estimate ~4 days installation effort.

- Use fuel cell PHEVs to maximize the electrical efficiency of a new park shuttle bus service at Hawaii Volcanoes National Park.

- Collaborate with existing data analysis groups at the national labs (SNL 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 SO\textsubscript{2} on vehicle performance.

- Identify areas that require further technical development such as air filtration systems.

- Transfer results to industry and government agencies.

- Produce hydrogen using an electrolyzer powered by renewable electricity from the Hawaii Electric Light Company at a special research rate.

- Design the initial installation to produce 10-20 kg of hydrogen per day @ 350 bar with the flexibility to expand production.

- Site the fueling station at KMC:
  - Department of Defense recreational facility located within HAVO.
  - KMC to provide shuttle bus operators.

Results

Contract Issued for the Supply of a “Turn-Key” Hydrogen Fueling Station

A major accomplishment this year was issuing a contract to Powertech for the supply of a “turn-key” hydrogen production and fueling station. The challenges involved included working closely with the Natural Sounds Program department of the NPS to develop an acoustic level specification for the system. The lack of industry data required a major effort by the project to conduct in-field acoustic measurements on existing equipment and extrapolate the results to develop a
specification for HAVO. This required almost six months of effort and delayed the request for proposal process by a like time frame. The benefit of the effort is that an aggressive acoustic specification of 35 dba at 75 meters (illustrated in Figure 1) was developed and our supplier can meet it. This will have application in the future to the overall hydrogen program as hydrogen production and fueling system will start moving from industrial to urban sites. In particular, cooling fans and compressors in particular will need to meet these reduced acoustic levels.

Identified Fuel Cell PHEV Shuttle Bus Market Gap

Working with HAVO, the Power Park team identified a market gap for shuttle bus-sized fuel cell PHEVs. The lack of a suitable off-the-shelf vehicle requires HAVO to convert an existing internal combustion engine shuttle bus and this is proving to be very costly and time-consuming. The project team assisted HAVO in obtaining addition funding ($600,000) from the State of Hawaii Hydrogen Investment Capital Special Fund (Hydrogen Fund) to help pay for non-recurring engineering for the bus conversions. This will result in a set of engineering designs that can be used to convert additional buses for other projects.

Progressed Multi-Party Legal Agreements

While the involvement of several agencies and organizations is highly desirable for outreach across many agencies, the requirement to negotiate suitable agreements among all the parties is time-consuming and has become a serious barrier to the timely implementation of the project. While considerable progress had been made in execution of a 4-way Memorandum of Understanding, and bilateral Memoranda of Agreement among the various federal and state agencies it, remains outstanding after almost a year of negotiations.

Utilize HAVO as Test Bed for Testing and Mitigating the Effects of $SO_2$ on Vehicle Performance

A significant advantage of the HAVO test site is the opportunity to test fuel cell vehicles in challenging environmental conditions and particularly in high $SO_2$ conditions. This is a challenge that must be addressed as fuel cell vehicles are introduced into general use. As illustrated in Figures 2 and 3, HAVO has extensive monitoring and data collection capabilities for $SO_2$. This
provides the opportunity to develop and test fuel cell vehicle air filtration systems.

**Conclusions and Future Directions**

- Based on unanticipated delays by HAVO in acquiring its shuttle buses, the Power Park team is developing alternative plans to deploy the hydrogen fueling station to support the October 2010 deployment of GM Equinox vehicles at Marine Corps Base Hawaii on Oahu until HAVO shuttle buses are ready. Preliminary discussions with both DOE and the State have been positive. Efforts will commence once written approval is obtained from both funding agencies.
- Subject to a new timetable for HAVO vehicles including availability in January 2012, complete KMC site prep in November 2011.
- Install the Power Park fueling station at HAVO – target: December 2011.
- Collect and analyze fueling station and vehicle data.
- Seek opportunities for expansion of fleet and/or additional hydrogen infrastructure.

**FY 2010 Publications/Presentations**

Objectives

- Quantify how much excess wind energy is available at the existing wind-diesel plant on St. Paul Island and 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.

Introduction

St. Paul Island is a remote speck in the Bering Sea 300 miles west of the Alaskan mainland, in the heart of America’s last rich fishing grounds. It is increasingly expensive, logistically challenging, and sometimes impossible to import fossil fuels to this location. The island has a class 7 wind resource and three Vestas 225 kW wind turbines that operate at a 47% capacity factor. TDX Power owns, operates and maintains the wind farm for the corporation, producing electricity and utilizing excess power for heat to a large industrial complex at the airport. TDX Power is in final negotiations with the City of St. Paul to sell wind energy to the city-owned electric utility, which now uses diesel to provide power for the 396 residents. TDX wants to stretch wind energy’s power to transportation and then add more wind turbines.

TDX evaluated the prospect of using wind energy to produce hydrogen for use in transportation, particularly the small buses used in our tourism business that take...
visitors to bird watching sites and northern fur seal rookeries. We researched the technical feasibility, commercial availability, environmental benefits, climate and geographic challenges, costs, additional applications for hydrogen, training needs and opportunities, operations and maintenance requirements, and the economic offset of diesel.

**Approach**

St. Paul Island has enough excess wind resource to produce fuel for transportation. Hydrogen could be the fuel of the future. TDX wanted to determine if hydrogen technology was ready for our remote location. We made site visits to two active hydrogen fueling stations and public transportation projects to collect real data and stories. We felt there were lessons to be learned by visiting facilities, site managers, fueling attendants, bus drivers, and bus riders face to face that cannot be found on project web pages. Our technical contractor visited the wind to hydrogen electrolysis project at the National Renewable Energy Laboratory to interview Kevin Harrison regarding the status of that project.

TDX contracted with ACEP to do a procurement study and produce a vendor and price list for the components we would need for a hydrogen demonstration project on St. Paul Island. TDX considers community education a critical piece of this project and conducts workshops and school events in St. Paul to present our findings and future plans.

**Results**

St. Paul Island has a class 7 wind resource and 47% availability for its one 225 kW Vestas wind turbine now in operation. Once interconnection of the two additional 225 kW turbines is complete, there will be a considerable amount of excess electricity available. Although plans are in process to tie two of the wind turbines into the city-owned community electric grid, there will still be excess power available. There is also a plan and space available to add three more wind turbines to the Petroleum Offshore Survey Support (POSS) Camp Wind Farm. St. Paul could become the first all-electric community run by wind energy.

The POSS Camp wind farm will produce an abundance of excess electricity when the two newest V27 wind turbines come on line [1]. Current power and production can be seen in Table 1.

According to the study completed by ACEP, the cost per mile driven of a hydrogen vehicle is considerably more than existing diesel technology (see Figure 1) [2]. Battery-powered electric vehicles are more expensive than diesel – at current prices – but show the most promise for near-term commercial availability. Battery technology is progressing rapidly.

Table 1. Power Production and Demand at POSS Camp Wind Farm (kWh)

<table>
<thead>
<tr>
<th>Turbines</th>
<th>Total Diesel Gen</th>
<th>Total Wind Turbine</th>
<th>POSS Camp Electrical Load Demand</th>
<th>Thermal Load Demand</th>
<th>Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>447,578</td>
<td>532,229</td>
<td>562,283</td>
<td>346,267</td>
<td>71,257</td>
</tr>
<tr>
<td>2</td>
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<td>1,596,687</td>
<td>562,283</td>
<td>346,267</td>
<td>1,135,715</td>
</tr>
</tbody>
</table>

Originally funded to demonstrate hydrogen technology, TDX opted to modify the grant to demonstrate plug-in electric vehicle (PEV) technology (see Table 2). Although the modification is not yet complete, TDX did invest in a Barefoot Motors ATV, introducing the vehicle to the community at the Wind Festival in September 2009.

The ATV does not perform as advertised, due to the more challenging environment on St. Paul Island. But the ATV works well enough that TDX is optimistic about the potential to expand the use of wind energy on island with PEV technology.

Currently, the POSS Camp uses the energy from only one of the three V-27 wind turbines. A plan is in progress to sell the energy from the other two to the City of St. Paul electric utility. The wind farm has space available for three more turbines. TDX assumes there will be a minimal increase in daily energy use for the demonstration project [3].

One concern is that the lowest wind resource months coincide with the height of tourist season (see Figure 2). TDX is prepared to add more wind turbines as use of PEVs becomes more widespread to solve this problem [4].

![Figure 1. Estimated Cost Per Mile Driven by Vehicle Type](image)
Conclusions and Future Directions

- PEV technology is available today, advancing rapidly, and looks to be economically feasible.
- TDX, with community input, chose to modify the existing grant to focus our demonstration efforts on PEVs.

- TDX has purchased a Barefoot Motors plug-in electric ATV, has ordered a Polaris plug-in electric ATV, and plans to contract with Miracle Energy Systems, Inc. to purchase or custom build an appropriate plug-in electric van or small truck.

FY 2010 Publications/Presentations


References


<table>
<thead>
<tr>
<th>Vehicles</th>
<th>Peak Charging</th>
<th>Daily Power Consumption</th>
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</thead>
<tbody>
<tr>
<td>4 buses</td>
<td>32 kw</td>
<td>160 kWh</td>
</tr>
<tr>
<td>20 light duty vehicles</td>
<td>40 kw</td>
<td>80 kWh</td>
</tr>
<tr>
<td>40 – 4 Wheelers</td>
<td>80 kw</td>
<td>200 kWh</td>
</tr>
<tr>
<td>Vehicle Totals</td>
<td>152 kw</td>
<td>440 kWh</td>
</tr>
</tbody>
</table>

**Typical Daily Load Conditions**

- Current Load: 1,575 kWh
- Future Load with Electric Vehicles: 2,035 kWh or a 25% increase in daily energy use.

**TABLE 2. PEV Type and Power Consumption**

**FIGURE 2. Wind Speed by Month for an 11-Year Period**
Objectives

- To advance commercialization of hydrogen-powered transit buses and supporting infrastructure.
- 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.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6) of the Fuel Cell 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

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestones from Section 3.6: Technology Validation of the Fuel Cell 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)

Approach

This project was originally developed in 2004 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 initial project approach was to design, engineer, build, and test the integrated fueling station at the “factory”; install it at a site that offered educational and technical resources; and provide an opportunity to showcase both the fueling station and advanced hydrogen vehicles. Through the five years of project development (2004 to 2008), 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 this current project (Texas Hydrogen Highway) to inform Texas target audiences on hydrogen and fuel cell applications. The assets in Austin are illustrating 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 station and bus are housed at the J.J. Pickle Research Center, University of Texas at Austin located in north Austin (Figures 1 and 2). The hydrogen fueling station is operated by the University of Texas technical staff, under the supervision of GTI personnel. 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

- Commissioning of the fuel station in February 2010:
  - The project team expended considerable effort for start-up of the station in Austin.
  - Performance and safety checks were conducted on the system during initial start-up which resulted in resolution of the following issues:
    - Pressure fluctuations in the system during automated start-up have led to on-site adjustment of the system controls.
    - Communications network link problems at the University of Texas led to a station 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.
- Station commissioning trials were completed and hydrogen was generated on-site for use by the fuel cell bus. All systems were deemed operational March 15, 2010.
- Completed and submitted fueling station safety plan to DOE.
- Held station showcase events for limited, invited visitors, which included bus rides and station tours.
- Conducted four Texas showcase events in Fall 2009 and early 2010 in coordination with various target groups. Conducted transit staff briefing and training in conjunction with these showcase events.
- Conducted briefing on the project for Texas legislative staff.
- Transit agency personnel from Capital Metropolitan Transportation Authority conducted interface meetings at both Capital Metro and UT-CEM to discuss hydrogen bus and fueling station operation and maintenance (March 24-25, 2010).
- Completed final Powertrain Systems Analysis Toolkit (PSAT, a vehicle simulation software package developed at Argonne National Laboratory) modeling of transit routes to verify vehicle suitability for deployment.
- Collaborated on fuel cell bus and electrified transportation modeling.
  - UT-CEM collaborated with the University of Texas Department of Mechanical Engineering and Georgia Tech on advanced energy storage and modeling techniques of electrified vehicles, including 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.
- Submitted grant request to Texas Commission on Environmental Quality to support hydrogen station operation as part of the U.S. Department of Transportation/Federal Transit Administration National Fuel Cell Bus Program, April 2010.
Future Directions

- Continue monitoring and evaluation of station and bus operations.
- Plan and conduct final outreach and showcase event in Austin with state and local government officials.
- Compile report on project milestones.

FY 2010 Publications/Presentations


Objectives

Develop Florida’s hydrogen and fuel cell infrastructure by:

- Creating partnerships for applied technology demonstration projects throughout the state.
- Sponsoring research and development in the production, storage and use of hydrogen and in the use and application of fuel cells.
- Facilitating technology transfer between the public and private sectors to create, building and strengthen high-growth potential, high technology companies.
- Developing industry support or potential for widespread applications.
- Developing unique hydrogen/fuel cell university level education programs.

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:

From the Fuel Cell section:

(C) Performance
(E) System Thermal and Water Management
(G) Start-up and Shut-down Time and Energy/Transient Operation

From the Education section:

(A) Lack of Readily Available, Objective, and Technically Accurate Information
(B) Mixed Messages
(E) Regional Differences

From the Technical Validation section:

(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 milestones from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 24 (Technology Validation): Validate a hydrogen cost of $3.00/gge (based on volume production). (4Q, 2009)

Accomplishments

- Project has solicited proposals to conduct research, development and demonstrative work.
- New program management in October 2009.
- Solicited new projects in October 2009.
- Selected three new projects in January 2010. Received DOE approval.
- Solicited additional new projects by issuing request for proposals in April 2010.
- Preliminary selection of five additional new projects made in May 2010.
Introduction

The contract for operation and management of the Florida Hydrogen Initiative (FHI) project was transferred from the FHI, a not-for-profit corporation, to the University of Central Florida (UCF) in October 2009. UCF’s Office of Research and Commercialization and UCF’s Finance and Accounting Division manages the contractual and financial aspects of the project and the issuance of subcontracts, per established procedures. Ms. Ashuantay Houston is in charge of the contractual and financial aspects of the project. Project management and technical oversight is provided by UCF’s principal investigator, Dr. David Block of UCF’s Florida Solar Energy Center (FSEC).

Approach

Following the change in operation and management of FHI, the project managers began the process of allocating the remaining funds (~$2.5 million) to new projects and finishing and/or completing old projects. Each of the FHI sub-project activities are designated as a Task number within the project. At the present time, there are nine tasks. The first six tasks are old projects. Tasks 1, 3, 4, 5, and 6 are now completed. Task 2 is continuing and Tasks 7, 8, and 9 are new tasks. The active tasks, including the two completed this year, are as follows:

• Task 3. Assessment of Public Understanding of the Hydrogen Economy through Science Center Exhibits, Hydrogen Exhibit, Orlando Science Center. This project is complete and final report submitted.
• Task 5. On-Site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications, FSEC/UCF and Chevron Technology Ventures. The project is complete and a final report written.
• Task 7. Chemochromatic Hydrogen Leak Detectors for Safety Monitoring, FSEC. New project.
• Task 9. Understanding Mechanical and Chemical Durability of Fuel Cell Membrane Electrode Assemblies, FSEC. New project.

Individual Project Descriptions

As stated above, FHI has funded individual projects which conduct the research, development and demonstration activities. Each of the individual projects are approved by DOE before work can begin. During the past year, one project was a continuing effort, two were completed, three new projects were approved and a request for proposal was issued. With this background, each of the six past year projects are described in the following sections.


The only active old task is Task 2 being done by Michael Fuchs of EnerFuel, Inc., 561-868-6720, x239. The project activities conducted in the past year are:

• Examined three new demonstration sites. Selected and received approval for a demonstration site of an electric vehicle charging station at Florida Atlantic University (FAU) in Boca Raton, FL. Secured the support of FAU to design, construct and evaluate the charging station and developed required documentation for DOE approval.
• New site activities include designing charging station using existing fuel cells and inverters and secured all permits necessary to begin construction phase and successfully incorporated the existing inverter/fuel cell systems into the design of the charge station.
• Future actions are to construct fuel cell demonstration site, operate charge station for period of three months, determine overall electrical efficiency, document system transient response to load changes, and determine overall performance and effectiveness of charging station.

Task 3. Assessment of Public Understanding of the Hydrogen Economy through Science Center Exhibits, Orlando Science Center, FL.

The H2Now exhibit has completed software and hardware ‘shakedown’ that resulted in a streamlined interface and communication and is functioning at 100% in the Orlando Science Center (OSC). The exhibit is so popular that exit intercept surveys that OSC regularly conducts have revealed that visitors like the exhibit and wish that there was more to it. In response, OSC has added a video presentation produced by the H2Now exhibit designers, IDEAS, Inc., titled “I Am Hydrogen” and developed a panel exhibit on other alternative energy resources. Future plans for H2Now include developing an interactive instructional video game based on hydrogen and other renewable energy sources. The video game was developed using a grant from Progress Energy Foundation. OSC has submitted its final report “Summative Evaluation Findings H2Now: (submitted with the 2009-01 Quarterly Report to DOE).

The learning objectives established for H2Now were established so that after participating in the exhibit, visitors would be able to:
VIII. Technology Validation

- Explain what hydrogen is, where it comes from, and some of its possible uses.
- Distinguish between truth and myth about hydrogen as an alternative energy source, and give specific examples.
- State a benefit and a challenge of hydrogen as an alternative energy source.
- Give an example of how hydrogen power is created, and how it can affect everyday life.
- Comment on a possible impact of hydrogen power on the future state of the world.

Evaluations to determine the extent to which H2Now meets educational objectives revealed that:
- 77% of the visitors surveyed either loved or liked the exhibit.
- 64% indicated that they ‘learned something’ or found the exhibit informative in the word choice section of the interview.
- 32% found the exhibit ‘interesting’ indicating that both cognitive and affective learning has clearly taken place.
- 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”.

Task 6. On-site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications

This project was conducted by N.Z. Muradov, A. T-Raissi, C. Linkous, K.K. Ramasamy, C. Huang, and F. Smith of the Florida Solar Energy Center, jointly with the Chevron Technology Ventures, LLC, Dr. James Stevens, Technical Advisor. The project was started in January 2008 and was completed in January 2010. The final report was submitted to DOE in April 2010.

The objective of the project was to develop a new on-demand forecourt hydrogen production technology by catalytically converting high-sulfur hydrocarbon fuels to an essentially sulfur-free gas. The removal of sulfur from reformate is critical since most catalysts used for the steam reformation have limited sulfur tolerance. The FSEC’s responsibilities included building, operating and validating the performance of a diesel pre-reformer as well as developing and demonstrating a small-scale desulfurization unit. Chevron Technology Ventures provided catalysts and know-how for the design and fabrication of the pre-reforming reactor. The pre-reformer was coupled with a regenerable Fe2+/Fe3+ redox/electrolysis system used for hydrogen sulfite removal from the pre-reformer effluent.

Results from laboratory tests showed that electrolysis of acidic FeSO₄ aqueous solution was highly efficient with a coulombic efficiency of 100% at a cell potential of 1.0 V and that the electrolytic process can be made to operate with a Pt-free anode to oxidize ferrous to ferric ions, thereby reducing the cost of the electrolytic scrubber. FSEC researchers have also developed a robust bi-functional catalyst for accomplishing the pre-reformation of the high-sulfur fuels (sulfur content as high as 5,240 ppmw) to short chain hydrocarbons (C1-C4, mostly propane) at an average yield of about 97%. Furthermore, results showed that after100 hours of continuous operation, the combined Fe2+/Fe3+ redox/electrolyzer H₂S scrubber and pre-reformer could achieve desulfurization efficiencies greater than 95% and removed sulfur down to less than 5 ppmv in the pre-reformer effluent. The project results were the development of a novel process 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.

New Projects Approved during Past Year

Beginning in October 2009 and ending in February 2010, a request for letters of interest (LOI) was issued to select three new projects for submission to DOE. The LOI request resulted in five proposal submittals that were evaluated by a proposal evaluation team of six technical experts.

The results of the evaluation team and discussions on each project’s merit with DOE resulted in selection of the following three new projects:

Task 7. Chemochromic Hydrogen Leak Detectors for Safety Monitoring – Dr. N. Mohajeri and Dr. N. Muradov, FSEC. The aim of this project is to develop and demonstrate a cost-effective, high specific chemochromic (visual) hydrogen leak detector for safety monitoring at any facility engaged in handling and use of hydrogen. The work will lead to a new generation of versatile chemochromic hydrogen detectors that employ “smart” materials that cost less, possess fast discoloration kinetics, are user-friendly, are reliable and have superior field worthiness.

Task 8. Development of High-Efficiency, Low-Cost Electrocatalysts for Hydrogen Production and Proton Exchange Membrane (PEM) Fuel Cell Applications – Dr. C. Huang, FSEC. The objectives of this project are to develop highly active metal alloys with low Pt loading and metal-metal oxide-based electrocatalysts having nanosized grains. The project will conduct research and development for enhanced hydrogen evolution at low cost. The new catalysts will be evaluated for their activity toward hydrogen evolution via electrolysis of water as well as applications for PEM fuel cells.

Task 9. Understanding Mechanical and Chemical Durability of Fuel Cell Membrane Electrode Assemblies – Dr. D. Slattery, FSEC. The objective of this project...
is to increase the knowledge base of the degradation mechanisms for membranes used in PEM fuel cells. Approaches to mitigate membrane degradation can be classified into three areas: membrane composition changes; radical quenching; and platinum band formation mitigation.

**Issuing of RFP for Final Projects**

The final activity of the year was the release of a request for proposals (RFP) for the remaining funds of $1,427,910. The RFP was released on March 17, 2010 with applications due by April 23, 2010. The RFP e-mail stated that FHI had about $1.5 million in funds that are to be awarded in competitive solicited projects and the RFP was sent to a large number of potential responders. Following the receipt of 19 proposals, a six-member review committee was established. The review committee met in May 2010 and a recommendation for the funding of five new projects has been submitted to DOE. Final DOE documentation material is now being developed.

**Conclusions and Future Directions**

The FHI project results have produced a stabilized project management, the completion of two projects, the continuation of one project, the awarding of three new projects and the preliminary selection of five additional new projects. At this time, the funding should be totally allocated. The future work will continue the monitoring and conducting of the eight new projects. There are no open issues.

**Patents Issued**


**FY 2010 Publications/Presentations**


IX. SAFETY, CODES & STANDARDS
Introduction

The Safety, Codes & Standards sub-program supports research and development (R&D) that provides critical information needed to define requirements and close gaps in codes and standards and safety to enable the widespread commercialization and safe deployment of hydrogen and fuel cell technologies. In FY 2010 the sub-program focused on continuing to identify risk management measures to reduce the risk and mitigate the consequences of potential incidents that could hinder the commercialization of these technologies.

The sub-program continues to promote collaborative activity among government, industry, standards development organizations (SDOs), universities, and national laboratories in an effort to harmonize regulations, codes and standards (RCS) both internationally and domestically. Communication and collaboration among codes and standards stakeholders is emphasized by the sub-program to maximize the impact of its efforts and activities in international RCS.

In addition to R&D, the sub-program’s safety activities focus on development of information resources and best practices. The sub-program utilizes extensive external stakeholder input—from the fire-protection community, academia, automobile manufacturers, and the energy, insurance, and aerospace sectors—to create and enhance safety knowledge tools for emergency responders and authorities having jurisdiction. Continual availability of safety knowledge tools, distributed via an array of media outlets to reach the largest number of safety personnel possible, is a renewed priority. The sub-program also supports the development and implementation of best practices and procedures to ensure safety in the operation, handling, and use of fuel cell and hydrogen technologies for Hydrogen Program-funded projects.

Goals

The sub-program’s aim is to provide the validated scientific and technical basis required for the development of codes and standards and to implement safety practices and procedures to allow for the safe deployment of hydrogen and fuel cell technologies. The goals are to:

- Conduct and facilitate the appropriate R&D for the development of scientifically and technically sound codes and standards that enable the safe use of hydrogen and fuel cell technologies.
- Facilitate the development and harmonization of domestic and international RCS by seeking the consensus of all major stakeholders via the sub-program’s continued support of R&D that produces critical data and information needed to define requirements and fill gaps in codes and standards.
- Ensure that safety is a critical priority in research, technology development, and market deployment of hydrogen and fuel cell technologies.
- Develop and implement safety practices and procedures that will ensure the safe operation, handling, and use of hydrogen and fuel cell technologies, and utilize these practices and lessons-learned to promote the safe use of hydrogen and fuel cell technologies in Hydrogen Program-funded projects.
- Promote widespread sharing of safety-related information, procedures, and lessons-learned with first responders, authorities having jurisdiction, and other stakeholders.
- Understand and mitigate risk, to facilitate the safe use and insurability of hydrogen and fuel cell technologies.

Objectives

The sub-program’s objectives are to:

- Support and facilitate the promulgation of essential codes and standards by 2015 to enable the widespread commercialization and market entry of these technologies.
Facilitate uniform implementation of requirements in codes and standards throughout the United States by 2015.

Support and facilitate the completion of all essential domestic and international RCS by 2020.


FY 2010 Technology Status

The sub-program continues to support R&D to provide the technical basis for codes and standards development with specific projects in a wide range of areas such as fuel specification, separation distances, materials and components compatibility, and hydrogen sensor technologies. Utilizing the results from this R&D, the sub-program continues to actively participate in discussions with SDOs such as the National Fire Protection Association (NFPA), International Code Council (ICC), Society of Automotive Engineers (SAE), Canadian Standards Association (CSA), and International Organization for Standardization (ISO) to promote domestic and international collaboration and harmonization of RCS. Figure 1 gives an overview of codes and standards development work:

![FIGURE 1. Overview of Codes & Standards Development Work](image)

The sub-program also utilizes the expertise of the Hydrogen Safety Panel to evaluate the safety plans and practices of Hydrogen Program-funded R&D 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 Program. The Hydrogen Safety Panel has taken the lead in reviewing fuel cell deployments under the American Recovery and Reinvestment Act (ARRA) by forming a team to conduct reviews of ARRA project safety plans, safety reviews, and site visits. As high-profile examples of early market deployments, it is especially important these projects are conducted in a safe and effective manner.

After initial pilot deployments of the advanced-level, prop-based course for first responders, the official course was rolled out to first responders in FY 2010. This rigorous eight-hour course uses a hydrogen fuel cell vehicle burn prop to provide first responders with hands-on experience and training. The course was developed with input from a steering committee made up of representatives from automobile manufacturers, energy companies, and the fire safety community. The course was deployed in three locations in August and September 2010.
The sub-program actively participates in the International Partnership for Hydrogen and Fuel Cells in the Economy Regulations, Codes and Standards Working Group and the International Energy Agency Hydrogen Implementing Agreement, both of which have been engaged in hydrogen safety work. Additionally, DOE continues to work with the Department of Transportation (DOT) to support its role as the U.S. representative to the UN ECE-WP29/GRPE to develop a global technical regulation for hydrogen-fueled vehicles.

**FY 2010 Accomplishments**

In FY 2010, the sub-program:

- Developed the technical basis for assessing the safety of hydrogen-based systems, which will be used in the development and modification of relevant codes and standards. This technical basis has introduced a risk-informed approach that enabled NFPA2 to update bulk gas storage separation distances in the 2010 edition of NFPA55.
- Completed additional materials and components compatibility work, including updates to the Technical Reference for Hydrogen Compatibility and completed testing to enable the deployment of 100-MPa stationary storage tanks; also supported the development of codes and standards for forklifts, including tank lifecycle testing, for use by the CSA Hydrogen Powered Industrial Truck Committee.
- Developed and published the “H₂ Safety Snapshot,” a quarterly newsletter promoting safety best practices.
- Developed and published a Web-based educational course addressing Hydrogen Safety Training for Researchers—the four-hour course has six modules and highlights best practices for the safe use of hydrogen in a research setting.
- 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—this includes the expansion of the Permitting Compendium for Hydrogen Facilities.
- Conducted hydrogen permitting workshops, which have reached over 250 code and permitting officials.
- Expanded outreach to code officials through four in-person workshops, an updated Introduction to Hydrogen Safety for Code Officials Web-based training course, and case studies documenting the permitting process for two early market fuel cell installations in conjunction with the Education sub-program. The codes and standards workshops, held in collaboration with local fire department and government organizations, were expanded to include additional modules on electric vehicles and infrastructure. The electronic learning package was updated with material on indoor hydrogen fueling to support the increasing number of fuel cell material handling equipment deployments. To support Market Transformation, the Education and Safety, Codes and Standards sub-programs were asked to evaluate, assist with and document the permitting of a backup-power fuel cell system and a fleet of fuel cell forklifts at two Department of Defense sites. The results were published as case studies to assist code officials and project developers in understanding the codes and standards and safety evaluations for similar early market installations.
- Continued to deploy the advanced-level, prop-based course for first responders in coordination with the Education sub-program. Two pilot sessions of the prop-based course were held at the

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4 [http://www.h2bestpractices.org/](http://www.h2bestpractices.org/)
Hazardous Materials Management and Emergency Response training center in 2009. The course was conducted three times in the state of California in 2010. More than 300 students from 18 states have been trained.

- Expanded the reach of the Web-based educational course *Introduction to Hydrogen Safety for First Responders.* This multimedia tutorial acquaints first responders with hydrogen, its basic properties, and how it compares with other fuels. The Web-based course has received over 17,000 unique visitors and is averaging 300–500 unique visitors each month from almost every state and many countries.

- Co-hosted, with the DOT, an international workshop for compressed natural gas (CNG) and hydrogen in December 2009. The workshop included participants from national laboratories and industry as well as international representatives from Brazil, India, Canada, China, and the United States. The workshop promoted the exchange of information among experts in CNG and hydrogen for vehicles, facilitated the sharing of lessons-learned from the deployment of these vehicles, and identified opportunities for international R&D collaboration.

- Held an Early Market Fuel Cell Technologies Workshop in April 2010 at Sandia National Laboratories (SNL). The workshop promoted the exchange of information among industry, government, national laboratories, SDOs, and other relevant stakeholders to enable the early market deployment of fuel cell technologies.

- Held a Vehicular Tank Workshop in April 2010 at SNL, which included participants from industry, government, national laboratories, SDOs, and other relevant stakeholders to coordinate R&D and RCS to enable the deployment of hydrogen storage tanks.

**Budget**

The sub-program received an appropriation of $8.8 million for FY 2010. This allowed for sustained progress in R&D, codes and standards development, and safety. The President’s FY 2011 budget request is $9 million, as shown below.

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FY 2011 Plans

The Safety, Codes & Standards sub-program will continue to work with codes and standards organizations to identify and address gaps to develop new hydrogen-specific codes and standards. To address these challenges, the sub-program will continue to support its rigorous technical R&D program.

In FY 2011, the sub-program will perform a technology status assessment of hydrogen sensors and their related targets. In addition, insurability for fuel cell and hydrogen technologies will be assessed through an international forum. In FY 2011 and beyond, the sub-program will continue to focus on critical safety R&D, such as assessment of materials compatibility for component designs, high-pressure tank cycle testing, and promoting a quantitative risk assessment approach to ensure the development of technically sound codes and standards. The sub-program will continue to promote the domestic and international harmonization of RCS.

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IX.1 National Codes and Standards Template

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• Smart Chemistry, Sacramento, CA
• Sloane Solutions, Oxford, MI
• CSA Standards, Cleveland, OH
• MorEvents, Englewood, CO
• GWS Solutions, Tolland, CT

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 hydrogen and fuel cell codes and standards.
- Support code development for the safe use of hydrogen and fuel cell technologies.
- Advance safety, code development, and market transformation issues through collaborations with appropriate stakeholders.
- Facilitate the safe deployment of hydrogen and fuel cell fuel technologies.

Technical Barriers

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

(A) Limited Government Influence on Model Codes
(B) Competition among SDOs and CDOs (Standards Development Organizations, Code Development Organizations)
(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
(N) Insufficient Technical Data to Revise Standards
(P) Large Footprint Requirements for Hydrogen Refueling Stations
(Q) Parking and Other Access Restrictions

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

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<th>Complete detailed scenario analysis risk assessments. (4Q, 2007)</th>
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<tr>
<td>3</td>
<td>Complete analytical experiments and data collection for hydrogen release scenarios as needed to support code development (Phase 1). (2Q, 2008)</td>
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<tr>
<td>4</td>
<td>Complete model of unintended release in complex metal hydrides. (2Q, 2008)</td>
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<tr>
<td>5</td>
<td>Materials compatibility technical reference updated. (2Q, 2009)</td>
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<tr>
<td>6</td>
<td>Collaborate with ICC and NFPA to develop first-order continuing education for code officials. (4Q, 2005)</td>
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Accomplishments

NREL has accomplished the following in support of section 3.7 of the DOE Fuel Cell 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. This report was published as a NREL technical report in FY 2010.
- Chemical sensor testing and validation: continued collaborations with key stakeholders; completed formal agreement with the European Commission’s Joint Research Centre (JRC) laboratory for testing hydrogen safety sensors and began round-robin testing with the JRC; continued testing commercially available sensors; participated on International Organization for Standardization (ISO) TC197 WG15 to develop a hydrogen sensor standard.
- Component testing: conducted validation testing of high-pressure release devices (HPRD). This work has been used to develop a HPRD standard by CSA America and will be complete in FY 2010. Also initiated compressed natural gas nozzle failure project, which could give useful information on designing hydrogen nozzles.
- Fuel quality specification: worked with ISO on technical specification 1 4687-2; coordinated testing and modeling to understand the effects of contaminants on fuel cell performance. Continued to support the promulgation of ASTM standards required to test contaminants to show compliance with the ISO standard.
- 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; added significant subcontracting responsibilities to support individuals and organizations responsible for codes and standards development.

Introduction

It is essential to develop and promulgate codes and standards in order to provide for the safe use of hydrogen and fuel cell technologies. With the help of key stakeholders, the DOE Fuel Cell Technologies Program and NREL are coordinating a collaborative national effort to prepare, review, and promulgate codes and standards for all hydrogen and fuel cell technologies.

Approach

The Fuel Cell Technologies Program recognizes that domestic and international codes and standards must be established to enable the timely commercialization and safe use of hydrogen and fuel cell technologies. The lack of codes and standards applicable to hydrogen and fuel cell technologies is an institutional barrier to deploying...
these technologies. It is in the national interest to eliminate this potential barrier. As such, the Hydrogen Codes and Standards sub-program 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 hydrogen and fuel cell 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**

The Safety Codes and Standards work is divided into three major areas:

1. National Template Implementation
2. Codes and Standards Research
3. Codes and Standards Training and Outreach

This report addresses the National Template Implementation

National Template Implementation, shows both the hierarchy for enforcing codes and standards and some of the progress made in promulgating the codes and standards required to implement hydrogen and fuel cell technologies (Figure 1).

In FY 2010 good progress was made in this implementation effort. National Fire Protection Association (NFPA) 2 Hydrogen Technologies Code was published as a Report on Proposal draft and the Hydrogen Technology Technical Committee met at NREL to act on comments to the draft. A final document will be issued in either December 2010 or July 2011 depending on whether there are any challenges to the document. NREL has supported the development of NFPA 2 in several ways including:

- Acting as a principal member of the technical committee.
- Funding subcontractors actively participating in the development of the document such as FP2 Fire Protection Engineering.
- Hosting meetings.

Another key codes and standards development area is the development of hydrogen fueling station component and system standards being performed by Canadian Standards Association (CSA) Standards. These H-4 series of documents consists of nine component standards and one system standard that address hydrogen dispensing. An NREL subcontractor is participating as a member of the CSA technical committee drafting these documents.

NREL continues to support the National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee. This effort, which is coordinated and directed by NREL, holds monthly meeting where SDOs, DOE laboratories, industry representatives, DOE and other interested parties are given topical information on codes and standards development activities.

**Conclusions and Future Directions**

NREL will continue to support the development of codes and standards by:

- Working with DOE 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.
• Performing outreach work to distribute information on hydrogen and fuel cell technologies to code officials, project developers, and other interested parties.
• Coordinating domestic codes and standards and international standards to ensure consistent requirements.

**FY 2010 Publications/Presentations**

8. High pressure Hydrogen Storage; Validation Testing of SAE performance Based System Level Requirements, Burgess, R. published in the proceedings of the National Hydrogen Association 2010 Annual Conference.
IX.2 Component Standard Research and Development

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Subcontractors:
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• Society of Automotive Engineers (SAE), Troy, MI

Project Start Date: Fiscal Year (FY) 2008
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Support development of new codes and standards required for commercialization of hydrogen technologies.
- Create code language that is based on the latest scientific knowledge by providing analytical, technical and contractual support.
- Participate directly on codes and standards committees to identify technology gaps, then work to define research and development needs required to close those gaps.
- Conduct laboratory testing to provide a basis for improved code language.
- Collaborate with industry, university and government researchers to develop improved analytical and experimental capabilities.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Codes and Standards section (3.7.4) of the Fuel Cell 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. (SDO = standards development organization)

(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 Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Codes and Standards section of the Fuel Cell 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. (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

- Completed validation testing of high-pressure composite overwrapped pressure vessel with induced flaws in support of ASME Boiler and Pressure Vessel code development.
- Completed validation testing of thermodynamic modeling used to generate SAE J2601 fill tables for hydrogen vehicle dispensing.
- Defined component level hydrogen compatibility testing being used to validate Canadian Standards Organization (CSA) hydrogen pressure relief device (HPRD) draft standard and initiated test program.
- Completed design/build/operations activities for NREL’s Sensor Testing Laboratory and initiated testing program responsible for supporting sensor development and commercialization.
- Established sensor test laboratory collaboration partners both domestically and internationally, entering into a long term agreement to develop sensor test protocol, conduct round robin test method validation and provide sensor commercialization support with European Joint Research Centre laboratory.

Introduction

Development of codes and standards has been identified as a key area needing support for the commercialization and growth of hydrogen technologies. NREL is providing research and development support to these codes and standards organizations through validation testing, analytical modeling, and product commercialization efforts. NREL has been tasked with these responsibilities as defined in the DOE multi-year RD&D plan.

Approach

NREL is participating on relevant codes and standards committees to help identify gaps and define research and development (R&D) needs to close those gaps. Working at the committee level allows us to quickly identify areas that need R&D support and to work directly with the technical experts in planning a path forward. This process is instrumental in avoiding delays and setbacks in the development of new codes and standards and in the revision of existing codes and standards. By providing support from a national lab we are able to help establish codes and standards language with solid technical basis.

Hydrogen safety sensors are a key component to commercialization of hydrogen technologies. NREL is tasked with building capability to test sensors for this growing market. 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 R&D, 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

NREL has been working on identifying gaps and supporting R&D efforts for developing new and improved hydrogen codes and standards. Results reported here are for efforts specifically directed at component level standards. There are four subject areas addressed in this report where significant achievements have been made during FY 2010. A summary of the four subject areas and corresponding gaps identified are presented in Table 1.

- Tanks: ASME Boiler and Pressure Vessel Code – ASME has developed new requirements that address the certification of tanks designed for stationary hydrogen storage applications. In developing these standards, new language has been developed for composite overwrapped pressure vessel (COPV) designs defining required testing to insure survivability in the event of material flaws. Flaw testing is based on best engineering
knowledge, however there was a need for validating these test methods. NREL worked with ASME in identifying the need and defining a series of validation tests. This work was subsequently conducted at Lincoln Composites. Testing included subjecting tanks to pressure cycling followed by a burst test to determine residual strength. Flaws were cut at depths up to 40% of the wall thickness in both longitudinal and transverse directions. Results of the testing are shown in Figure 1. Post test burst data show that current design COPV tanks are able to maintain better than a two times safety factor with a worst case flaw.

![FIGURE 1. ASME Flawed Cylinder Testing, Burst Pressure vs. Cycling and Depth of Flaw](image)

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**TABLE 1. Hydrogen Component Standard Summary**

<table>
<thead>
<tr>
<th>Hydrogen Component Requirements</th>
<th>Technology Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanks ASME Boiler and Pressure Vessel Code New addition to test standard for composite overwrapped pressure vessels</td>
<td>High pressure performance testing being developed to insure survivability with flaw added to exterior surface requires testing to be used as basis for code language</td>
</tr>
<tr>
<td>Interface SAE J2601 Fueling Protocol New non-communication fill tables for hydrogen vehicle fueling are designed to insure temperature limits are not exceeded</td>
<td>Tables developed by thermodynamic modeling need to be validated with actual performance test data</td>
</tr>
<tr>
<td>PRD CSA HPRD1 Pressure Relief Device New performance based standard for temperature activated pressure relief device</td>
<td>Hydrogen service suitability test, designed to insure PRD operation is not compromised by hydrogen effect on materials, requires validation testing</td>
</tr>
<tr>
<td>Safety Sensors Hydrogen leak detection NFPA 52 section 9.4.7.4 requires use of hydrogen leak detection for safe alarm and shutdown</td>
<td>DOE 2007 sensor workshop identified hydrogen safety sensor performance gaps relative to end user needs</td>
</tr>
</tbody>
</table>

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Interface: SAE J2601 Fueling Protocol – SAE standards for fueling rates in non-communication fill scenarios have been developed and are incorporated into the SAE J2601 standard, recently released as a technical information report. These fill rates are needed to insure against overfilling or exceeding temperature limits in the COPV tank. Fill tables have been developed based on thermodynamic modeling provided by a team of automotive manufacturers. The thermodynamic models take into account effects of Joule-Thomson heating, friction heating, thermal mass, pre-cooling and initial thermodynamic state. Validation testing was required to provide a sound basis for the data provided in the tables. NREL and SAE worked on defining a series of tests that include 35 and 70 MPa tanks, -20°C and -40°C pre-cooling and tank sizes ranging from 1.4 liter up to 9.8 liter internal volume. Fill cycle testing was conducted at Powertech labs. Results were shared with the SAE interface committee and it was determined that results showed good correlation and that there was no further modification to the tables required.

**PRD: CSA HPRD1 Pressure Relief Device** – Pressure relief devices have been identified as a key safety component on hydrogen storage systems. Inadvertent opening can result in a failure mode where there is a release of the entire contents of the storage vessel. Component standards for HPRD certification testing are being put in place to insure that these components have end of life reliability. NREL and CSA have worked toward defining scope of supply required to validate hydrogen service suitability testing as part of the CSA HPRD1 draft standard. Testing includes pneumatic cycle testing in hydrogen on three valves of three different designs. Also included in the test program are three surrogate designs made from materials that are known to show poor performance in hydrogen service. Post test metallurgical examination will be conducted to determine the extent of hydrogen related material degradation. Test components have been procured and testing has started. Completion of the contracted test program is scheduled for the end of FY 2010.

Hydrogen Safety Sensors – DOE has published performance targets for hydrogen safety sensors in the multi-year RD&D plan. NREL 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 140 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. NREL has completed the design and build of a new custom test apparatus with capability for an expanded range of environmental test conditions and capacity to test
multiple sensors concurrently. Figure 2 shows the new test apparatus.

NREL is currently working directly with sensor manufacturers, testing both commercially available product and near term prototype designs. In order to validate our test methods we have started a round robin test program with our sensor lab collaboration partner, the Joint Research Centre lab in the Netherlands. Selected sensors are being tested in both labs in order to show sensor performance is independent of any facility to facility differences. NREL is also collaborating with other national and international partners, including national laboratories, universities and codes and standards development organizations.

Conclusions and Future Directions

NREL has completed (or is near completion of) validation testing in support of ASME, SAE and CSA standards and will continue to work closely with codes and standards development organizations to close gaps and promulgate codes and standards that are based on the latest technical knowledge.

In addition to continuing to support component level codes and standards development, NREL will undertake a number of initiatives including:

• Identifying gaps to hydrogen technology commercialization.
• Developing national laboratory capabilities needed to provide a sound basis for component level codes and standards content.
• Focusing efforts toward working directly with sensor manufacturers in order to reach performance targets defined in the DOE multi-year RD&D plan.
• Expanding sensor laboratory capabilities to test over a wider range of environmental conditions and to add long-term exposure and response time test apparatus.
• Further our efforts on national and international collaboration in order to provide a path toward commercialization of hydrogen components.

FY 2010 Publications/Presentations

IX.3 Codes and Standards Training and Outreach and Education for Emerging Fuel Cell Technologies

Objective

- Conduct research and development (R&D) needed to establish sound technical requirements for hydrogen and fuel cell codes and standards.
- Support code development for the safe use of hydrogen and fuel cell technologies.
- Advance safety, code development, and market transformation issues through collaborations with appropriate stakeholders.
- Facilitate the safe deployment of hydrogen and fuel cell fuel technologies.

Technical Barriers

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

(A) Limited Government Influence on Model Codes
(B) Competition among SDOs and CDOs (Standards Development Organizations, Code Development Organizations)
(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
(N) Inadequate 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

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

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Complete detailed scenario analysis risk assessments. (4Q, 2007)</td>
</tr>
<tr>
<td>4</td>
<td>Complete analytical experiments and data collection for hydrogen release scenarios as needed to support code development (Phase 1). (2Q, 2008)</td>
</tr>
<tr>
<td>5</td>
<td>Complete model of unintended release in complex metal hydrides. (2Q, 2008)</td>
</tr>
<tr>
<td>6</td>
<td>Materials compatibility technical reference updated. (2Q, 2009)</td>
</tr>
<tr>
<td>9</td>
<td>Collaborate with ICC and NFPA to develop first-order continuing education for code officials. (4Q, 2005)</td>
</tr>
</tbody>
</table>
Accomplishments

NREL has accomplished the following in support of section 3.7 of the DOE Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

1. Codes and standards workshops: expanded codes and standards workshops from Fiscal Year (FY) 2009 to cover more subject matter, including a new module on electric vehicles and infrastructure requirements for electric vehicles. Presented four workshops in FY 2010 partnering with local fire departments and government organizations.
2. Web-based information compendium: expanded compendium to include other vehicle fuels and to include updated code official training course that includes material on indoor hydrogen fueling.

Introduction

It is essential to develop and promulgate codes and standards in order to provide for the safe use of hydrogen and fuel cell technologies. With the help of key stakeholders, the DOE Fuel Cell Technologies Program and NREL are coordinating a collaborative national effort to prepare, review, and promulgate codes and standards for all hydrogen and fuel cell technologies.

Approach

The Fuel Cell Technologies Program recognizes that domestic and international codes and standards must be established to enable the timely commercialization and safe use of hydrogen and fuel cell technologies. The lack of codes and standards applicable to hydrogen and fuel cell technologies is an institutional barrier to deploying these 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 hydrogen and fuel cell 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

The Safety Codes and Standards work is divided into three major areas:

1. National Template Implementation
2. Codes and Standards Research
3. Codes and Standards Training and Outreach

This report will address codes and standards outreach.

Codes and Standards Training and Outreach

NREL has several active training and outreach projects in FY 2010 including the following:

- Codes and Standards workshops.
- Update of code official on-line training course.
- Analysis of two emerging fuel cell technology projects (funded through the Education subprogram).

NREL conducted four Codes and Standards workshops in FY 2010. These workshops were held in Tampa, FL, New Orleans, LA, San Francisco, CA and Los Angeles, CA. All four were held in collaboration with local fire service departments or organizations. These workshops were targeted at code officials and project developers who would be working on fuel cell or hydrogen technology projects.
The proceedings from these workshops are posted at the Hydrogen Program Safety, Codes and Standards Web page. Generally, the workshops have been effective at getting information to individuals who will be directly involved in hydrogen and fuel cell projects. These individual proceedings include plan reviews for officials of fire departments and project managers responsible for getting hydrogen and fuel cell projects built.

The Code Official training course that was placed on-line in FY 2009 was amended to include material on indoor fueling operations. Indoor fueling is a special concern because of the developing use of hydrogen-fueled forklifts that are typically fueled indoors.

Another key project is two case studies that address emerging fuel cell technologies. The first project is an evaluation of codes and standards and safety issues associated with a fuel cell system used to supply backup power at a military base and the second is an evaluation of indoor fueling and forklift operations at a military storage facility. The analysis and findings from these projects will be published as an NREL technical report that would assist code officials and project developers in codes and standards and safety evaluations in similar projects.

Figure 1 shows the how the work done in the outreach activities feeds into the research projects and codes and standards development work.

**Conclusions and Future Directions**

NREL will continue to support the development of codes and standards by:

- Working with DOE 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.

![FIGURE 1. Structure of Safety, Codes and Standards Work at NREL](image-url)
• Continuing R&D collaborations with national and international stakeholders on vehicle codes and standards activities.
• Performing outreach work to distribute information on hydrogen and fuel cell technologies to code officials, project developers, and other interested parties.
• Coordinating domestic codes and standards and international standards to ensure consistent requirements.

FY 2010 Publications/Presentations


8. High pressure Hydrogen Storage; Validation Testing of SAE performance Based System Level Requirements, Burgess, R. published in the proceedings of the National Hydrogen Association 2010 Annual Conference.
IX.4 Hydrogen Safety Sensors

Objective

- Develop a low-cost, low-power, durable, and reliable hydrogen safety sensor for vehicle and infrastructure applications.
- Demonstrate working technology through application of commercial and reproducible manufacturing methods and rigorous life testing results guided by materials selection, sensor design, and electrochemical research and development investigation.
- Recommend sensor technologies and instrumentation approaches for engineering design.
- Disseminate packaged prototypes to DOE laboratories and commercial parties interested in testing and fielding advanced commercial prototypes while transferring technology to industry.

Multi-Year Program Plan Technical Barriers from the Hydrogen Safety section (3.8) of the Fuel Cell Technologies Program

- Liability Issues: Potential liability issues and lack of insurability affecting the commercialization of hydrogen technologies: Need for reliable H₂ safety sensor.


(G) Expense of Data Collection and Maintenance

Technical Targets

- Sensitivity: 1 vol% in air.
- Accuracy: 0.04-4% ± 1%.
- Response Time: <1 min at 1% and <1 sec at 4%; recovery <1 min.
- Temperature: -40°C to 60°C.
- Durability: 5 years without calibration.
- Cross-Sensitivity: Minimal interference to humidity, H₂S, CH₄, CO, and volatile organic compounds.

Accomplishments

- New zirconia-based mixed potential sensor with 0-4 vol% hydrogen sensitivity was demonstrated utilizing a machined, dense indium-tin oxide (ITO) working electrode (In₂O₃: SnO₂; 90%: 10%), a Pt wire counter electrode, and porous yttria-stabilized zirconia (YSZ) electrolyte were prepared using ceramic tape casting methods. The response of these devices to hydrogen concentrations up to 2% in air was studied from 600 to 740°C.
- Durability testing of over 1,700 hrs was accomplished on pre-commercial tape-cast sensors.
- Potential manufacturing platform were investigated for early prototypes.
- Developed a miniaturized, low-power, robust H₂ sensor prototype conducive to commercialization.
- Stable response over time achieved in the sensor prototype by modifying Pt morphology.
- Completed long-term testing of H₂ sensor (4,000 hrs) including 100 hrs of accelerated stress testing.
- Evaluated sensor electrode materials and design to further improve long-term stability and prevent sensor-aging effects.
- Investigated the suitability of lanthanum strontium manganate (LSM) as a pseudoconuter electrode to replace Pt electrode for long-term stability and reliability.
- Explored alternate modalities such as impedancemetric detection for H₂ screening.
Introduction

Recent developments in the search for renewable energy coupled with the advancements in fuel cell powered vehicles have augmented the demand for hydrogen safety sensors [1]. There are several sensor technologies that have been developed to detect hydrogen, including deployed systems to detect leaks in manned space systems and hydrogen safety sensors for laboratory and industrial usage. Among the several sensing methods electrochemical devices [2-8] that utilize high temperature-based ceramic electrolytes are largely unaffected by changes in humidity and are more resilient to electrode or electrolyte poisoning. The desired sensing technique should meet a detection threshold of 1% (10,000 ppm) H₂ and response time of ≤1 sec [9] targets for infrastructure and vehicular. Further, a review of electrochemical hydrogen sensors by Korotcenkov et al. [10] and the report by Glass et al. [11] suggest the need for inexpensive, low-power, and compact sensors with long-term stability, minimal cross-sensitivity, and fast response. As part of the Hydrogen Code and Standards sub-program, Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL) are working together to develop and test inexpensive, zirconia-based, electrochemical (mixed potential) sensors for H₂ detection in air. Previous work conducted at LLNL showed [8] that ITO electrodes produced a stable mixed potential response in the presence of up to 5% of H₂ in air with no response to CO₂ or water vapor. The sensor also showed desirable characteristics with respect to response time and resistance to aging, and degradation due to thermal cycling.

In this investigation, the development and testing of an electrochemical H₂ sensor prototype based on ITO/YSZ/Pt configuration is detailed. The device fabricated on an alumina substrate integrates a resistive Pt heater to achieve precise control of operating temperature while minimizing heterogeneous catalysis. Targeting fuel cell-powered automotive applications, the safety sensor was subjected to interference studies, temperature cycling, operating temperature variations, and long-term testing over 4,000 hrs. The sensor responded in real time to varying concentrations of H₂ (1,000 to 20,000 ppm). Among the interference gases tested such as NO, NO₂, NH₃, CO, and propylene (C₃H₆), the sensor showed cross-sensitivity to C₃H₆. Analyzing the overall device performance over 4,000 hrs of testing for 5,000 ppm of H₂, (a) the sensitivity varied between 0.135 to 0.17 V with a minimum low of 0.12 V, (b) the baseline signal ranged from 0 to 0.04 V, and (c) the response rise time fluctuated between 3 to 47 s.

The salient features of the H₂ sensor prototype developed by LANL are (a) the low power consumption, (b) compactness to fit into critical areas of application, (c) simple operation, (d) fast response, (e) a direct voltage read-out circumventing the need for any additional conditioning circuitry, and (f) conducive to commercialization.

Approach

The sensor design approaches from LANL and LLNL were used to develop devices with superior performance.

LANL Design: Controlled Electrode/Electrolyte/Gas Interface

At LANL, electrochemical potentiometric modality is utilized for designing the sensors. Mixed potential sensors are a class of electrochemical devices that develop an open-circuit electromotive force due to the difference in the kinetics of the redox reactions of various gaseous species at each electrode/electrolyte/gas interface, referred to as the triple phase boundary [12]. Therefore these sensors have been considered for the sensing of various reducible or oxidizable gas species in the presence of oxygen. Based on this principle, a unique sensor design was developed. The uniqueness of the LANL sensor [13] derives from minimizing heterogeneous catalysis (detrimental to sensor response) by avoiding gas diffusion through a catalytically active material and minimizing diffusion path to the 3-phase interface (electrode/electrolyte/gas referred to as tripe phase boundary). Unlike the conventional design of these devices that use a dense solid electrolyte and porous thin film electrodes (similar to the current state-of-the-art zirconia-based sensors and fuel cells), the LANL design uses dense (either metal wires, oxide pellets or thin film) electrodes and porous electrolytes (bulk or thin film). Such a sensor design facilitates a stable and reproducible device response, since dense electrode morphologies are easy to reproduce and are significantly more stable than the conventional porous morphologies. Moreover, these sensors develop higher mixed potentials since the gas diffusion is through the less catalytically active electrolyte than the electrode. Further, the choice of electrodes is primarily based on their O₂ reduction kinetics. Sensors fabricated at LANL will typically involve one electrode with fast (Pt) and another with slow (Au or LaCrO₃) O₂ reduction kinetics aimed to improve the sensitivity.

LLNL Design

In the LLNL design, a new impedance-based measurement technique, originally developed for electrochemical NOₓ sensors, was shown to generate more stable sensor responses and may be able to offer a way to compensate for cross-sensitivity effects. The technique is based on the measurement of parameters related to the complex impedance of the sensor in the frequency range of 1 Hz to 10 kHz. Measurements
are typically made at a single frequency selected to maximize the desired sensitivity, although measurements performed at additional frequencies have been shown to be useful for correcting the response to interfering gases. LLNL has also found in the NOx sensor studies that it may be possible to use a wider variety of electrodes for the sensor in impedance-based sensing. Additional possible advantages included better tolerance to mechanical defects (such as delamination) and better longer-term stability.

Results

(a) Potentiometric Sensing

Figure 1 shows the schematic of the fabricated sensor with integrated Pt heater. The plan and cross-sectional view of the sensor schematic along with the four post (two electrodes, two heater pads) metal connections are shown in the top and bottom part of Figure 1, respectively. After obtaining the sensor platform from ESL Electro-Science Laboratories (fabricated using a patented LANL design), the ITO electrode was deposited.

The ITO working electrode was sputter deposited onto the sensor body using a commercially available 2" diameter radio frequency magnetron sputtering target (Alfa, In2O3: SnO2; 90%: 10%) in an off-axis orientation. After ITO deposition, the YSZ electrolyte layer was prepared using e-beam evaporation. Tosoh-8z YSZ powder was pressed into a pellet, which was then sintered at 1,200°C for 6 hrs. The sintered pellet was used as the evaporation source. An alumina platform with four metal posts connecting the sensor electrodes and heater was housed in a low volume quartz tube with a gas inlet and outlet. Humidity was added to the system by passing the gas through a bubbler. The heater voltage was set to 6.5 V, which corresponded to an operating temperature of approximately 535°C following a polynomial trend, \( Y = 4.941 \times 2 + 45.85 \times + 28.16 \) (\( Y \) represents the operating temperature in degrees and \( x \) represents the heater voltage).

The ITO and Pt electrode achieve different steady-state redox potentials when exposed to a mixture of \( \text{H}_2 \) and \( \text{O}_2 \) determined by the kinetic balance of the following electrochemical reactions:

\[
\frac{1}{2} \text{O}_2 + 2e^- \leftrightarrow \text{O}^{2-} \quad (i)
\]

\[
\text{H}_2 + \text{O}^{2-} \leftrightarrow \text{H}_2\text{O} + 2e^- \quad (ii)
\]

The electrode that favors the second reaction over the first develops a large non-Nernstian potential. However, the non-electrochemical oxidation (heterogeneous catalysis) of \( \text{H}_2 \) lowers the differential voltage developed between the electrodes signifying the importance of materials selection and localized heating.

In this investigation, the alumina substrate is integrated with a screen-printed Pt heater for precise control over the operating temperature. In addition, the use of metal oxide electrode enables a higher mixed potential. The derived the mixed potential equation for a \( \text{H}_2 \) sensor as a function of air/hydrogen concentration as:

\[
E_m = E_o + mAlnC_{\text{H}_2} - nAlnC_{\text{O}_2} \quad (iii)
\]

\( E_m \) is the developed mixed potential, \( E_o \) is the electrode potential at equilibrium, \( m \) and \( n \) are constants, \( A \) is a constant associated with the catalytic activity of the electrode material through their dependence on the charge-transfer coefficient and the standard rate constant, and \( C \) stands for the concentration of \( \text{H}_2 \) or \( \text{O}_2 \). As inferred from equation (iii), the mixed potential linearly relates with logarithmic concentrations of \( \text{H}_2 \). Such an observation is noticed in this investigation.

Figure 2a shows the staircase sensor response with varying concentrations of \( \text{H}_2 \). The sensor response was seen to linearly vary with logarithmic concentrations of \( \text{H}_2 \) and seems to follow a mixed potential device behavior.

For interference studies, 100 ppm of gases such as NO, NO2, CO, NH3 and C3H6 were used as analytes. Figure 2b shows the cross-sensitivity response indicating a strong signal from 100 ppm of C3H6. The concentration of C3H6 was further increased to 500 ppm to observe any augment in the undesired signal. Absence of any
significant increase in the C\textsubscript{3}H\textsubscript{6} response with higher concentration suggests that the tested concentration range of C\textsubscript{3}H\textsubscript{6} must have coincided with the saturation region of the device (characterized by the logarithmic flat sensor response). Also, the occurrence of a non-electrochemical heterogeneous process rather than electrochemical oxidation of C\textsubscript{3}H\textsubscript{6} cannot be ruled out.

Life cycle characterization of the sensor was initiated since the device exhibited the appropriate sensitivity and selectivity to H\textsubscript{2}. Table 1 summarizes the different sensor testing conditions over 4,000 hrs. The variation in the sensor response (Figure 3) subjected to different thermal treatments can be attributed to thermal expansion mismatch between the electrodes (ITO, Pt) and the electrolyte (YSZ). For a typical ceramic-metal system involving high-temperature applications, the recommended rule for materials selection involves the

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**TABLE 1. Summary of the Life Cycle Testing Experiments**

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 300</td>
<td>Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas</td>
</tr>
<tr>
<td>301 - 390</td>
<td>Temperature Cycling 6.5 V to 0 to 6.5 V, Three Cycles, Maintaining Humidity Level and Base Gas</td>
</tr>
<tr>
<td>391 - 822</td>
<td>Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas</td>
</tr>
<tr>
<td>823 - 894</td>
<td>Operating Temperature Variations – 6.5 to 5.75 V, Maintaining Humidity Level and Base Gas</td>
</tr>
<tr>
<td>895 - 1900</td>
<td>Static Conditions – No humidity, No Base Gas, Set Voltage – 6.5 V</td>
</tr>
<tr>
<td>1901 - 2296</td>
<td>Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas</td>
</tr>
<tr>
<td>2297 - 3249</td>
<td>Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas</td>
</tr>
<tr>
<td>3250 - 4000</td>
<td>Stress Testing – Temperature Cycling 6.5 V to 0: 100, 500, 1000, and 10000 Cycles, Sensor Response Measurement Before and After Each Cycle</td>
</tr>
</tbody>
</table>

---

**FIGURE 2.** (a) Sensor response upon exposure to various concentrations of H\textsubscript{2} in air (6.5 V—535°C, 200 SCCM, 0 hrs) and (b) Cross-sensitivity studies comparing sensor response from 10,000 ppm of H\textsubscript{2} to 100 ppm of interferents and 500 ppm of C\textsubscript{3}H\textsubscript{6}.

**FIGURE 3.** Lifetime testing of sensor response and response time upon exposure to 5,000 ppm of H\textsubscript{2} over 4,000 hrs (6.5 V—535°C, 200 SCCM, air)
use of metal, that have similar and/or smaller thermal expansion coefficients than that of the ceramic. Though intermediate layers (such as an insulator or metal composites) have been added in the past to match the coefficient of thermal expansion (CTE) of the metal and the ceramic, certain applications that involve charge transfer process demand a direct ceramic-metal contact. Considering the materials specific to this application, the thermal expansion coefficients of ITO, 8z-YSZ, and Pt from published literature were found to be 6.2 x 10-6/°C, 9.6 x 10-6/°C, and 10.53 10-6/°C respectively. The CTE of both ITO and Pt electrode deviate from that of YSZ. Such a variation in CTE of the materials may be responsible for the different levels of sensor response observed in Figure 3. The variation in the sensor response subjected to different thermal treatments is also shown in Figure 3. As the response time of the device is governed by the speed of the competing oxygen reduction and electrochemical oxidation reactions, it is postulated that surface stress on ITO due to CTE mismatch and H2 oxidation slows down the reaction represented in equation (ii) upon different thermal treatments.

Analyzing the overall device performance from 0 to 4,000 hrs upon exposure to 5,000 ppm of H2, (a) the sensitivity varied between 0.135 to 0.17 V with a minimum low of 0.12 V, (b) the baseline signal ranged from 0 to 0.04 V, and (c) the response rise time fluctuated between 3 to 47 s. It should be noted that the rise time includes the time constant of the test set-up, which is calculated as 1 s. The absence of any dramatic deterioration in the sensor response over time is attributed to a stable three-phase interface (electrode/electrolyte/gas). As the interfacial regions contain the electrochemically active sites, it is vulnerable to microstructural changes during sensor operation as these regions are also the sites for mass transport and diffusion. These microstructural changes (for example, due to annealing/heating) can be a major factor inducing sensor drift. Even well designed interfaces contribute to the electrical losses of devices and hence limit the overall sensor performance. Hence, it is critical to engineer the interface through materials selection and processing for the development of a reliable and stable sensor.

(b) Impedancemetric Sensing

Based on preliminary results, impedance-based response was evaluated using a test cell with a stacked electrode configuration consisting of a porous ITO sensing electrode on the bottom, porous YSZ electrolyte, and dense LSM counter electrode on the top. Results of impedance-based testing indicated reasonably stable performance to over 150 hrs of testing with resolution of 0.25, 0.5, 1, and 2 vol% H2. However, the sensitivity for the impedance-based method was lower than that of the potentiometric signal. Nevertheless, another important result of the impedance-based sensing experiments was characterizing the overall influence of applied signals (alternating and direct current, ac and dc) on the stability of the sensor response during long-term testing. Further investigation is necessary to understand how applied signals may temporarily influence sensing behavior, and the development of a novel strategy using electrical measurement and conditioning protocols, both alternating current and direct current, will be explored to improve sensor performance.

Conclusions

- Improved electrode materials with potentially better performance were investigated where dense electronically conducting oxide (LSM) counter electrode showed better long-term stability.
- An alternate impedancemetric sensing modality was explored to evaluate improvements in long-term performance and stability.
- A pre-commercial H2 sensor prototype was fabricated on an alumina substrate with ITO and Pt electrodes and YSZ electrolyte with an integrated Pt heater to achieve precise operating temperature and minimize heterogeneous catalysis.
- During the initial 4,000 hrs of long-term testing for the prototype with optimized platinum electrode, the sensor response to 5,000 ppm of H2 varied at a maximum of ca. +10%/-7% from its original value of 0.135 V (0 hrs). The response rise time fluctuated between 3 to 47 s.
- The extended sensor response stability over time may be attributed to a stable, engineered three-phase interface.
- The salient features of the investigated H2 sensor prototype include (a) conducive to commercialization, (b) low power consumption, (c) compactness to fit into critical areas, (d) simple transduction mechanism, and (e) fast response.

Future Directions

- Postmortem analysis of H2 prototype sensor tested for 4,000 hrs (Aug. 2010 - Oct. 2010).
- Fabrication and lifetime performance evaluation (minimum 5,000 hours) of advanced prototypes (Aug. 2010 - Feb. 2011).
  - Investigation of composite electrode compositions with novel impregnation technique for improved stability. Such a rationale is based on controlling properties at the interface between the electrode and electrolyte. The composite electrode compositions, containing both electrode and electrolyte material may decrease...
thermal expansion mismatch at the interface and improve stability. Further, the novel impregnation technique uses an already sintered backbone of electrolyte material where the electrode material is added in a separate low-temperature process step (previous work has shown this approach to not only improve thermal expansion matching (as anticipated with a composite structure), but also improve electronic/ionic conduction paths).

- Cross-sensitivity studies, stability evaluation using LSM electrodes in advanced prototypes (Sep. 2010 - Dec. 2010).
  - Need to configure radio frequency magnetron sputter system and optimize deposition conditions for lanthanum strontium manganese oxide (LSMO) thin film deposition. This material will replace Pt as a sensor pseudo-reference counter electrode. Then, sputter masks (for low- and high-temperature depositions) needs to be prepared for sensor electrode and electrolyte film patterning during deposition. Also, a modified mount needs to be machined to fix position of sensor substrate relative to mask. This will permit a high degree of reproducibility for placement of electrodes/electrolyte from sensor to sensor. Finally, several ITO and LSMO calibration runs needs to be performed to characterize rates/structure/morphology/conductivity.

- Characterize and understand the sensing mechanism(s) in various modalities and apply to future devices and optimize next generation of pre-commercial prototypes (Sept. 2010).

- Investigate and identify packaging schemes for field and laboratory testing (Nov. 2010 - Jan. 2011).

- Independent testing and comparison of the performance of packaged prototype $H_2$ sensor with a commercial device (Feb. 2011 - May 2011).
  - Initiate and pursue collaboration and independent testing work with Dr. William Buttner from National Renewable Energy Laboratory. Then, acquisition of best available technology $H_2$ sensor (thermal conductivity detector-based technology, $\$2000.00$ unit cost) for comparison performance/stability testing with the low-cost LANL/LLNL device needs to be completed.
  - Further, a new, customized test chamber assembly needs to be constructed to test $H_2$ sensors (both experimental and commercial) under diffusion conditions while permitting continuous sampling and measurement of $[H_2]$ local to sensors using gas chromatography.

**FY 2010 Patent Application**


**FY 2010 Publications and Presentation**


**References**


IX.5 Materials and Components Compatibility

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Start Date: Fiscal Year (FY) 2003
End Date: Project continuation and direction determined annually by DOE

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Technical Barriers
This project addresses the following technical barriers from the Codes and Standards section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration 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

Contribution to Achievement of DOE Codes and Standards Milestones
This project will contribute to achievement of the following DOE milestones from the Codes and Standards section of the Fuel Cell 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). This project enables the development and implementation of codes and standards by providing expertise and data on hydrogen compatibility of structural materials.


Accomplishments

- Completed cutting-edge measurements and report on fracture threshold measurements of tank steels in H2.
- Testing completed on stationary tank materials to meet immediate needs for market transformation.
- Testing performed on forklift tank materials to meet immediate needs for market transformation.
- Measurements performed to illuminate pathway to optimization of procedures in American Society of Mechanical Engineers (ASME) Article KD-10 standard.
- Updated “Technical Reference for Hydrogen Compatibility of Materials” to include single-phase nickel alloys.
- Initiated testing and analysis effort to evaluate the cycle-life of steel tanks and inform the design qualification standards for hydrogen-powered industrial trucks (e.g. forklifts).
Introduction

A major barrier to 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 optimized materials qualification methodologies and assembling 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 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. Results from this materials testing illuminate the pathways to optimize materials qualification methods, enabling efficient, high-quality testing to support rapid technology deployment.

Approach

The focus of the Materials and Components Compatibility project is to optimize materials characterization methodologies, generate benchmark data for materials to enable technology deployment, and compose the Technical Reference on Hydrogen Compatibility of Materials. Two activities proceed in parallel: generating new data and understanding through materials testing, and identifying and compiling existing data from technical documents. 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 identify pathways to improve the test methods and to ensure the data are suitable for implementation in structural design. The qualification methods developed in this program are then validated on real components to enable effective incorporation into codes and standards.

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 (CSA), Society of Automotive Engineers, and the 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

The Technical Reference is an evolving document, where individual chapters are published via Web site (http://www.ca.sandia.gov/matlsTechRef/) and updated as information is collected. In addition, a formal report (SAND2008-1163) has been distributed to stakeholders and will be revised periodically. When available, the data featured in the Technical Reference are those that enable application of design standards such as ASME Article KD-10 and ASME B31.12. In addition, permeability data are needed to calculate the rate of hydrogen release from containment structures. There are currently 22 material-specific chapters whose content has been informed by input from stakeholders including industry and standards development organizations. In FY 2010, a new chapter on single-phase nickel alloys was incorporated. The data contained in this reference is often used for materials selection in technology design and for standards development and will continue to be an enabling product of the Codes and Standards program element.

Material Measurements

Efforts in FY 2010 focused on improving methods for measuring fatigue crack growth rates of structural metals in high-pressure hydrogen gas and generating high-demand fatigue crack growth data to enable the implementation of ASME Article KD-10 for short-term technology deployment. We developed and evaluated a new load cell capable of operation in high-pressure hydrogen gas. The performance of the load cell was then assessed by conducting a fatigue crack growth test on the line pipe steel X52 in high-pressure hydrogen gas. In this case, the fatigue crack growth test was conducted using control software that required a feedback signal from the load cell. The test was successfully conducted, and the resulting fatigue crack growth (da/dN) vs stress-intensity factor range (AK) data from the test are displayed in Figure 1. Test systems capable of measuring fatigue crack growth rates under high-pressure hydrogen are rare, and the implementation of this platform at Sandia establishes a valuable capability that will be leveraged to generate critical data for hydrogen service materials.

The need to determine the cycle-life of steel hydrogen storage tanks on lift trucks emerged as a high priority during FY 2010. In response, a new activity was initiated to establish cycle-life prediction methodologies
FIGURE 1. Fatigue crack growth rate data measured for X52 line pipe steel in 3,000 psi (21 MPa) hydrogen gas at a load cycle frequency of 1 Hz and load ratio of 0.5. This fatigue crack growth test represents the successful performance of the new strain gauge-based load cell in the test system.

and support standards development for lift-truck tanks. One of the cycle-life prediction methodologies explored in this lift-truck tank activity is based on structural analysis, i.e., ASME Article KD-10. This analytical framework for calculating the cycle life of steel hydrogen pressure vessels requires measurements of fatigue crack growth data for the steel in hydrogen gas. Since one objective of the Materials and Components Compatibility activity has been to measure fatigue crack growth rates for pressure vessel steels in hydrogen gas, this activity is well positioned to contribute critical data for the lift-truck tank effort. The lift-truck tanks are fabricated from the DOT 3AAX (4130X) steel, which we evaluated previously while measuring the sustained-load cracking thresholds of pressure vessel steels. The parameters for the fatigue crack growth tests were developed in consultation with several industry partners. Based on these interactions, the hydrogen gas test pressure and initial stress-intensity factor range were selected as 6,500 psi (45 MPa) and about 9 MPa m\(^{1/2}\), respectively, for the fatigue crack growth tests. Two variables that are known to affect measured fatigue crack growth rates in hydrogen gas are the load cycle frequency and the load ratio, i.e., ratio of minimum applied load to maximum applied load (R). Since the rationale for specifying values of load cycle frequency and load ratio are still being developed for fatigue crack growth testing in hydrogen gas, it was decided to test the 4130X over a range of load cycle frequencies and load ratios.

A summary of the fatigue crack growth test matrix, the measured fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) curves, as well as the status for each test on the 4130X steel are provided in Table 1 and Figure 2. The table indicates that three heats of 4130X are included in the test matrix, in which each steel heat was supplied by a different industry partner. Results in Figure 2 show that the fatigue crack growth rates in hydrogen gas exhibit a complex dependence on the applied stress-intensity factor range. The fatigue crack growth rate relationships (da/dN vs. ΔK) are being used, along with data generated in the full-scale tank tests, to better understand crack initiation in hydrogen gas and to validate the engineering analysis method for design and qualification of steel tanks for use in hydrogen, especially the lift-truck application. Heats 2 and 3 in Table 1 represent specimens taken from the tanks that are being tested in the full-scale tests.

Fatigue crack growth testing of ASME SA-372 Grade J in hydrogen gas at 100 MPa pressure has also been a recent focus of testing activities. Results from this testing directly impact market transformation, since our industry partner will use the data to qualify a stationary hydrogen tank design for a refueling station. Sandia was approached by the industry partner since no commercial test facilities exist in North America with capabilities to execute the testing required by the ASME Article KD-10 code at the service pressure of 100 MPa. Our testing is designed to meet the requirements of the ASME code for hydrogen tanks: three heats of steel tested at a frequency of 0.1 Hz. The low specified test frequency is intended to accommodate the kinetics of hydrogen transport in the steel, but the resulting extended test durations can present a challenge. Table 1 summarizes the matrix for the SA-372 Grade J fatigue testing, and includes the durations for tests completed on both the SA-372 Grade J as well as the 4130X. The da/dN vs. ΔK relationships from the completed test matrix on the SA-372 Grade J steel are plotted in Figure 2. Fatigue crack growth tests in air can be characterized by a power law relationship over a wide range of ΔK, which is represented by a line in a log-log plot such as Figure 2.

Component Testing and Codes and Standards Advocacy

Members of the Sandia Materials and Components Compatibility team were actively involved in the development of standards for lift truck tanks, CSA Hydrogen Powered Industrial Trucks (HPIT) 1. An experimental and analysis project was initiated in FY 2010 to perform hydrogen pressure-cycle testing and engineering analysis of commercial Type 1 hydrogen pressure vessels to build consensus for design methodologies and code development processes for high-frequency refueling applications. The effort provides the technical basis for CSA HPIT 1. The project addresses fatigue crack initiation and growth in steel tanks used in high-cycle applications. The tanks under test are sourced from two fuel cell forklift partner companies and tank manufacturers. We are developing design methodologies for steel tanks in this environment and validating the methodologies with experiments that emulate the real environment of the storage tank.
TABLE 1. Summary of Fatigue Crack Growth Tests for Tank Steels

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield strength (MPa)</th>
<th>Test conditions</th>
<th>Test duration (hours)†</th>
<th>completion</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Frequency (Hz)</td>
<td>Load ratio, R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4130X Heat 1</td>
<td>600</td>
<td>1</td>
<td>0.5</td>
<td>8</td>
<td>FY 2010 Q1 Investigate frequency and R-ratio</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>0.1</td>
<td>21</td>
<td>FY 2010 Q1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>52</td>
<td>FY 2010 Q1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td>340</td>
<td>FY 2010 Q2</td>
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<tr>
<td>4130X Heat 2</td>
<td>765</td>
<td>1</td>
<td>0.5</td>
<td>14</td>
<td>FY 2010 Q2 Investigate frequency and R-ratio</td>
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<tr>
<td></td>
<td></td>
<td>1</td>
<td>0.1</td>
<td>23</td>
<td>FY 2010 Q2</td>
</tr>
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<td></td>
<td></td>
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<td>0.5</td>
<td>62</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td>(56)*</td>
<td>FY 2010 Q2</td>
</tr>
<tr>
<td>4130X Heat 3</td>
<td>544</td>
<td>Specimens prepared, not yet tested</td>
<td>n/a</td>
<td>Extend range of tested YS; same steel as tank testing</td>
<td></td>
</tr>
<tr>
<td>SA372 Grade J Heat 1</td>
<td>642</td>
<td>1</td>
<td>0.5</td>
<td>3</td>
<td>FY 2009 Q2 Benchmark steel; effect of YS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.2</td>
<td>40</td>
<td>FY 2010 Q3 Qualify steel according to ASME KD-10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>56</td>
<td>FY 2010 Q2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>&gt;100</td>
<td>FY 2010 Q3</td>
</tr>
<tr>
<td>SA372 Grade J Heat 2</td>
<td>731</td>
<td>1</td>
<td>0.5</td>
<td>3</td>
<td>FY 2009 Q2 Benchmark steel; effect of YS</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.2</td>
<td>135</td>
<td>FY 2010 Q3 Qualify steel according to ASME KD-10</td>
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<tr>
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<td>0.5</td>
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<td>0.5</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>60</td>
<td>FY 2010 Q3</td>
</tr>
</tbody>
</table>

† excludes preparation and analysis
* unintended interruption of test
YS – yield strength; Q1 – first quarter; Q2 – second quarter; Q3 – third quarter

FIGURE 2. Fatigue crack growth rate (da/dN) vs. stress-intensity factor range (√K) relationships measured for 4130X tank steel (Heat 1) in 6,500 psi (45 MPa) hydrogen gas and for SA-372 Grade J tank steels (Heats 1-3) in 15,000 psi (103 MPa) hydrogen gas.
IX. Safety, Codes & Standards

A tank cycling apparatus was developed in a high-pressure facility at Sandia (Figure 3). This is a closed-loop cycling manifold that allows efficient hydrogen utilization. The system has the engineering and administrative controls in place to accommodate tank failure, which is desired in order to understand life-cycles of steel pressure vessels. A periodic pressure profile involves a 2 minute fill to 6,350 psi, a 2 minute hold, and a 2 minute vent which was deemed appropriate by the CSA HPIT 1 Materials working group. This accelerated fatigue cycling allows for up to 250 cycles per day. The test manifold is designed to operate up to 10 tanks in parallel. A test plan was developed in conjunction with the CSA HPIT 1 Materials working group. Two different tanks are under test from two separate manufacturers. Both as-manufactured tanks as well as tanks with engineered defects are tested to understand how cracks imitate and grow through the tank walls. Output from this project provides data in the area of crack initiation in components and validation of performance-based design qualification methods as will be codified in CSA HPIT 1 and the GTR.

Conclusions and Future Directions

In FY 2010:

- A report was completed on fracture threshold measurements of tank steels in hydrogen gas. The data has enabled revision of the ASME Article KD-10 tank standard.
- Fatigue crack growth testing was conducted on tank steels in hydrogen gas following ASME Article KD-10 to meet immediate needs for technology deployment in refueling stations and forklifts.
- We determined that the application of the ASME Article KD-10 standard indicates a path for optimization by establishing fatigue crack growth test frequencies that shorten test duration without compromising data quality.

Future Work:

- Update “Technical Reference” chapters on ferritic steels with new data.
- Establish ability to test properties of materials at variable temperature and pressure.
- Complete and distribute report on results from fatigue crack growth and fracture threshold testing of SA372 Grade J tank steel in hydrogen.
- We will complete fatigue crack growth testing of forklift tank steels in hydrogen to provide data for tank testing activity and enable standards development.
- Establish optimum load cycle frequencies for fatigue crack growth testing of steels in high-pressure hydrogen to enable standards revision.
- Complete first phase of materials qualification standard development for vehicle components (i.e., fittings, regulators, etc.) in collaboration with international partners.
- Conduct testing on additional materials (e.g., aluminum) that impact market transformation (FY 2011–2012).
- Complete materials qualification standard development for vehicle components (i.e., fittings, regulators, etc.).

FY 2010 Publications/Presentations


IX.6 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 and share lessons learned from hydrogen incidents and near-misses, with the goal of preventing similar safety events from occurring in the future.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section of the Fuel Cell Technologies (FCT) 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 has already met the following DOE milestones from the Hydrogen Safety section of the FCT Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 18: Publish safety bibliography and incident databases (3Q, 2006).

Accomplishments

Hydrogen Safety Best Practices

- We enhanced the best practices content for outdoor storage of hydrogen cylinders in the Laboratory Safety/Laboratory Design section.
- We made Management of Change (MOC) more visible by adding a new page on the Web site and adding links to that page from three other Web pages.
- We drafted a new section called Hydrogen Properties that is focused on hydrogen combustion and liquid hydrogen expansion.
- We updated the Hydride Storage and Handling Section of Laboratory Safety/Laboratory Operations to cover the risks related to large-scale experiments with metal hydrides.
- We added approximately 50 links to safety event records in the Incident Reporting and Lessons Learned database to illustrate the kinds of incidents and near-misses that can occur if hydrogen safety best practices are not followed.

Hydrogen Incident Reporting and Lessons Learned

- We added 37 new safety event records, for a total of 177 records currently in the database. The new records came from DOE projects, private companies, and member countries of the International Energy Agency (IEA) Hydrogen Implementing Agreement (HIA) Task 19 (Hydrogen Safety).
- We created a new feature on the Web site called the Lessons Learned Corner to analyze and present hydrogen safety themes illustrated with database content.

Introduction

PNNL has developed and continues to improve two software tools to support the Hydrogen Safety, Codes and Standards Sub-Program. This report covers the Hydrogen Safety Best Practices online manual (http://

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 teams with hydrogen safety experts at Los Alamos National Laboratory (LANL), Sandia National Laboratories (SNL), the Hydrogen Safety Panel, and other subject matter experts to compile hydrogen-specific best practices from a variety of references. 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 includes encouraging DOE-funded project teams and others to voluntarily submit incidents and near-misses and to provide specific lessons learned. We continue to pursue the addition of new records by actively seeking news reports on hydrogen incidents and searching existing databases and other sources for hydrogen-related safety event records. We contact private-sector companies who experience hydrogen-related safety events to solicit their permission to publish such records. We continue to maintain a mechanism for online submission of records. Specific safety event records are linked to Best Practices online manual content to emphasize safe practices for working with hydrogen and avoiding future incidents. Expert review of all safety events and lessons learned is provided by PNNL subject matter experts and the Hydrogen Safety Panel.

Results

Hydrogen Safety Best Practices – We enhanced the best practices content for outdoor storage of hydrogen cylinders in the Laboratory Safety/Laboratory Design section. The Hydrogen Safety Panel identified the need for more detailed content and recommendations as the result of conducting a number of safety review site visits to facilities and discussing safe practices for outdoor cylinder storage.

MOC content is now more visible because we added a new page on the Web site and provided links to that page from three other pages (Safety Culture/Formalized Procedures; Equipment Maintenance and Integrity; and Development of Operating Procedures). Multiple references are provided on the new MOC page, including publications by the American Institute of Chemical Engineers Center for Chemical Process Safety and the U.S. Chemical Safety and Hazard Identification Board. Links to incidents in our Incident Reporting and Lessons Learned database are provided to illustrate what can happen if MOC procedures aren’t rigorously followed.

Hydrogen Incident Reporting and Lessons Learned - We added 37 new records to the database during the past year from DOE projects, private companies, and member countries of IEA HIA Task 19 (Canada, France, Germany, Italy, Japan, The Netherlands, Norway, Switzerland, the U.K., and the U.S.). We now have 177 records in the database, and about 15 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.

Conclusions and Future Directions

Hydrogen Safety Best Practices - Our future work includes improving existing Web site content as well as drafting new content. Ideas for new content come from the Hydrogen Safety Panel, other national laboratories, technical reviewers at the DOE Annual Merit Review, and actual Web site users. For example, a new section on indoor refueling of forklifts is planned.
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 are drafting a new section that is focused on technicians and young engineers with limited or no knowledge of hydrogen properties and behavior. This new section will be practical and concise, formatted as a series of bullets showing what to do and what not to do, and include lots of photos and graphics to enhance the material. It will be highlighted on the Web site with a link that says “Starting Point for Those Not Familiar with Hydrogen” and will cover Hydrogen Basics, Hydrogen Hazards, and Design and Operation of Hydrogen Systems. It will also include links to existing Web site sections for further information.

We are also adding new content on working safely with chemical hydrides (analogous to the metal hydride section discussed earlier). The section has been drafted and reviewed by PNNL research staff working with chemical hydrides, and a revised version will be reviewed by Hydrogen Safety Panel members.

PNNL continues to monitor website 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. Web site utility is enhanced 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, in part through identifying additional sources of hydrogen safety event data and lessons learned. A significant part of our effort involves working with the national laboratories, universities, and private-sector firms that experience hydrogen incidents and 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 Web site usage and respond to user feedback.

We will also continue to encourage all DOE-funded projects, universities, private-sector organizations, and others to voluntarily submit records of their hydrogen incidents and near-misses. Success requires that people use the database and submit information without fear of negative consequences from reporting and publicizing safety events. We will continue to maintain confidentiality for the organizations that voluntarily submit safety event records.

FY 2010 Publications/Presentations


References

IX.7 Hydrogen Fuel Quality

Tommy Rockward (Primary Contact),
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DOE Technology Development Manager:
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Project Start Date: October 1, 2006
Project End Date: September 30, 2011

Objectives

- Test the effects of critical constituents (NH₃, CO, and H₂S) 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.
- Collaborate with international experts to determine levels of constituents for the development of an international standard for H₂ fuel quality.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Codes and Standards section (3.7) of the Fuel Cell 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 and 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 baseline test procedures for commercial membrane electrode assemblies (MEAs).
- Continued providing data sets to and interacting with fuel cell modelers.
- Performed multiple experiments using both common commercially-available and LANL ‘in-house’ MEAs.
- Tested critical constituents (NH₃, CO, and H₂S) and presented data sets to the working group and interacted with fuel cell modelers at various meetings.
- Participated in the development of the North American Team’s perspective on the levels of the critical constituents in the hydrogen fuel specification.

Background

LANL scientists have continued their support of the DOE/Energy Efficiency and Renewable Energy Office of Fuel Cell Technologies, in the Safety, Codes and Standards sub-program, through their expertise in the various disciplines such as materials physics and applications, chemistry, and modeling.

There has been an on-going effort to harmonize at the international level, a standard for hydrogen fuel quality, specifically for vehicle applications. This effort is being coordinated by the ISO Technical Committee on Hydrogen (TC197) in Working Group 12 (WG-12). 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

We attempt to address two important concerns as the standard is being developed and finalized. The first is to recall that the current level of the constituents in the hydrogen fuel specification was based on detection limits. Since the specification origination, analytical techniques have improved considerably, inherently lowering these detectable limits. And, the other concern is that experimental data were collected using different membrane electrode assemblies (MEAs).
This was mainly due to the lack of a commercial supplier to provide platinum loadings desired by the WG-12. We previously developed and performed baseline test protocols for the commonly agreed upon commercial MEAs. Our previous results with the most deleterious critical constituents (NH₃, CO, and H₂S) employed LANL's MEAs and showed unacceptable performance losses. These tests were conducted at the original specification levels. More recently, the WG-12 tentatively agreed to lower both H₂S and CO levels in the fuel specification. Our results shown reflect test with both LANL and the common MEAs at the initial and reduced levels. Table 1 shows the initial and reduced critical constituents taken from the fuel specification.

<table>
<thead>
<tr>
<th>Previous Levels</th>
<th>Current levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃: 0.1 ppm</td>
<td>NH₃: 0.1 ppm</td>
</tr>
<tr>
<td>H₂S: 0.004 ppm</td>
<td>H₂S: 0.001 ppm</td>
</tr>
<tr>
<td>CO: 0.2 ppm</td>
<td>CO: 0.1 ppm</td>
</tr>
</tbody>
</table>

**Results**

Test using NH₃, CO, and H₂S as isolated contaminants, in addition to testing combinations of these contaminants were continued. Experiments were conducted using 0.1 mg Pt/cm² at the anode and 0.2 and 0.4 mg Pt/cm² at the cathode electrodes for LANL and the common MEAs, respectively. We used 50 cm³ hardware from Fuel Cell Technologies (Albuquerque, NM) with Nafion® (NRE212) as the membrane and our catalyst was 20% Pt/C (ETEK) for the LANL cell and commercial MEAs were provided by W.L. Gore & Associates. In each result shown we operated the cell in constant current mode at 80°C with 85% utilization for the hydrogen and 50% for the air. In Figures 1 and 2, fuel cells with the common MEA were exposed to 4 ppb H₂S and the ISO critical contaminant mixture (NH₃, CO, and H₂S) in the anode feed stream while operating at 100% relative humidity (RH), respectively. After approximately 100 hours of exposure to H₂S, the voltage decay begins and slowly increases over time. This is consistent with an accumulative effect that has been observed with sulfur-platinum interactions. A similar phenomenon occurs in Figure 2, except after 100 hours the decay rate is higher than a fuel cell operating with just a sulfur containing compound. This indicates that the critical contaminants as a mixture are more detrimental to fuel cell performance.

We also probed the impact of RH on fuel cell behavior in the presence of these critical contaminants. Figure 3 illustrates the results of varying the level of humidification. Clearly, the left graph show a slower voltage decay rate and the extent of performance losses is much lower. This implies that the local water will definitely play a major role in the fuel cell behavior operating in the presence of the more soluble impurities.

As mentioned earlier, the initial specification was reduced and tests at those levels (see Table 1) are currently underway. Our preliminary results are shown in Figure 4. Parallel testing with both LANL and the common MEA are being investigated. Results shown are not conclusive, however, they show promise.
FIGURE 3. LANL MEA tested with 4 ppb H₂S, 100 ppb NH₃, and 200 ppb CO at 80°C in a fuel cell operating at 0.8 A/cm² with (a) 50% RH and (b) 100% RH.

FIGURE 4. Results using the common MEA with 1 ppb H₂S combined with 100 ppb NH₃ (left figure) and 200 ppb CO (right figure) at 80°C for a fuel cell operated at 1 A/cm².
IX.8 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:  2004  
Project End Date:  Project continuation and direction determined annually by 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 Fuel Cell Technologies (FCT) 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 contributes to achievement of the following DOE milestones from the Hydrogen Safety section of the FCT Program Multi-Year Research, Development and Demonstration Plan:

• Milestone 8: Complete investigation of safe refueling protocols for high pressure systems. (1Q, 2012)  
• Milestone 20: Update peer-reviewed Best Practices Handbook (4Q, 2008/ongoing)

Related milestones in Task 3 (Failure Modes), 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

• Reviewed 50 safety plans since July 1, 2009 for projects in hydrogen storage, fuel cells, production and delivery and manufacturing and updated the DOE/Panel-prepared safety planning guidance resource [1].  
• Conducted safety review site visits for two hydrogen storage projects; completed and submitted five safety evaluation reports for site visits previously conducted [2-6]; conducted nine follow-up interviews for previously issued safety evaluation reports and submitted interview reports.  
• 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
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, demonstration and deployment work of the DOE FCT 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 Fiscal Year (FY) 2004 and the first meeting was held in Washington, D.C., December 11-12, 2003. Two meetings of the Panel were held in FY 2010 as noted above. The 13th meeting (Washington, D.C.) included a topical session on fuel cell applications in the materials handling market with presentations by Air Products, Nuvera Fuel Cells and Plug Power. Panel project work in this application is planned (see Conclusions and Future Directions). The 14th meeting (Aiken, SC) included presentations/discussion with participating organizations in the Hydrogen Storage Engineering Center of Excellence lead by SRNL and facility visits to Bridgestone Firestone and GENCO, both employing fuel cell forklifts for materials handling.

Current Panel membership is noted in Table 1.

<table>
<thead>
<tr>
<th>Richard A. Kallman, Chair</th>
<th>City of Santa Fe Springs, CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steven C. Weiner, Program Manager and Panel Coordinator</td>
<td>PNNL</td>
</tr>
<tr>
<td>Addison Bain</td>
<td>NASA (ret)</td>
</tr>
<tr>
<td>Harold Beeson</td>
<td>NASA White Sands Test Facility</td>
</tr>
<tr>
<td>David J. Farese</td>
<td>Air Products and Chemicals, Inc.</td>
</tr>
<tr>
<td>William C. Fort</td>
<td>Shell Global Solutions (ret)</td>
</tr>
<tr>
<td>Don Frikken</td>
<td>Becht Engineering</td>
</tr>
<tr>
<td>Michael Pero</td>
<td>Hydrogen Safety, LLC</td>
</tr>
<tr>
<td>Glenn W. Scheffler</td>
<td>GWS Solutions of Tolland, LLC</td>
</tr>
<tr>
<td>Andrew J. Sherman</td>
<td>Powdermet Inc.</td>
</tr>
<tr>
<td>Ian Sutherland</td>
<td>General Motors</td>
</tr>
<tr>
<td>Robert G. Zalosh</td>
<td>Firexplo</td>
</tr>
<tr>
<td>Nicholas F. Barilo, Technical Support</td>
<td>PNNL</td>
</tr>
<tr>
<td>Edward G. Skolnik, Technical Support</td>
<td>Energetics, Inc.</td>
</tr>
</tbody>
</table>

The Panel conducted safety reviews for the projects noted in Table 2 since the last reporting (safety reviews have been conducted for 41 projects since March 2004). Preliminary reports have been issued for all safety reviews and completed final reports with recommendations are referenced. Final reports were also issued for safety reviews previously conducted [2-6].

The Panel established a follow-up protocol to interview project teams in order to identify actions, findings and conclusions regarding safety review recommendations as one means for measuring the value of this work. Action on report recommendations represents a rich source of safety knowledge that can have broader benefits to others. Table 2 identifies the follow-up interviews that have been conducted and Table 3 summarizes the conclusions for the first eight follow-up interviews.

The Panel concluded that all interviewees have improved the safety aspects of the work they are conducting. Overall, nearly 90% of the
recommendations – 58 in number – have been implemented in some manner or are in progress for the set of eight project interviews. A presentation given at the 2010 World Hydrogen Energy Conference noted that “the mechanism used by the Panel for seamless discussion and knowledge sharing at the project level augments the prime responsibility of any organization to ensure the safe conduct of work” [7].

The Hydrogen Safety Panel contributes to PNNL’s ongoing work in updating and adding new technical content to two safety knowledge tools, the Hydrogen Incident Reporting and Lessons Learned database (www.h2incidents.org) and the Hydrogen Safety Best Practices Web site (www.h2bestpractices.org). For example, the Panel supported work to add content on laboratory safety aspects for hydrogen storage in cylinders, management of change procedures and additional information on hydrogen properties. Panel members also reviewed technical content for the new feature, the Lessons Learned Corner, in the above mentioned database. A second review of “Safety Training for Researchers,” an online training tool developed by Lawrence Livermore National Laboratory, was completed prior to release by DOE.

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, best practices and lessons learned can be brought to bear on the safe conduct of project work.

The Panel will undertake a number of additional initiatives in FY 2011 including:

- Safety plan reviews and safety review site visits for American Recovery and Reinvestment Act fuel cell deployment projects in specialty vehicle, auxiliary

<table>
<thead>
<tr>
<th>Program Area</th>
<th>Project Title</th>
<th>Contractor</th>
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</thead>
<tbody>
<tr>
<td>Storage</td>
<td>High-Throughput Synthesis and Testing of Porous COF and ZIF Materials for On-Board Vehicular Hydrogen Storage</td>
<td>University of California, Los Angeles</td>
</tr>
<tr>
<td>Storage</td>
<td>Development of Improved Composite Pressure Vessels for Hydrogen Storage</td>
<td>Lincoln Composites, Lincoln, NE</td>
</tr>
<tr>
<td>Storage</td>
<td>*Effect of Gaseous Impurities on Long-term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage</td>
<td>University of Nevada, Reno</td>
</tr>
<tr>
<td>Cross-Cutting</td>
<td>*Hydrogen Technology Program: Ammonia Borane Tasks</td>
<td>Purdue University, West Lafayette, IN</td>
</tr>
<tr>
<td>Fuel Cells, Storage</td>
<td>*Hydrogen Fuel Cell and Storage Technologies (FCAST) and Solar Hydrogen Generation Research (SHGR) Projects</td>
<td>University of Nevada, Las Vegas</td>
</tr>
<tr>
<td>Technology Validation</td>
<td>*California Hydrogen Infrastructure Project Hydrogen Fueling Station</td>
<td>Air Products/University of California, Irvine</td>
</tr>
<tr>
<td>Technology Validation</td>
<td>*Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation Project</td>
<td>Chevron Technology Venture/Alameda-Contra Costa Transit, Oakland, CA</td>
</tr>
<tr>
<td>Fuel Cells</td>
<td>*Fuel Cell Testing</td>
<td>Argonne National Laboratory, Argonne, IL</td>
</tr>
<tr>
<td>Fuel Cells</td>
<td>*High Temperature, Low Relative Humidity Membrane Program</td>
<td>University of Central Florida, Cocoa, FL</td>
</tr>
<tr>
<td>Production and Delivery</td>
<td>*Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming Over Co-Based Catalysts</td>
<td>Ohio State University, Columbus, OH</td>
</tr>
<tr>
<td>Production and Delivery</td>
<td>*Water-Gas Shift Reaction via a Single-Stage Low-Temperature Membrane Reactor</td>
<td>Membrane and Process Technology Inc., Pittsburgh, PA</td>
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<table>
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<th>Category</th>
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<th>Partial or In Progress</th>
<th>No Action</th>
<th>Total Recommendations</th>
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<td>Safety Vulnerability/ Mitigation Analysis</td>
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<td>3</td>
<td>4</td>
<td>20</td>
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<td>System/ Facility Design Modifications</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>9</td>
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<tr>
<td>Equipment/ Hardware Installation and O&amp;M</td>
<td>5</td>
<td>4</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>Safety Documentation</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Training</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Housekeeping</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Emergency Response</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Total</td>
<td>37</td>
<td>21</td>
<td>7</td>
<td>65</td>
</tr>
</tbody>
</table>

0&M - operation and maintenance
and back-up power, portable and combined heat and power applications.

- Conduct follow-up teleconferences with all project teams for which safety review site visit reports have been issued in order to identify actions taken, findings, conclusions and other learnings.
- Assist PNNL in various technical aspects for future issues of *H2 Safety Snapshot*, a safety bulletin to be published every quarter.
- Consider additional topics for study consistent with the Hydrogen Safety Panel’s charter to identify safety-related data and knowledge gaps.

The 15th and 16th meetings of the Hydrogen Safety Panel are planned for April 2011 and September 2011, respectively.

**FY 2010 Publications/Presentations**


**References**


IX.9 Hydrogen Release Behavior

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Start Date: Fiscal Year (FY) 2002
End Date: Project continuation and direction determined annually by DOE

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

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 the effectiveness of ventilation, active sensing, and similar engineered safety features.

(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 Fuel Cell 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 Refueling Stations
(Q) Parking and Other Access Restrictions

Contribution to Achievement of DOE Codes and Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Codes and Standards section of the Fuel Cell 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).
- **Milestone 8:** Complete investigation of safe refueling protocols for high pressure systems. (1Q, 2012)
- **Milestone 9:** Complete risk mitigation analysis for advanced transportation infrastructure systems. (1Q, 2015)
- **Milestone 12:** Complete research needed to fill data gaps on hydrogen properties and behaviors. (2Q, 2010)

Accomplishments

- We determined that implementation of barriers can be effective in reducing risk and separation distances to the facility lot line.
- Analysis of $\text{H}_2$ releases and delayed ignition deflagration have been performed for partially confined spaces (tunnels).
- Experiments have shown that entrained particulates originating from tanks or piping are likely a source of spontaneous ignition.
- The Sandia turbulent entrainment model for cold hydrogen jets has been validated against high-momentum jet data (from Forschungszentrum Karlsruhe tests).
Introduction

The purpose of this 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

We develop an understanding of combustion behavior and thermal effects from the unintended releases of hydrogen in the built environment. We consider ignition characteristics, barrier wall interactions, partially confined spaces (tunnels, garages, warehouses), and liquid hydrogen handling. Technical information is disseminated through a variety of public channels and is used by codes and standards developers writing for the International Code Council and National Fire Protection Agency (NFPA). International partnerships for vetting technical data and analysis methods occur through activities such as International Energy Agency Task 19 on Hydrogen Safety and the European HYPER project. Efforts in FY 2010 have focused on developing the basis for regulations and codes and standards development in the area of hydrogen releases in enclosures, ignition mechanisms, and liquefied hydrogen release behavior.

Results

Risk Analysis

Using risk information in the code development process enables rapid and effective hydrogen and fuel cell technology deployment. In FY 2010 we evaluated the use of barrier walls to reduce the risk (and thus separation distances) for hydrogen facilities. The use of properly designed barriers will remove the potential for direct contact with jet flames, reduce the distance of unignited jets, reduce the isosurfaces for various thermal radiation heat fluxes, and not result in any substantial increase in pressure that would harm people or structures. Thus, barriers provide a means to reduce the risk to the public from unintended releases of hydrogen. This reduction in risk also allows for the opportunity to reduce the separation distances at a hydrogen facility. Estimates of the risk reduction potential were generated by using the risk model developed for evaluation of the separation distances selected for incorporation into the NFPA-2 and NFPA-55 hydrogen standards [1] and the consequence results reported in [2,3]. The system configurations and associated leakage frequencies utilized in [1] were utilized in the barrier risk assessment, thus allowing for direct comparison of the risk with and without a barrier. The barrier wall was assumed to be 2.4 m high and separated from the hydrogen equipment by 1.22 m. The barrier wall was assumed to be 2.4 m high and separated from the hydrogen equipment by 1.22 m. Table 1 provides a comparison of the risk to an individual located at the facility lot line from a leak equivalent to a 3% of the maximum flow area in the hydrogen system.

<table>
<thead>
<tr>
<th>System Pressure (MPa)</th>
<th>Leak Diameter (mm)</th>
<th>Separation Distance to Facility Lot Line w/o Barrier (m)</th>
<th>Individual Risk at Facility Lot Line (fatalities/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.83</td>
<td>9.09</td>
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<td>1.24</td>
<td>10.4</td>
<td>3.5E-5 1.0E-5</td>
</tr>
</tbody>
</table>

1 Leak diameter corresponds to 3% of the largest flow area in the system.
2 Separation distance specified in NFPA-55, based on selected leak diameter.

As indicated in Table 1, the presence of a barrier can be used to reduce the risk to a person standing at the facility lot line. The use of a barrier can also be used to reduce the separation distances. For a risk level equivalent to the risk without a barrier, the separation distance to the facility lot line can be shortened to approximately 3.5 m for the leak diameters shown in Table 1.

Unintended Releases of Hydrogen in Partially Enclosed Spaces

Code language is being developed for the use of hydrogen in partially enclosed spaces. In FY 2010, we evaluated the release of hydrogen in enclosures to inform the code development processes in NFPA 2, 52, and 502. Experiments were performed in a scaled tunnel test facility (Figure 1) to provide model validation data for release simulations resulting from the venting of the thermally-activated pressure relief device (PRD) on a hydrogen vehicle in a full-scale tunnel. The tunnel test facility had a cross-sectional area that was approximately 1/2.53 that of the full-scale transversely ventilated tunnel. The release diameter was designed to match the scaled mass flow rate versus scaled time tank blow-down curve from the full-scale release. Measurements were made of the hydrogen concentration, flame speed, and ignition delay overpressure in the scaled tunnel resulting from the release produced by activation of three simulated...
PRD vents on the bottom of the scale-model vehicle. As part of the work a dispersion model and deflagration model of the test tunnel and vehicle geometry were developed. These models were used prior to the tests to estimate the placement of concentration and pressure sensors in the tunnel test geometry and to determine the amount of expected overpressure from ignition of the hydrogen releases. Pretest ignition deflagration simulations of the test tunnel geometry using three-dimensional concentration maps from the dispersion simulations indicated that the maximum overpressure would be approximately 0.5 barg and that a peak in the overpressure would occur with increasing ignition delay time as observed in the full-scale tunnel simulations. Figure 1 shows a comparison of the peak overpressures measured in the experiments for different ignition delay times as compared to the model simulations. The ignition overpressure simulations are found to be in good agreement with the experimental data.

The same modeling approach was used in the full-scale tunnel simulations and the pretest simulations of the scaled-tunnel experiments. The good agreement between the scaled-tunnel test experimental data and pretest simulations provide validation of the simulation approach and full-scale tunnel modeling results. Results were reported to NFPA 502 – the standard for road tunnels.

Auto-Ignition of Unintended Hydrogen Releases

Understanding ignition mechanisms and the probability of ignition is a vital aspect of the QRA. Ignition source in a large percentage of reported hydrogen release incidents is not easily identified. Due to this uncertainty, these events are often referred to as auto-ignition events. One of the most likely ignition sources for these events is ignition of the hydrogen/air mixture by electrostatic discharge resulting from the presence of charged particles in the flow. It is known from industrial experience that significant particle charge can develop during the high-speed flow of particle-laden gases through piping. During FY 2010, experiments were carried out to investigate the generation of static charge on iron-oxide particles in hydrogen gas flowing through pipes and the potential for these charged particles to induce an ignition event in the release. The objective of these experiments was to determine whether a static charge accumulation on iron oxide particles entrained in a hydrogen jet release could lead to a spark discharge ignition or a corona discharge ignition. Experiments were performed by adding particles to a high-pressure release of hydrogen gas flowing through a 10 foot steel pipe prior to exiting to ambient air through a nozzle.

A series of tests were performed where a circular ungrounded plate was placed in close proximity to a grounded probe in the particle-laden jet release (see Figure 2). In this configuration the ungrounded plate is charged by induction or particulate impact until the charge is high enough to arc to the nearby grounded probe. In this configuration, six ignitions occurred and in case when only 0.1 gram of iron (III) oxide particles were introduced into the flow ignition occurred in three out of four tests. In the case when no particles were introduced into the flow ignition did not occur. In addition, ignition did not occur when both probes were maintained at comparable floating electrostatic potentials. No corona-discharge events were observed during the test matrix. The results of these tests show that entrained particulates can be a source leading to spontaneous ignition in hydrogen gas releases.

Liquid Hydrogen Releases

Separation distances for liquid hydrogen systems are being specified in codes such as NFPA 2. We have developed an engineering model that can be utilized
to provide the basis for these separation distances. In FY 2010, this model was validated against high-momentum jet data from Forschungszentrum Karlsruhe of Germany. Forschungszentrum Karlsruhe conducted several experiments in which room temperature and 80 K under-expanded jets of hydrogen were vented into still air at ambient conditions. Hydrogen concentration was measured at several locations along the centerline. These jet releases were simulated using the Sandia turbulent entrainment model for cold hydrogen jets. Since the releases were choked, a source model was used to extrapolate choked conditions at the actual leak diameter to a source diameter where the pressure was atmospheric. Predicted centerline concentrations for hydrogen were compared with the Forschungszentrum Karlsruhe measurements as shown in Figure 3. Centerline concentrations for both room temperature and 80 K jets were well-reproduced by the model. The comparison shown in Figure 3 represents a validation for the cold- and ambient-temperature single phase hydrogen jet model and the high momentum source model. Further validation of the model for colder jets in which the release is two-phased will be made as validation data becomes available.

Conclusions and Future Directions

This project provides key understanding to enable the deployment of early-market hydrogen systems. In FY 2010:

- We analyzed the use of barriers to reducing risk and separation distances to the facility lot line.
- We performed analysis of H\(_2\) releases and delayed ignition deflagration for partially confined spaces (tunnels):
  - A preliminary risk analysis indicates that the level of potential risk from H\(_2\) vehicles accidents does not significantly increase the level of individual risk.
  - Tunnel release modeling approach validated with scaled-tunnel experiments.
- We completed experiments that identified entrained particulates as a likely a source of spontaneous ignition.
- We validated the Sandia turbulent entrainment model for cold hydrogen jets against high-momentum jet data (from Forschungszentrum Karlsruhe tests).

This project will continue to enable hydrogen and fuel cell technology deployment through developing the defensible technical basis for codes and standards. We will perform work to:

- Complete risk and consequence analysis of indoor refueling and operation of hydrogen powered industrial trucks.
- Analyze risk of unintended releases involving other confined spaces (e.g. sheds).
- Incorporate data from existing demonstration and projects into the QRA of hydrogen technologies.
• Improve the existing predictive model of ignition in turbulent flames to include sustained flame light-up probability.
• Understand ignition behavior due to environmental particulate entrainment and other mechanisms.
• Develop an understanding of high-momentum low-temperature hydrogen plume behavior in support of NFPA 2 separation distance activities.
• Perform risk analysis of advanced storage materials in support of NFPA 2 activities.

**FY 2010 Publications/Presentations**


**References**


IX.10 Risk-Informed Separation Distances for $H_2$ Facilities

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Start Date: Fiscal Year (FY) 2002
End Date: Project continuation and direction determined annually by DOE

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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 the effectiveness of ventilation, active sensing, and similar engineered safety features.

(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 Fuel Cell 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 Refueling Stations
(Q) Parking and Other Access Restrictions

Contribution to Achievement of DOE Codes and Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Codes and Standards section of the Fuel Cell 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).
- **Milestone 9**: Complete risk mitigation analysis for advanced transportation infrastructure systems. (1Q, 2015)

Accomplishments

Provided methods, data, and analytical support to International Organization for Standardization (ISO) technical committee (TC) 197 working group (WG) 11 Task Group 1 for the implementation of a risk-informed approach to determine separation distances for refueling facilities.

✨ ✨ ✨ ✨ ✨ ✨

Introduction

The development of a set of safety codes and standards for hydrogen facilities is necessary to ensure they are designed and operated safely. To help ensure that a hydrogen facility meets an acceptable level of risk, code and standard development organizations (SDOs) are utilizing risk-informed concepts in developing hydrogen codes and standards. Two SDOs, the National Fire Protection Association (NFPA) and the ISO have been developing standards for gaseous hydrogen.
facilities that specify the facilities have certain safety features, use equipment made of material suitable for a hydrogen environment, and have specified separation distances. Under DOE funding, SNL has been supporting efforts by both of these SDOs to develop the separation distances included in their perspective standards. Important goals in these efforts are to use a defensible science-based approach to establish these requirements and to the extent possible, harmonize the requirements. The successful approach to risk-inform the separation distances in the NFPA standards [1] is a model for establishment of additional requirements by NFPA and other SDOs. In fact, ISO has generally adopted the SNL approach to determine the separation distances in ISO 20100, “Gaseous hydrogen – Fuelling stations” [2]. The efforts to support development of the ISO separation distances by providing methods, data, and analytical support to the ISO TC197 WG11 task group on separation distances are described subsequently. Differences between the approaches and data utilized in NFPA and ISO assessments are highlighted.

Approach

The approaches used in establishing the NFPA and ISO separation distances for gaseous hydrogen facilities are very similar but do have some important differences. Both use Quantitative Risk Assessment (QRA) techniques to evaluate the risk from unintended releases of hydrogen. The risk from the operation of a facility is the product of the frequency and consequences of all credible accidents and can be estimated using QRA. A QRA can be used to identify and quantify scenarios involving the unintended release of hydrogen, identify the significant risk contributors, and to identify potential accident prevention and mitigation strategies to reduce the risk to acceptable levels. A key mitigation feature is the use of separation distances. Under DOE sponsorship, SNL developed the data and methods that were used in quantifying both the frequency and consequence portions of the QRAs performed in both the NFPA and ISO analyses.

A significant difference between the NFPA and ISO approaches is that the NFPA approach is risk-informed while the ISO approach is more properly characterized as risk-based. A risk-informed process utilizes risk insights obtained from QRAs combined with other considerations to establish code requirements. Other considerations used in this risk-informed process include the results of deterministic analyses of selected accident scenarios, the frequency of leakage events at hydrogen facilities, and the use of safety margins to account for uncertainties in the data, methods, and scope of the risk evaluation. In contrast, a risk-based approach only utilizes risk to develop the requirements.

The separation distances in both the NFPA and ISO analysis are based on the selection of a hydrogen leak size that if ignited, would result in unacceptable risk to a person, structure, or equipment. It is generally accepted that separation distances should not be used to provide protection against rare events such as large, catastrophic ruptures. Separation distances should be selected to cover leakage events that may be expected to occur during the facility lifetime, especially small leaks that may occur frequently. It is also desirable to establish separation distances that are not too short and consequently result in unacceptable risk levels. In particular, the associated risk from leakage events that would result in consequences beyond the designated separation distances should be acceptable as determined by consensus. The risk-informed process used in the NFPA approach for selecting the separation distances explicitly included consideration of both the frequency of the selected leak size and the risk from larger leaks. In contrast, the ISO approach only included the evaluation of risk from leakage events (the frequency of expected leakage events was implicitly evaluated in the risk assessment but was not used in making any decisions). It is noted that in both analyses, some of the separation distances were not based on risk arguments. For example, in the ISO analysis the separation distances for large volume systems (i.e., >100 kg hydrogen) was based on the subjective argument that the distances should be greater than for the smaller systems.

The ISO risk-based approach utilizes the conceptual framework shown in Figure 1. In this approach, the cumulative risk from different leak diameters resulting in one or more specified consequence are evaluated against the separation distances required to protect people, equipment, or structures from a specified level of harm. The ISO analysis also included risk to structures and components with the potential for structural or component damage assumed to result in a fatality. The accidental releases of hydrogen were limited to leakage events from four types of components

![FIGURE 1. Risk-Based Approach for Establishing Safety Distances](image-url)
(valves, compressors, hoses, and joints – pipes and tanks were excluded because they were not important risk contributors in the NFPA analysis). The consequences in both the ISO and NFPA analyses were limited to the effects of ignited hydrogen jets and exposure to an ignited hydrogen jet was assumed to result in harm to a target independent of the exposure period. In the ISO QRA, two selected risk acceptance criteria were used to establish the risk-based separation distances using the framework in Figure 1. The separation distances were generated for one of two selected consequence parameters that can result from a hydrogen jet: (1) the extent of the 4% hydrogen envelope or, (2) the exposure to an ignited hydrogen flame. Hydrogen leaks resulting in risk values equal to the risk criteria were used to select the separation distances for both consequence parameters.

In contrast, the leak diameter used as the basis for the separation distances in the NFPA approach was selected to encompass at least 95% of possible leakage events in typical hydrogen gas storage facilities. As a second criterion, the leak diameter was selected such that an event would not likely occur during the life time of the facility due to a low occurrence frequency (i.e., approximately 1E-2/yr). Although larger leaks would not be expected to occur, if they did, it would be desirable that the risk from these larger leaks to a member of the public standing at the selected separation distance be acceptable. Thus, the cumulative risk to the public from larger leaks was evaluated and compared to a single risk guideline, as opposed to the two risk criteria in the ISO approach, using the framework depicted in Figure 1. A risk guideline is essentially a soft risk criterion that allows consideration of uncertainty in the risk assessment when selecting the separation distances when using the framework in Figure 1. The NFPA risk evaluation included separate scenarios involving either early and late ignition of a hydrogen jet and added the risk to an individual from both scenarios to determine the separation distances (the ISO analysis only included one or the other scenario to evaluate the separation distances for each target but this was compensated for by using a higher ignition probability that was equal to the average of the early and late ignition probabilities used in the NFPA analysis for a large release).

The risk measure evaluated in the NFPA QRA was the frequency of a fatality to a person assumed to be constantly present at the facility lot line from an ignited hydrogen jet. The fatality risk from all possible leaks in the modeled facility was evaluated and used to help select a single leak size (expressed as a percentage of the largest flow area in the system) that was used to determine the separation distance for all exposures included in the separation table. In contrast, the ISO analysis included the frequency of exposure of structures and equipments to hydrogen jets (to prevent escalation of a leakage event into a major incident; escalation was assumed to result in a human fatality) in addition to the potential for exposure of humans that would result in fatalities. Thus, different leak diameters were evaluated for different exposures and used to establish the resulting separation distances.

The performance of the QRAs in both assessments required selection of risk criteria/guidelines, establishment of needed data (component leakage frequencies and hydrogen ignition probabilities), and selection of a consequence model. Reference 1 provides a survey of fatality risk criteria that was used to select the risk guidelines utilized in the NFPA assessment. The selected fatality risk guideline of 2E-5/yr was based on three inputs: maintaining the risk at an equivalent level to gasoline stations, using a value that is consistent with countries that have established risk criteria, and limiting the risk from hydrogen releases to a fraction of the risk to an average person from accidental causes. The ISO analysis is using a slightly lower fatality risk criteria of 1E-5/yr for some exposures and a lower risk criteria of 4E-6/yr for selected “critical” exposures believed by some in ISO TC197 WG11 task group to require additional protection (e.g., large volumes of flammable liquids and air intakes in occupied buildings). There is no documented basis for the critical exposure criteria. It is also important to note that the ISO analysis used the two fatality risk criteria listed above for the criteria of exposure of equipment and structures to hydrogen jets based on the assumption that equipment damage would result in a fatality.

In both analyses, data and models generated by SNL were utilized. The hydrogen jet model developed by Houf and Schefer [3] was used in both the NFPA and ISO assessment to evaluate the harm distances associated with hydrogen jets. However, there are some differences in the two analysis in the data used in evaluating the frequency of ignited hydrogen jets. For example, different hydrogen ignition probabilities were used. The NFPA utilized ignition probabilities that changed with leak size and whether the ignition occurred immediately or was delayed. The ISO risk model included a single ignition model that was independent of leak size or ignition time. Although the selected ISO ignition probability was conservative, its use skews the actual risk profile and the resulting selection of the separation distances.

The component hydrogen leakage frequencies utilized in the NFPA were generated using a Bayesian statistical approach [4]. A Bayesian statistical method was selected for use in the data analysis for three reasons. First, this approach allows for the generation of leakage rates for different sizes of leaks which is a critical requirement for estimating the size of a leak to use as the basis for establishing separation distances. Second, it also generates uncertainty distributions for the leakage rates that can be propagated through the QRA.
models to establish the uncertainty in the risk results. Finally, it provides a means for incorporating limited hydrogen-specific leakage data with leakage frequencies from other sources (e.g., the nuclear and petroleum industries) to establish estimates for leakage rates for hydrogen components. An example of the generated hydrogen component leakage frequencies is provided in Figure 2. The component leakage distributions utilized in the ISO analysis are linear versions (on a log-log plot) of the values generated by SNL that as depicted in Figure 2 are conservative over the majority of the leak size range. The linearization of the SNL data distributions was performed to simplify the ISO analysis and allow for a method to generate alternate separation distances for facilities that are substantially different than the example facility used to establish the ISO separation distance table. However, the ISO linear leak frequency distributions actually used in the risk analysis were shifted an order of magnitude when used in the ISO risk analysis (illustrated in Figure 2). The shifting of the leak frequency distributions results in underestimating the risk associated with each leak size and under prediction of the resulting separation distances by a factor of 3 (e.g., it uses the risk for 100% leaks to generate the separation distance for 10% leaks).

Both the ISO and NFPA QRAs also require establishment of representative facilities for evaluating the frequencies of hydrogen leaks and the resulting risk. The NFPA analysis was focused on establishing separation distances for gaseous bulk hydrogen storage systems whereas the ISO analysis was for gaseous fuelling stations. A single facility description was used in the ISO evaluation while four configurations were used in the NFPA evaluation. Two operating pressures were evaluated with the ISO model while four pressures (one per model) were evaluated in the NFPA analysis. Thus, the representative facilities and pressures used in the analysis were substantially different. These differences also resulted in different separation distance table formats in the ISO and NFPA standards.

The NFPA example facilities had multiple components with diameters ranging from 7 mm to 52.5 mm. The ISO analysis used a single component (8 mm) in the facility. In addition, the NFPA analysis assumed that the entire facility was collocated while the ISO analysis divided the facility into modules that were assumed to be adequately separated. The risk from leaks for each module was evaluated and compared with the risk criteria. By separating the gaseous fuelling station in this fashion, the risk to an individual can be underestimated for stations that are not separated. These differences in the assumed facility separation result in significant differences in the estimated leak frequencies and associated risk for the facilities. It also makes it difficult to compare the resulting separation distances.

### Results

Comparison of the separation distances generated in the ISO and NFPA analysis is not possible due to the differences in the scope of the application (i.e., bulk storage versus fuelling station) and the differences in the separation distance table format used in the specific standards (pressure ranges and exposures). However, it is informative to compare the leak size, in terms of the percentage of the flow area, used to determine the separation distances. As indicated in Table 1, the fraction of the flow area used to determine the ISO separation distances for both the regular and critical exposures (i.e., based on a 1E-5/yr and 4E-6/yr risk criterion, respectively) are substantially less than the 3% of the flow area utilized by NFPA (calculated using a 2E-5/yr risk guideline). There are several contributors to the difference including different risk criteria, different facility configurations, separation of the gaseous fuelling station into separate modules, different ignition probabilities, and most importantly, the difference in the application of the hydrogen leak frequencies. Table 1 shows that the leak area would increase by an order of magnitude if the linear leak frequency distributions generated by ISO TC197 WG11 task group were not shifted in the ISO risk assessment. The resulting leak sizes for the ISO regular exposures are closer to the value selected for the NFPA standards.

### Conclusions and Future Directions

As indicated above, the efforts to harmonize the ISO and NFPA approaches was generally successful as both used essentially the same risk approach for evaluating separation distances developed by SNL. Similarly, the SNL consequence models and the hydrogen leak frequency distributions were combined to provide an adequate estimate of the risk associated with hydrogen leaks. However, further work is needed to refine the separation distances and to better understand the impact of different factors on the risk associated with hydrogen leaks.
data generated by SNL were used in both evaluations, although generally conservative approximations of the leak frequencies were generated for the ISO analysis. However, the application of the ISO leak frequency distributions in the QRA underestimates the risk and associated separation distances. International harmonization of regulations, codes and standards enables global market penetration of hydrogen and fuel cell technologies. Toward this end, efforts will continue to evaluate the effect of other differences between the NFPA and ISO analyses in order to harmonize the methodologies and the resulting separation distances to the greatest extent possible.

### References


Objectives

The goal of the Hydrogen Safety Task is to survey and analyze effective risk management techniques, testing methodologies, test data, contribute to development of fundamental knowledge on hydrogen related to hydrogen safety and develop targeted information products that will facilitate the accelerated adoption of hydrogen systems.

The specific objectives of this task are to:

• Survey risk assessment methodologies based on case studies provided by collaborative partners;
• Survey available test data, develop recommendations on modeling and testing methodologies, and share future test plans around which collaborative testing programs can be conducted thus avoiding duplication of work among collaborative partners;
• Collect information on the effects of component or system failures of hydrogen systems; and
• Use the results obtained to develop targeted information packages for selected hydrogen energy stakeholder groups.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section (3.8) of the Fuel Cell 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

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

• Milestone 2: Develop sensors meeting technical targets (4Q, 2012)
• Milestone 7: Complete Risk mitigation analysis for baseline transportation infrastructure systems (1Q, 2012)
• Milestone 8: Complete investigation of safe refueling protocols for high pressure systems (1Q, 2012)
• Milestone 9: Complete risk mitigation analysis for advances transportation infrastructure systems (1Q, 2012)
• Milestone 12: Complete research needed to fill data gaps on hydrogen properties and behaviors (2Q, 2010)

Accomplishments

In 2009, the task continued to compare experimental data with risk analysis methods to validate the models and further close the knowledge gaps identified in earlier work. The subtask also completed the development of the Hydrogen Technical Experimental (HyTEx) database. Starting in late 2009, the populating of the database with data from participating countries was begun. Technical progress
on the development of Risk Informed Approval Criteria for hydrogen projects to provide a solid basis for Risk Informed Codes and Standards was completed.

- Established a list of relevant engineering models that had been used to evaluate the safety of hydrogen systems, categorized them, and performed a comparative analysis with actual testing data.
- Several dispersion models were further developed in 2009 by extending their capabilities to include surface and transient effects (November 2009).
- Developed a more detailed thermal radiation model.
- Completed development of the HyTEX database.
- Task participants presented many papers at technical conferences on subjects that dealt with the collaborative work.
- The International Energy Agency (IEA) Hydrogen Implementing Agreement Co-organized the September 2009 Third International Conference on Hydrogen Safety and Task 19 members presented more than 10 technical papers.

Introduction

Acceptability of new systems is traditionally measured against regulations, industry and company practices and the judgment of design and maintenance engineers, however contemporary practice also incorporates systematic methods to balance risk measurement and risk criteria with costs. Management decisions are increasingly relying on quantitative risk assessment (QRA) for managing the attainment of acceptable levels of safety, reliability and environmental protection in the most effective manner. QRA is being applied more frequently to individual projects and may be requested by regulators to assist in making acceptance and permitting decisions. This task was approved by the executive committee of the IEA Hydrogen Implementing Agreement in October 2004. The Task is currently comprised of 11 participating countries.

Approach

This task, aimed at reducing the barriers to widespread adoption of hydrogen energy systems, is being accomplished within three subtasks:

Subtask A. Risk Management - To survey QRA methodologies and compare assessments of hydrogen systems with conventional fuels to develop recommendations for modeling and testing methodologies around which collaborative testing programs can be conducted. Subtask A Risk Management is concentrating on the following four activities:

- Develop uniform risk acceptance criteria and establish link with risk-informed codes and standards.
- Develop a list of appropriate engineering models and modeling tools. Develop simple but realistic physical effects models for all typical accident phenomena (i.e., jet fires, vapor cloud explosions, flash fires, boiling liquid expanding vapor explosions, pool fires, etc.) for education and training, design evaluation and simplified quantitative risk analysis purposes.
- Develop a methodology for consistent site risk assessment based on the hydrogen quantitative risk assessment (HyQRA) approach.
- Release updates to all published products: risk assessment methodology survey, knowledge gaps white paper and review and comparison of risk assessment studies.

Subtask B. Testing and Experimental Program - To conduct a collaborative testing program to evaluate the effects of equipment or system failures under a range of real life scenarios, environments and mitigation measures. This subtask will summarize and ultimately coordinate and guide the experimental programs being conducted within the 11 countries participating in the task. The approach is to identify such testing programs, the facilities being used, and to coordinate the activities to fill in the data and knowledge gaps for the development of risk informed codes and standards. Subtask B focuses on both testing and experimental data, i.e., testing data as collected by checking the performance of applications and equipment and experimental data as collected by experiments with hydrogen release, ignition, fire, explosions and preventive and protective measures.

Subtask C. Information Dissemination - To disseminate results of the task through targeted information packages for stakeholders. An important aspect of information dissemination is to ensure that the review and vetting of all work products for Task 19 are consistent with the requirements and procedures for producing, approving and distributing various types of IEA reports and other information products. A protocol has been adopted by Task 19 partners and is being applied appropriately for Task 19 work. It is expected that several of these Subtask C products will be updated and enhanced over the course of the period covering Task 19 through October, 2010.

Results

In 2009, the task continued to compare experimental data with risk analysis methods to validate the models and further close the knowledge gaps identified in earlier work. The subtask also completed
the development of the HyTEx database. Starting in late 2009, the populating of the database with data from participating countries was begun. Technical progress on the development of Risk Informed Approval Criteria for hydrogen projects to provide a solid basis for Risk Informed Codes and Standards was completed.

Risk Management

Prior to 2009, the task had established a list of relevant engineering models that had been used to evaluate the safety of hydrogen systems and categorized them. In 2009 they were compared to each other to assess their limitations and validity. Part of this effort was achieved through comparing the engineering models to actual testing data. Several dispersion models were further developed in 2009 by extending their capabilities to include surface and transient effects. A more detailed thermal radiation model was also developed that would account for crosswinds.

Testing and Experimental Program

An inventory of existing testing and experimental data is in progress and the participants have started sharing information during and beyond the Task 19 meetings. This has been extended (and will be in the future activities) by a search by the partners for any data existing in their respective countries and around the world. In order to secure a continuing refinement of the survey, the data and/or references will be stored in the HyTEx database. The Subtask B databases HyTEx, HYPRO and HYTEF will be used as a source of information for any missing data in relation to the knowledge gaps as defined by and resulting from the Subtask A activities. If data is not available this could give rise to recommendations on new testing and experimental programs. The existing data can also be checked on its relevance and completeness. A first set of knowledge gaps has been identified in Subtask A and described in the white paper ‘Knowledge Gaps in Hydrogen Safety.’ Currently identified knowledge gaps are: spontaneous ignition, protective barriers and consequence modeling.

Development of Targeted Information Packages for Stakeholder Groups

The targeting of information packages for selected hydrogen energy stakeholder groups is central to the work and objectives of Task 19, currently focused on risk assessment methodologies and studies, testing and experimental programs, safety training and knowledge resources and hydrogen facility siting. Information packages can take a variety of forms: IEA publications, publicly available Web-based tools, databases and documents for use by Task 19 partners.

Conclusions and Future Directions

The current task is scheduled to be completed in October 2010 and a new task on hydrogen safety is being developed to continue to build on the very effective collaboration of this six-year effort. It is anticipated that one of the major outcomes of this ongoing work will a technical and credible basis for the development of risk informed codes and standards that will not be unnecessarily restrictive. This will eliminate a major barrier to the widespread commercial adoption of hydrogen energy systems. Future work will support this goal by improving hydrogen risk assessment methodologies and quantitative risk analysis and closing knowledge gaps with regard to consequences of hydrogen related accidents and incidents, the effects of mitigation methods, and failure probabilities of system components.

FY 2010 Publications/Presentations

Objectives

- Select and finalize the hydrogen sensor chemistry that possesses the optimum sensitivity, reliability, reproducibility, and aging performance.
- Design and fabricate optoelectronic board for hydrogen leak sensor.
- Assemble and test the optoelectronic interface for the sensor prototype.
- Test and validate the fully packaged prototype performance at the National Renewable Energy Laboratory (NREL).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section of the DOE Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP), page 38-7:

(D) Liability Issues: Potential liability issues and lack of insurability are serious concerns that could affect the commercialization of hydrogen technologies.

Barriers addressed by this project from other sections of the MYRDDP include:

- Delivery:
  (I) Hydrogen Leakage and Sensors (page 3.2-20)
- Storage:
  (H) Balance of Plant (BOP) Components (page 3.3-14)
- Manufacturing R&D:
  (F) Low Levels of Quality Control and Inflexible Processes (page 3.5-11)
- Technology Validation:
  (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data (page 3.6-8)

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to the achievement of the following DOE milestones from the Hydrogen Safety/Leak Detection Technology section of the Fuel Cell Technologies Program MYRDDP:

- Milestone 2: Develop sensors meeting technical targets. (4Q, 2012)
- Milestone 3: Develop leak detection devices for pipeline systems. (4Q, 2015)

Accomplishments

This continuation of a project that was initiated on June 1st, 2008 has been extended through November 2010. The initial work focused on exploring a family of colorimetric hydrogen sensor formulations and physical embodiments for different venues and markets. These included porous glass “optrodes” for integration with optical fiber sensors, polymer integrated optic chip sensors, and fully-distributed fiber optic sensors. Work on the latter has been presented by R.G. Zalosh and N.F. Barilo [1] from the Pacific Northwest National Laboratory at the International Hydrogen Conference in France, 2009.

In the past year, IOS has focused on developing and testing an optrode-based point H₂ detector technical accomplishments for the past 12 months are summarized below:

- A process for reproducible fabrication of hydrogen sensor substrates was optimized and tested. The statistical variance in different batches of sensor elements was observed to be (~0.04±0.01) from batch-to-batch.
The development of the optoelectronic readout device was finalized. Two generations of fully functional hydrogen sensor prototype devices were fabricated, tested and optimized.

Signal processing algorithms were developed to linearize optrode response under various environmental conditions. The algorithms are currently undergoing validation and optimization testing before release of the final version.

The hydrogen sensor was tested and validated, for reversibility, repeatability, accuracy, and environmental dependence, confirming IOS results at NREL.

IOS presented a briefing, and a working prototype unit, during the 2010 Hydrogen and Vehicle Technologies Annual Merit Review in Washington, D.C. During this review, we met with a number of parties interested in the hydrogen sensor and its performance.

Introduction

Hydrogen safety is an important key to commercializing hydrogen energy technologies, and to facilitate the use of hydrogen as a green energy source. The principal objective of this DOE project is to integrate IOS’ proprietary hydrogen indicator chemistry with optical and optoelectronic designs, and advanced signal processing, to create a prototype point-sensor system with well-defined sensing characteristics for various markets, including fuel cell-powered passenger vehicles, hydrogen generation and refueling stations, storage locations, and other situations.

Each IOS hydrogen sensor uses an optoelectronic platform to monitor an optically conductive matrix hosting a colorimetric indicator. Upon hydrogen exposure, the sensor element changes color, and the sensor uses the resulting optical signal to calculate hydrogen concentration.

IOS’ hydrogen sensor approach is unique in many aspects. First, it uses an intrinsically safe sensing element that functions without the heat required by many electronic hydrogen sensors, and can be remotely read without any electrical connection. Second, the unit has a faster response time and higher sensitivity levels, over a wide range of environmental conditions (i.e., temperature and humidity) than its counterparts. The sensor module can also be cabled to a readout unit for remote monitoring applications.

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 three sensor matrices revealed that, overall, the more technologically mature porous glass optrodes performed the best, and thus the optrodes were chosen as the hydrogen indicator matrix for the final product prototype. Sensor prototypes, each designed to accommodate both a hydrogen-sensitized optrode and an undoped porous glass “reference optrode,” were fabricated and tested. The optrode response time is rapid (time to reach 90% of full scale: T90 ≈ 5-8 seconds); software routines have been developed to provide a user-settable detection alarm at low hydrogen levels (down to 0.02% hydrogen in air).

Results

Optrode development focused on optimizing the optrode substrate fabrication steps to achieve the optimum response characteristics, a reproducible fabrication process, longer shelf-life times, and better resistance to chemical gas interferences. The operational specifications are summarized in Table 1.

<table>
<thead>
<tr>
<th>TABLE 1. Summary of Current Optrode Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Range</td>
</tr>
<tr>
<td>LOD\textsubscript{inj}, LOD\textsubscript{exch}</td>
</tr>
<tr>
<td>Accuracy</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Response Time:</td>
</tr>
<tr>
<td>Alarm Measurement T\textsubscript{90}</td>
</tr>
<tr>
<td>Recovery Time T\textsubscript{90}</td>
</tr>
<tr>
<td>Environmental Correction</td>
</tr>
<tr>
<td>Temperature Range, Operating</td>
</tr>
<tr>
<td>Humidity Range, Operating</td>
</tr>
<tr>
<td>Product Life</td>
</tr>
</tbody>
</table>

LOD – limit of detection; RH – relative humidity

The design, fabrication, assembly, and testing of the optoelectronic readout unit resulted in the construction of two hardware generations. After successfully testing and characterizing the first generation development prototype, we then developed the second generation (final prototype) unit shown in Figure 1. Among other requirements, the new version was designed with scaled up manufacturability and mass production in mind. Multiple user-friendly features, such as the replaceable sensor module, were also added. Figure 1 shows the fully functional final prototype in an anodized aluminum enclosure. The new prototype is smaller than the
The new device can be powered with a wall plug adapter, a universal serial bus, or the built-in rechargeable battery. This unit is an ideal handheld device that can also be used as a wall mounted unit. The detachable sensor module is mounted on a printed circuit board that was adapted from the design of a secure digital memory card, which is commonly used in today’s consumer electronics. The sensor module is inserted into the main measuring module using a push-pull locking and removal mechanism. The replaceable sensor module containing a hydrogen-sensitive optrode and a reference optrode is shown in Figure 1.

Repeatability/Reversibility

Excellent signal reversibility and repeatability are now being observed for our optimized optrodes, as illustrated by the test data shown in Figure 2. High degree of reproducibility in sensor fabrication was achieved by controlled sensors preparation protocol. Figure 3 illustrates the signal changes for two various batches, error bars represent the standard deviation from the average value (~0.04±0.01).

Environmental Stability

The detection and quantification of hydrogen was observed under a wide range of humidity and temperature, as shown in Figure 4; some degree of dependence on RH was noted, while at different temperatures, variations in the relative humidity were also observed (from 30 to 45%), and therefore, the sensor signal was not only affected by the temperature, but also by the humidity. Because of this factor, an accurate calibration curve for temperature dependence alone cannot be extracted from these tests; however, we have qualitatively identified the thermal dependence of the sensor.
Reproducible Fabrication/Longevity Studies

Fabricated hydrogen sensor optrodes were placed in long-term longevity studies where the optrodes were exposed to various levels of hydrogen (0.2 and 1.0%) at standard conditions (RH ~40%, and T=25°C). The signal change at a fixed hydrogen concentration showed no noticeable change over an aging period of five months (see Figure 5). We envision that a minimum longevity time of one year can be obtained. The accuracy and precision of hydrogen optrode measurements are listed in Table 2. A high degree of optrode fabrication reproducibility was achieved; data summarizing the inter-batch performance versus the intra-batch performance is shown in Figure 6.

Conclusions and Future Directions

We have developed sensitive, stable, reversible colorimetric hydrogen optrodes, and incorporated them in unique compact, hydrogen sensor units. Future directions include:

- “Map” the temperature/humidity parameter space using formally designed experiments to provide complete coverage.
- Develop, test, and optimize data processing algorithms to fully compensate for environmental effects.
- Perform field tests to validate sensor performance in a variety of environments and applications.
- Explore commercial possibilities for the different hydrogen sensor embodiments.
Special Recognitions & Awards/Patents Issued

An application is currently under examination in the United States Patent Office (USPTO); during this quarter, IOS did not receive any communications from the USPTO on this matter.

FY 2010 Publications/Presentations


References


FIGURE 6. Response of Different Optrodes from Two Batches to 0–2% H₂ in Air at 40-45% RH
IX.13 Hydrogen Safety Training for First Responders

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  Dennis McCall, James Bryan, Scott Jones
• California Fuel Cell Partnership (CaFCP), Sacramento, CA
  Jennifer Hamilton

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

Objectives

• Support the successful demonstration and deployment of hydrogen and fuel cell technologies by providing technically accurate hydrogen safety and emergency response information to first responders.

• Provide a one-day first responder training course, “Hydrogen Emergency Response Training for First Responders,” that integrates the use of DOE’s mobile hydrogen fuel cell vehicle (FCV) prop (initial offering in Fiscal Year [FY] 2009).

• Continue to support the Web-based awareness-level course, “Introduction to Hydrogen Safety for First Responders,” (initial offering in FY 2007).

• Disseminate first responder hydrogen safety educational materials at appropriate conferences to raise awareness.

Technical Barriers

This project addresses the following technical barriers from both the Education (ED) and Safety (SAF) sections of the Fuel Cell Technologies (FCT) Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of Readily Available, Objective, and Technically Accurate Information (ED)

(C) Disconnect Between Hydrogen Information and Dissemination Networks (ED)

(D) Lack of Educated Trainers and Training Opportunities (ED)

(H) Lack of Hydrogen Knowledge by Authorities Having Jurisdiction (SAF)

(I) Lack of Hydrogen Training Facilities for Emergency Responders (SAF)

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 FCT Program Multi-Year Research, Development and Demonstration Plan:

• 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).

• Milestone 4: Update “awareness-level” information package for first responders (4Q, 2009).

Accomplishments

• Prop-Based Course: Three sessions were held at the Hazardous Materials Management and Emergency Response (HAMMER) facility in June 2009, August 2009, and April 2010 to train 66 students from 14 states. Extremely positive feedback reinforced the value of this course.

• Awareness-Level Course: Our Web site still averages 500-500 unique visits per month from almost every state and some foreign countries. We registered the course on the TrainingFinder Realtime Affiliate Network (TRAIN) Web site for broader dissemination to first responders. TRAIN is a central repository for public health training courses.
Almost 30,000 TRAIN users identify themselves as emergency responders [1].

- **Outreach**: Compact discs (CDs) of the awareness-level course, laminated posters, and Firehouse article reprints were distributed through the DOE Energy Efficiency and Renewable Energy Information Center [2]. PNNL and HAMMER hosted booths at two key first responder conferences.

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**Introduction**

Safety in all aspects of a future hydrogen infrastructure is a top priority, and safety concerns influence all DOE hydrogen and fuel cell projects. Despite the most concerted effort, however, no energy system can be made 100% risk-free. Therefore, for any fuel and energy system, a suitably trained emergency response force is an essential component of a viable infrastructure. The FCT Program Office has identified training of emergency response personnel as a high priority, not only because these personnel need to understand how to respond to a hydrogen incident, but also because firefighters and other emergency responders 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 (OSHA) and National Fire Protection Association (NFPA) 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 in FY 2006-2007. A more advanced course and materials to facilitate education were developed in FY 2008-2009, complementing the design, construction, and operation of a fuel cell vehicle prop (developed under PNNL’s Hydrogen Safety project). In addition, PNNL has implemented outreach efforts to key stakeholder groups to facilitate delivery of the training to a broad audience.

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**Approach**

PNNL works with subject matter 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. The PNNL team works with DOE to make stakeholder groups aware of training opportunities and to provide “live” training when appropriate. The prop-based course has been given at the HAMMER facility, but plans are in progress to deliver the course at three training centers in California during 2010 in order to reach larger audiences in areas where hydrogen and fuel cell technologies are being deployed.

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**Results**

**Prop-Based Course**: 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. Course evaluation forms are distributed and feedback obtained at each class to help us improve the course content and delivery. Based on feedback from the three class sessions held this year (June 2009, August 2009, and April 2010), we concluded that first responders are comfortable with hydrogen and prepared to operate in a safe and effective manner, if a hydrogen incident should occur in their jurisdiction.

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, HAMMER, and the CaFCP for DOE. The figure shows a team of firefighters responding to a multi-vehicle accident involving a hydrogen FCV and two conventional vehicles.

**Web-Based Course**: Since the online course was launched in January 2007, there have been more than 17,000 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 users 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 positive.
**Outreach**: To distribute information and raise awareness about hydrogen safety and the DOE-sponsored courses, PNNL and HAMMER staff participated in two major first-responder conferences in FY 2010:

- Fire Department Instructor’s Conference, April 2010, Indianapolis, IN.
- Fire Rescue International, August 2010, Chicago, IL.

Booths were set up to display and disseminate posters, announcements of course offerings, hydrogen safety literature, and awareness-level course CDs.

**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 incident. The in-depth prop-based course builds on that success and is very useful in giving first responders a hands-on experience with simulated FCV incidents that integrates well with classroom training. PNNL will continue to update both courses as needed to reflect current applications and markets for hydrogen and fuel cells.

There is an identified need for the prop course curriculum to achieve a better balance between the vehicles and stationary facilities modules, through the development of some type of prop for stationary applications of fuel cells. A virtual hydrogen fueling station model having dual capabilities to simulate both outdoor fueling of passenger FCVs and indoor fueling of hydrogen forklifts could address that need. We are planning to develop a virtual model with the following capabilities and attributes:

- Visualizations of outdoor and indoor hydrogen dispensing systems.
- Text pop-ups describing the key components of outdoor and indoor hydrogen fueling stations (e.g., compressor, cylinder storage, dispenser).
- Animations of 30-second emergency response scenarios that could occur at outdoor and indoor fueling stations (e.g., various hydrogen leaks and fires).
- Narration of scripts for outdoor and indoor fueling scenarios.

The prop course will be offered at three first responder training facilities in California in FY 2010 (Sunnyvale Public Safety Department in Sunnyvale, Rio Hondo Community College Fire Academy in Santa Fe Springs, and the Orange County Fire Authority in Irvine). The prop will be transported to California in its trailer and left at each site for about a week. Three classes will be given at each site, resulting in a total of ~300 first responders trained. In future years, the prop will be transported to other locations across the country for use in delivery of this course at training centers in areas that have emerging deployments of hydrogen and fuel cell technologies. PNNL will also work with DOE and other stakeholders to determine what, if any, additional types of educational courses and materials are warranted, and to develop and implement plans to provide education to specific groups.

**FY 2010 Publications/Presentations**


**References**

Objectives

- Prepare safety training materials for researchers unfamiliar with hydrogen technology.
- Prepare advanced safety training materials for personnel in charge of hydrogen systems.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section (3.8) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (H) Lack of Hydrogen Knowledge by Authorities Having Jurisdiction
- (I) Lack of Hydrogen Training Facilities

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

- Milestone 17. Identify user needs for safety bibliography and incident databases. (1Q, 2006)

Accomplishments

- Delivered a final version of the Web-based class that incorporated reviewers’ comments.
- Started working toward a hands-on safety class for technical personnel.

Introduction

LLNL has been conducting hydrogen research for more than 50 years, starting with national security applications and continuing with hydrogen energy research. For many of these years, LLNL was designated as the pressure safety training facility for the whole DOE complex and other government institutions such as the National Aeronautics and Space Administration. Many technicians and researchers visited LLNL to receive appropriate training on many aspects of pressure safety, including hydrogen technology, cryogenics, leak detection, and vacuum technology.

The national security hydrogen and high-pressure research conducted at LLNL demanded unique testing facilities, and these were built with funding from DOE defense programs. These facilities include a high-pressure laboratory equipped with four hydrogen-compatible test cells, each rated for 80,000 psi, and 4 pounds of trinitrotoluene (TNT) equivalent stored energy. LLNL also has a high explosive test facility (Site 300) for high-energy experiments with many pounds of TNT-equivalent and many kilograms of hydrogen. Experiments in Site 300 are typically conducted in outdoor firing tables and monitored from the safety of a bunker. The remote location of this facility protects employees and property from any hazard.

These unique facilities and the expertise necessary to operate them are now being made available for hydrogen energy research through the development of training materials that may contribute to safe operation within the many institutions working for the Hydrogen Program.

Approach

We are planning to pursue a two-pronged approach to hydrogen safety training:

- Most researchers participating in the Hydrogen Program can benefit from basic training on hydrogen and pressure safety. This Web-based training can be completed in ~2 hours.
- Pressure operators in charge of setting up experimental equipment require comprehensive education on all aspects of hydrogen operation, in addition to the Web-based training on hydrogen fundamentals.
Results

We have developed a Web-based class with basic safety information for hydrogen researchers available through the following link: http://www.h2labsafety.org.

Readers are invited to take the class and submit comments to the authors that may improve the learning experience and/or update the class information.

The class takes ~2 hours for completion, and includes six modules:

- **Introduction** (5 minutes): course description, navigation, study guides.
- **Hydrogen Properties** (20 minutes): buoyancy, dispersion, ignition, flame and leak detection, ventilation, ignition sources, protective equipment.
- **Pressure Safety** (60 minutes): pressurized systems (Figure 1), system components, stored energy considerations and calculations, basic design criteria, material properties, pressure ratings, safety factors, gas cylinder use and storage.
- **Cryogenic Safety** (15 minutes): cryogenic fluid properties, thermal hazards, pressure hazards, expansion charts, asphyxiation, liquid air, safety measures.
- **Emergency Response** (15 minutes): hydrogen posted signs, alarms, emergency crews, emergency instructions.
- **Codes and Standards** (15 minutes): importance, organizations developing codes relevant to hydrogen, applicability, local and external resources.

Each module is followed by a quiz. After successful completion of all module quizzes (85% passing grade) the student will receive class credit. If a module quiz is failed, the student has the opportunity to review the module and retake that quiz.

This is a self-paced course that may take several hours to complete. However, it is not necessary to complete the course at one time. This course will track progress, allowing students to leave the course and continue where they left off when they return.

Navigation through the class is simple: from any location the student can easily jump to different modules at any time by pressing the “menu” button in the upper part of the screen.

The pressure safety module is the longest and most demanding module of the course. To better assist the student in learning the information, this module provides practice questions as a preview of the module quiz. We recommend students to carefully go through these practice questions to be better prepared for the end of module quiz.

In addition to the Web-based fundamentals class, we are also working on the development of a hands-on hydrogen safety class for pressure operators. This comprehensive training includes basic hydrogen safety, regulators, relief devices, leak detection, and cryogenics safety, followed by hands-on assembly and test of a hydrogen pressure system and a final evaluation. Training can be conducted during a three-day session at LLNL or at remote institutions with appropriate facilities.

While work in this more comprehensive “hands-on” class is just starting, we have been able to prepare two working tables and instructional materials including segmented pressure components (regulators, valves, FIGURE 1. A Screen Image from the Pressure Safety Module of the Web-based “Hydrogen Safety Class for Researchers”

Working table  Pressure vessels  Regulator

Relief device  Pressure gauge  CGA fitting

FIGURE 2. A Working Table and Different Pressure Components Cut to Illustrate Internal Structure and Operability
gauges; Figure 2). We anticipate Fiscal Year (FY) 2011 completion and start of instruction.

**Conclusions and Future Directions**

- We are contributing to safe hydrogen operations by developing instructional materials for researchers and operators.
- Web-based class (now complete) addresses the need of laboratory researchers handling small amounts of hydrogen.
- Hands-on class (in process) will present in-depth information for technical personnel tasked with installing and testing hydrogen systems.
- Participation from the hydrogen community will improve the class through suggestions, bug reports, etc.
IX.15 Optically Read MEMS Hydrogen Sensor

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Start Date: August 2007
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop sensing technology that achieves DOE research and development (R&D) targets for hydrogen safety sensors.
- Characterization of response time, recovery time, sensitivity and accuracy within the operating temperature range.
- Demonstrate sensor performance and compliance with safety goals.
- Establish partnership to develop pre-commercial sensor prototype.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Safety section (3.8.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (October 2007):

(D) Liability Issues
(E) Variation in Standard Practice of Safety Assessments for Components and Energy Systems

Technical Targets

The long-term project objective is to achieve commercialization and regulatory acceptance of fiber-reinforced polymer 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:

- Measurement Range: 0.1%-10%
- Operating Temperature: -50 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
- Resistant to interferents (e.g., hydrocarbons)

Accomplishments

- Developed new highly porous nanoparticle palladium-coated microcantilever sensor arrays.
- Developed a new wet chemical Pd film deposition technique on Ag/Cr coated cantilever sensors using a galvanic PdCl₂ exchange reaction.
- Demonstrated that large sensor surface area in comparison with film volume leads to very fast sensor response and recovery times.
- Completed selectivity, sensitivity, response and recovery time and regeneration analyses of the nanoporous Pd coated sensors and demonstrated excellent response characteristics.
- Demonstrated excellent stability, repeatability and life measurements that have been observed during more than a year of operation.
- Fabricated first field portable instrument to demonstrate operational performance of the Pd based sensors.
- Identified sensor commercialization partners and are negotiating commercialization agreements.

Introduction

Utilization of hydrogen as a transportation fuel requires comprehensive safety management during its storage, handling and use. Although safety-by-design and passive mitigation systems are the preferred methods for safety management, it is vitally important to develop technologies that can detect hydrogen releases and alert to system failures. The DOE Fuel Cell Program’s Hydrogen Safety sub-program recognizes the need to develop and commercialize hydrogen sensors that provide the appropriate response time and the sensitivity and accuracy necessary for use in safety applications, thereby reducing risk and helping to establish public confidence in the hydrogen infrastructure.

This project addresses the above needs by developing, proving and commercializing a hydrogen detection device based on nanostructured thin film...
palladium microcantilever arrays. This hydrogen sensor has been shown to provide major performance improvements over existing and other recently developed sensors. The overall objective is to develop sensor technology that achieves DOE R&D targets for hydrogen safety sensors at lower cost and with the potential for wide-area hydrogen gas detection.

**Approach**

Microcantilever-based chemical sensors were first seriously explored as a trace gas sensing technology in 1990s with the first reported use of Pd coated microcantilevers for sensing H2 occurring in 2000. Adsorption of a gas onto a thin film surface can cause large changes in stress and consequent bending of a thin cantilever structure. This bending response can be sensitively detected using piezoresistive, capacitive and optical techniques such that sub part-per-billion (ppb) sensitivities are achievable. Microcantilever-based chemical sensors have been shown to have high sensitivity, wide dynamic range and fast response times. Optically read microcantilever sensors are particularly advantageous in the presence of combustible or explosive gases and vapors (e.g. H2) due the possibility of vapor ignition when using heated or electrically operated sensors. Other advantages of this sensing technique include very low power consumption, and their potential use in distributed wide area sensor networks allowing multiple low cost chemical sensors to be located at storage or processing facilities (e.g. in the H2 fuel economy) or on H2-powered or transportation vehicles [1].

One of the most challenging aspects of detecting and quantifying the amount of a low concentration gas or vapor in the environment is the effect of potential interferents on the gas sensor response. Interferents can lead to false positive responses or suppressed responses to the gas being detected. One approach to overcoming this problem is the use of a multiplexed sensor array, with each sensor having a distinct sensitivity response to the gas or vapor of interest and any potential interferents. A much simpler approach is to use a single sensor, or small array of sensors, to sense a single gas species, as the computational processing of the array responses is much less intensive than for the multiplexed sensor array. The single sensor mode of operation is feasible if a coating can be found that responds primarily to the gas species of interest with minimal response to any potential interferents. Palladium has previously been used as a sensing medium in a number of sensor technologies due to its strong and reasonably unique response to H2. The possibility of using Pd-coated microcantilever sensors to detect H2 leaks has been examined in several previous studies.

Approach

The issue with most previous thin film Pd studies, and reasonably unique response to H2. The possibility of using Pd-coated microcantilever sensors to detect H2 leaks has been examined in several previous studies. The single sensor response and recovery times are far longer than acceptable for most applications; response times for these microcantilever-based H2 sensor studies varied from a few minutes to as long as 1 hour. The long response and recovery times are attributed to the long diffusion time for elemental hydrogen to diffuse into and out of the palladium film to form palladium hydride.

Our approach is to use a new nanostructured Pd/Ag alloy that we developed specifically for the hydrogen sensing application. Microcantilever sensors coated with this alloy have fast, near ideal response characteristics when monitoring low concentration H2 gas. In particular, the response and recovery times measured with these sensors are far shorter (<10 s) than those reported in all previous microcantilever-based H2 sensor studies. The development work performed to optimize the performance of our sensor consisted of efforts to increase the sensitivity and dynamic range, to minimize the response and recovery times, to improve its resistance to interferents, and to increase its accuracy, repeatability and lifetime. We are presently working on the development of a prototype that can be performance-evaluated by third parties and adapting the sensor system for use in wide-area sensing.

**Results**

We conducted sensitivity and performance measurements of the Pd-Ag functionalized, optically read microcantilever using a benchtop setup consisting of the microcantilever in a gas flow cell, an optical readout system, a flow control valve and sample loop, and a LabVIEW®-based data acquisition system. The threshold and dynamic range test results revealed a lower-limit-detection of 0.01% (100 ppm) H2 in argon, with three orders of magnitude dynamic range. Response and recovery times for 4% H2 in argon were <3 s and <10 s, respectively. Over an eight-month period the sensor accuracy and repeatability remained constant within ±2%, indicating that the projected operational lifetime of this early version of the sensor could be as long as several years. Measurements of sensor specificity to common impurities and carrier gases (CO2, CH4, H2O, N2, He, CO) showed that in all cases, the responses from the interferents were an order of magnitude or more smaller than that observed for H2 at similar concentrations (see Figure 1). This degree of discrimination against interfering species will be adequate in all but the most demanding applications.

As illustrated in Table 1, in laboratory tests completed to date, we demonstrated that our microcantilever-based H2 sensors meet all but the most stringent requirements for automotive sensing applications.
We have demonstrated that Pd-Ag functionalized, optically read microcantilever H₂ sensors have nearly ideal attributes required for distributed low cost sensing of hydrogen leaks in many applications. These include high sensitivity, wide dynamic range, adequate response and recovery times and repeatable response. These sensors have been operating in a laboratory environment for more than a year without noticeable changes in sensitivity, specificity and response and recovery times. Work is also progressing on the development of low-cost portable detector prototypes that can be used to validate the expected performance of this potentially lower cost, better performing sensing technique. To this end, we have developed and done preliminary performance studies on two generations of portable instrumentation with encouraging results. We plan to report on these studies at a later date.

**Conclusions and Future Directions**

In the next project year we plan to:

- Improve H₂ sensor response in several areas:
  - Faster response/recovery times: shorten recovery from 3-10 s to <1 sec.
  - Improve specificity by reducing response to water vapor.
  - Continue studies on potential interferents such as CO, EtOH, CH₄, H₂S.
  - Perform studies on multi-component mixtures.
- File patents applications on techniques, methods, coatings, applications.
- Finalize commercialization partnership agreements.

**TABLE 1.** ORNL microcantilever-based H₂ sensor meets all requirements for stationary and automotive applications and possibly exceeds performance of other recent sensors.

<table>
<thead>
<tr>
<th>Performance Requirement*</th>
<th>ORNL Measured Performance</th>
<th>Competitor #1 (IOS)</th>
<th>Competitor #2 (LANL)</th>
</tr>
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<tbody>
<tr>
<td>Sensitivity Range</td>
<td>&lt; 0.1% to &gt; 4%</td>
<td>0.01 – 10%</td>
<td>0.2 – 10%</td>
</tr>
<tr>
<td>Survivalivity Limit</td>
<td>100%</td>
<td>Linear response to 100% H₂</td>
<td>unknown</td>
</tr>
<tr>
<td>Response Time</td>
<td>Automotive: &lt; 3 sec</td>
<td>1-3 sec</td>
<td>&gt; 5 sec</td>
</tr>
<tr>
<td></td>
<td>Stationary: &lt; 30 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recovery Time</td>
<td>Automotive: &lt; 3 sec</td>
<td>3-10 sec</td>
<td>&gt; 5 sec</td>
</tr>
<tr>
<td></td>
<td>Stationary: &lt; 30 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature Range</td>
<td>Automotive: -40°C to +125°C</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Stationary: -20°C to +50°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure Range</td>
<td>Automotive: 62-107 kPa</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Stationary: 80-110 kPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient Relative Humidity</td>
<td>Automotive: 0 – 95%</td>
<td>0-100% - little response to changes in humidity</td>
<td>significant response to changes in humidity</td>
</tr>
<tr>
<td></td>
<td>Stationary: 20 – 80%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interferent Resistance</td>
<td>No false positive responses</td>
<td>Excellent</td>
<td>poor – H₂S, CO, CH₄</td>
</tr>
<tr>
<td>Power Consumption</td>
<td>&lt; 1 Watt</td>
<td>0.2-0.5 Watt</td>
<td>0.5 watt</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>Room temperature</td>
<td>Room temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Lifetime</td>
<td>Automotive: 6,000 hr</td>
<td>Demonstrated</td>
<td>Unknown</td>
</tr>
<tr>
<td></td>
<td>Stationary: &gt; 5 years</td>
<td>&gt; 12 months</td>
<td></td>
</tr>
<tr>
<td>Accuracy and Repeatability</td>
<td>Automotive: 5-10%</td>
<td>&gt; +/- 5%</td>
<td>&gt; +/- 5%</td>
</tr>
<tr>
<td></td>
<td>Stationary: 10%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

LANL - Los Alamos National Laboratory
• Complete fabrication and preliminary testing of a field portable instrument.
• Implement commercialization plan with commercial partner.
• Begin tech transfer to commercialization partner for preproduction prototype development.
• Manage preproduction instrument fabrication at commercialization partner facilities.
• Test pre-commercialization prototype at National Renewable Energy Laboratory Hydrogen Sensor Laboratory.

FY 2010 Publications/Presentations

References
X. EDUCATION
Introduction

The Education sub-program seeks to support and facilitate hydrogen and fuel cell demonstration, deployment, and early market introduction 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

<table>
<thead>
<tr>
<th>Target Audience</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code Officials</td>
<td>Code officials must be familiar with hydrogen to facilitate the permitting process and local project approval.</td>
</tr>
<tr>
<td>First Responders</td>
<td>Firefighters, as well as law enforcement and emergency medical personnel, must know how to handle potential incidents; their understanding can also facilitate local project approval.</td>
</tr>
<tr>
<td>Local Communities/General Public</td>
<td>Local communities will be more likely to welcome hydrogen and fuel cell projects if they are familiar with hydrogen.</td>
</tr>
<tr>
<td>Potential End-Users</td>
<td>Potential early adopters need information about commercially available hydrogen and fuel cell products and the opportunities for incorporating the technology into their operations.</td>
</tr>
<tr>
<td>State and Local Government</td>
<td>A broad understanding of hydrogen supports decision-making on current opportunities for near-term deployment and lays the foundation for long-term change.</td>
</tr>
<tr>
<td>Representatives</td>
<td></td>
</tr>
<tr>
<td>Teachers and Students</td>
<td>Teachers are looking for technically accurate information and usable classroom activities.</td>
</tr>
<tr>
<td>University Faculty and Students</td>
<td>Graduates are needed for research in government, industry, and academia.</td>
</tr>
</tbody>
</table>

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 fuel cell technologies and how they fit in the portfolio of energy and efficiency options. To aid with market introduction, the sub-program helps to develop an accurate understanding of hydrogen safety, to recognize opportunities for deployment in near-term markets, and to understand the role of early markets in facilitating use of hydrogen and fuel cell technologies.

Goals

Educate key audiences about hydrogen and fuel cell technologies to facilitate near-term demonstration and long-term commercialization and market acceptance.

Objectives

- By 2011, expand availability of university curricula developed under Fiscal Year (FY) 2008 solicitation projects and expand availability of case studies for near-term market applications.
- By 2012, complete analysis to identify domestic employment and workforce development opportunities for early market hydrogen and fuel cell applications.

FY 2010 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 2010, the sub-program conducted several sessions of a hands-on “prop course” for firefighters. This advanced-level, one-day course builds on a 2007 introductory course, “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. It 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 registered on the Training Finder Realtime Affiliate Network (TRAIN) Web site, a central repository for health training courses, to reach out to the 30,000 emergency responder members of TRAIN.

The Education sub-program and the Safety, Codes and Standards sub-program expanded the code and permitting official e-learning package with indoor fueling information and developed permitting case studies, in support of increasing early market deployments. Like the introductory course for first responders, “Introduction to Hydrogen Safety for Code Officials” is a five-module, Web-based course that provides a general overview of hydrogen, its properties, and its applications; the course also includes information on the technology and equipment tailored to the needs of code and permitting officials. The case studies were based on actual forklift and backup power deployments supported by the Hydrogen Program, and were developed to assist code officials and project developers in the permitting and safety evaluation of similar installations. Additionally, the in-person code official workshop curriculum was updated to include modules on electric vehicles and infrastructure, to provide a more comprehensive perspective on future transportation technologies.

In FY 2010, an early market outreach education project conducted hydrogen education sessions accompanied by hands-on forklift demonstrations at material handling equipment dealerships, customer sites, community colleges, and regional green-business expos to educate facilities managers, operators, maintenance personnel, safety groups, first responders, authorities having jurisdiction, technical and community colleges, and the general public on the benefits of fuel cell forklifts. In parallel, month-long demonstrations of two hydrogen fuel cell–powered lift trucks at five major retailers in geographically diverse locations provided real-world experience and showcased the economic and environmental benefits of fuel cells. As evidence of the project’s success, one site has decided to acquire over 100 fuel cell forklifts as a result of their experience with the demonstration units.

The Education sub-program continued its efforts to reach out to and partner with state and local governments through seven outreach projects. These 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 their second year, these projects finalized or are finalizing the resource development phase and have moved into the deployment phase. Many groups have been using the results of their research to work directly with state agencies to implement policies, programs, and best practices that can support the growth of hydrogen and fuel cell markets in local economies.

In FY 2010, the Education sub-program’s five university projects targeted a broad student audience through general education courses, specialized science and engineering courses, minor and concentration programs, curricula modules, internships, labs, lab kits, and textbook chapters. Also in their second year, these projects are finalizing development of curriculum and have moved into teaching, reviewing, and refining the course materials. Some projects are leveraging the newly formed core of hydrogen and fuel cell undergraduates by implementing student-taught middle school and high school workshops in addition to outreach targeted toward community college students. The next phase of deployment will involve publicly disseminating these teaching resources to other universities and colleges for adoption into their curricula.

“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," is deploying a six-unit science curriculum and laboratory kit on hydrogen and fuel cells through professional development workshops and science teacher conferences across the country.
FY 2010 Accomplishments

- Deployed three sessions of the advanced-level prop-based course for first responders, in coordination with the Safety, Codes and Standards sub-program. After three sessions at the Hazardous Materials Management and Emergency Response training facility, DOE has trained 66 first responders from 14 states; an additional three courses are planned in California.

- In coordination with the Safety, Codes and Standards sub-program, increased accessibility of the “Introduction to Hydrogen Safety for First Responders” Web-based course by registering the course on the TRAIN Web site, a central repository for health training courses. Since its launch in January 2007, over 17,000 unique visitors have accessed the course, with an average of 300 to 500 users each month; user groups 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.

- Expanded outreach to code officials through four in-person workshops, an updated “Introduction to Hydrogen Safety for Code Officials” Web-based training course, and case studies documenting the permitting process for two early market fuel cell installations in coordination with the Safety, Codes and Standards sub-program. The codes and standards workshops, held in collaboration with local fire department and government organizations, were expanded to include additional modules on electric vehicles and infrastructure in coordination with the DOE Vehicle Technologies Program. The e-learning package was updated with material on indoor hydrogen fueling to support the increasing number of fuel cell material handling equipment deployments. In support of the Fuel Cell Technologies Program, teams were asked to evaluate, assist with, and document the permitting of a backup fuel cell system and a fleet of fuel cell forklifts at two Department of Defense sites. The results were published as case studies to assist code officials and project developers in understanding the codes and standards and safety evaluations for similar early market installations.

- Outreach efforts continued for both first responder courses with the dissemination of hydrogen safety literature and course compact disks, 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.

- Conducted nearly 20 hydrogen education sessions with hands-on forklift demonstrations at material handling dealerships, customer sites, community colleges and regional green business expos to educate facilities management, operators, maintenance personnel, safety groups, first responders, authorities having jurisdiction, technical and community colleges, and the general public on the benefits of fuel cell forklifts. In parallel, month-long demonstrations of two hydrogen fuel cell-powered lift trucks at five high-profile geographically diverse locations provided real-world experience and showcased the economic and environmental benefits of fuel cells.

- Continued state and government outreach projects in states with an active hydrogen and fuel cell presence; these projects involved work with the Clean Energy State Alliance, Technology Transition Corporation, and state organizations in Connecticut, Texas, Ohio, South Carolina, and Virginia. These seven projects have conducted over 80 workshops, seminars, briefings, and Webinars across the country; they have also produced fact sheets, newsletters, best practice guides, Web sites, video segments, print articles, and an installation analysis tool to educate government officials and help decision-makers identify and assess opportunities for future deployments.

- Taught over 25 courses, labs, and curriculum modules at California State University, Los Angeles; Humboldt State University; University of California, Berkeley; Michigan Technological University; the University of Central Florida; and the University of North Dakota for general science and engineering programs and specialized hydrogen and fuel cell concentrations. These universities are developing senior design projects, building labs, and sponsoring teaching assistantships and internships to provide hands-on experience with the technologies. Lab kits, textbook modules, problem set workbooks, and course curricula will be integrated into existing science and engineering teaching materials and shared on the Internet to introduce hydrogen and fuel cell technologies to university students across the country.
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 sub-program has reached over 8,000 middle school teachers through workshops and conference sessions in 35 states.

Eleven high school science teachers in Connecticut, Georgia, New York, South Carolina, and southern California used the Hydrogen Technology and Energy Curriculum (HyTEC) to teach over 860 students about the science and engineering of hydrogen and fuel cells and their role in addressing energy needs. An additional 240 teachers were introduced to these course materials at science teacher conferences across the country.

Continued audience-targeted Fuel Cell Technologies Program exhibit outreach to early end-user conferences (e.g., U.S. Conference of Mayors, North American Material Handling Logistics Tradeshow, Next Generation Data Center), and hydrogen and fuel cell conferences (e.g., National Hydrogen Association Conference and Expo, Fuel Cell Seminar).

Published the final results from the 2008/2009 Hydrogen Knowledge and Opinions survey and analysis. This effort follows the baseline survey conducted in 2004 and includes a separate survey of code officials—an audience that had been previously incorporated into the state and local officials survey population but has since been prioritized as a separate key target audience essential to the early adoption of fuel cells.

**Budget**

In FY 2010 the Education sub-program returned from the Vehicle Technologies Program to be a part of the Fuel Cell Technologies Program, with an appropriation of $2.0 million. The FY 2009 appropriation allowed for full funding of many of the education portfolio projects. The work of these projects continued in FY 2010 and many of these projects were reviewed in the FY 2010 Annual Merit Review. The FY 2010 appropriation allowed for support of existing projects across the education portfolio, including outreach to state and local government officials, university hydrogen and fuel cell education programs, in addition to ongoing efforts to educate first responders, code officials, and teachers and students at the middle and high school levels.
**FY 2011 Plans**

In FY 2011, the Education sub-program will continue to focus on facilitating the introduction of hydrogen and fuel cell technologies into early markets. Future efforts will begin to examine workforce development needs and include nearer-term employment needs and projections with the Systems Analysis sub-program.

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Fuel Cell Technologies Program  
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Washington, D.C. 20585-0121  
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E-mail: Carole.Read@ee.doe.gov
X.1 Hydrogen Safety Training for First Responders

Objectives

- Support the successful demonstration and deployment of hydrogen and fuel cell technologies by providing technically accurate hydrogen safety and emergency response information to first responders.

- Provide a one-day first responder training course, “Hydrogen Emergency Response Training for First Responders,” that integrates the use of DOE’s mobile hydrogen fuel cell vehicle (FCV) prop (initial offering in Fiscal Year [FY] 2009).

- Continue to support the Web-based awareness-level course, “Introduction to Hydrogen Safety for First Responders,” (initial offering in FY 2007).

- Disseminate first responder hydrogen safety educational materials at appropriate conferences to raise awareness.

Technical Barriers

This project addresses the following technical barriers from both the Education (ED) and Safety (SAF) sections of the Fuel Cell Technologies (FCT) Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of Readily Available, Objective, and Technically Accurate Information (ED)

(C) Disconnect Between Hydrogen Information and Dissemination Networks (ED)

(D) Lack of Educated Trainers and Training Opportunities (ED)

(H) Lack of Hydrogen Knowledge by Authorities Having Jurisdiction (SAF)

(I) Lack of Hydrogen Training Facilities for Emergency Responders (SAF)

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 FCT Program Multi-Year Research, Development and Demonstration Plan:


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

- **Prop-Based Course**: Three sessions were held at the Hazardous Materials Management and Emergency Response (HAMMER) facility in June 2009, August 2009, and April 2010 to train 66 students from 14 states. Extremely positive feedback reinforced the value of this course.

- **Awareness-Level Course**: Our Web site still averages 300-500 unique visits per month from almost every state and some foreign countries. We registered the course on the TrainingFinder Realtime Affiliate Network (TRAIN) Web site for broader dissemination to first responders. TRAIN is a central repository for public health training courses. Almost 30,000 TRAIN users identify themselves as emergency responders [1].
Outreach: Compact discs (CDs) of the awareness-level course, laminated posters, and Firehouse article reprints were distributed through the DOE Energy Efficiency and Renewable Energy Information Center [2]. PNNL and HAMMER hosted booths at two key first responder conferences.

Introduction

Safety in all aspects of a future hydrogen infrastructure is a top priority, and safety concerns influence all DOE hydrogen and fuel cell projects. Despite the most concerted effort, however, no energy system can be made 100% risk-free. Therefore, for any fuel and energy system, a suitably trained emergency response force is an essential component of a viable infrastructure. The FCT Program Office has identified training of emergency response personnel as a high priority, not only because these personnel need to understand how to respond to a hydrogen incident, but also because firefighters and other emergency responders 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 (OSHA) and National Fire Protection Association (NFPA) 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 in FY 2006-2007. A more advanced course and materials to facilitate education were developed in FY 2008-2009, complementing the design, construction, and operation of a fuel cell vehicle prop (developed under PNNL’s Hydrogen Safety project). In addition, PNNL has implemented outreach efforts to key stakeholder groups to facilitate delivery of the training to a broad audience.

Approach

PNNL works with subject matter 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. The PNNL team works with DOE to make stakeholder groups aware of training opportunities and to provide “live” training when appropriate. The prop-based course has been given at the HAMMER facility, but plans are in progress to deliver the course at three training centers in California during 2010 in order to reach larger audiences in areas where hydrogen and fuel cell technologies are being deployed.

Results

Prop-Based Course: 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. Course evaluation forms are distributed and feedback obtained at each class to help us improve the course content and delivery. Based on feedback from the three class sessions held this year (June 2009, August 2009, and April 2010), we concluded that first responders are comfortable with hydrogen and prepared to operate in a safe and effective manner, if a hydrogen incident should occur in their jurisdiction.

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, HAMMER, and the CaFCP for DOE. The figure shows a team of firefighters responding to a multi-vehicle accident involving a hydrogen FCV and two conventional vehicles.

Web-Based Course: Since the online course was launched in January 2007, there have been more than 17,000 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 users 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 positive.

FIGURE 1. FCV Prop Training Exercise
**Outreach:** To distribute information and raise awareness about hydrogen safety and the DOE-sponsored courses, PNNL and HAMMER staff participated in two major first-responder conferences in FY 2010:

- Fire Department Instructor’s Conference, April 2010, Indianapolis, IN.
- Fire Rescue International, August 2010, Chicago, IL.

Booths were set up to display and disseminate posters, announcements of course offerings, hydrogen safety literature, and awareness-level course CDs.

**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 incident. The in-depth prop-based course builds on that success and is very useful in giving first responders a hands-on experience with simulated FCV incidents that integrates well with classroom training. PNNL will continue to update both courses as needed to reflect current applications and markets for hydrogen and fuel cells.

There is an identified need for the prop course curriculum to achieve a better balance between the vehicles and stationary facilities modules, through the development of some type of prop for stationary applications of fuel cells. A virtual hydrogen fueling station model having dual capabilities to simulate both outdoor fueling of passenger FCVs and indoor fueling of hydrogen forklifts could address that need. We are planning to develop a virtual model with the following capabilities and attributes:

- Visualizations of outdoor and indoor hydrogen dispensing systems.
- Text pop-ups describing the key components of outdoor and indoor hydrogen fueling stations (e.g., compressor, cylinder storage, dispenser).
- Animations of 30-second emergency response scenarios that could occur at outdoor and indoor fueling stations (e.g., various hydrogen leaks and fires).
- Narration of scripts for outdoor and indoor fueling scenarios.

The prop course will be offered at three first responder training facilities in California in FY 2010 (Sunnyvale Public Safety Department in Sunnyvale, Rio Hondo Community College Fire Academy in Santa Fe Springs, and the Orange County Fire Authority in Irvine). The prop will be transported to California in its trailer and left at each site for about a week. Three classes will be given at each site, resulting in a total of ~300 first responders trained. In future years, the prop will be transported to other locations across the country for use in delivery of this course at training centers in areas that have emerging deployments of hydrogen and fuel cell technologies. PNNL will also work with DOE and other stakeholders to determine what, if any, additional types of educational courses and materials are warranted, and to develop and implement plans to provide education to specific groups.

**FY 2010 Publications/Presentations**


**References**

X.2 Education for Emerging Fuel Cell Technologies

Objectives

- Conduct research and development (R&D) needed to establish sound technical requirements for hydrogen and fuel cell codes and standards.
- Support code development for the safe use of hydrogen and fuel cell technologies.
- Advance safety, code development, and market transformation issues through collaborations with appropriate stakeholders.
- Facilitate the safe deployment of hydrogen and fuel cell fuel technologies.

Technical Barriers

This project addresses the following technical barriers from the Education section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of Readily Available, Objective, and Technically Accurate Information
(B) Disconnect Between Hydrogen 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 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

18. Develop end-user workshop materials for use at events. (4Q, 2009)
19. Develop short courses for end-users at technical colleges. (4Q, 2011)

Accomplishments

NREL has accomplished the following in support of section 3.9 of the DOE Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Codes and standards workshops: Expanded codes and standards workshops from Fiscal Year (FY) 2009 to cover more subject matter, including a new module on electric vehicles and infrastructure requirements for electric vehicles. Presented four workshops in FY 2010 partnering with local fire departments and government organizations.
- Web-based information compendium: Expanded compendium to include other vehicle fuels and to include updated code official training course that includes material on indoor hydrogen fueling.

Introduction

It is essential to develop and promulgate codes and standards in order to provide for the safe use of hydrogen and fuel cell technologies. With the help of key stakeholders, the DOE Fuel Cell Technologies Program and NREL are coordinating a collaborative national effort to prepare, review, and promulgate codes and standards for all hydrogen and fuel cell technologies.

Approach

The Fuel Cell Technologies Program recognizes that domestic and international codes and standards must
be established to enable the timely commercialization and safe use of hydrogen and fuel cell technologies. The lack of codes and standards applicable to hydrogen and fuel cell technologies is an institutional barrier to deploying these technologies. It is in the national interest to eliminate this potential barrier. As such, the Program works with domestic and international standards development organizations (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 hydrogen and fuel cell 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**

The Safety Codes and Standards work is divided into three major areas:

- National Template Implementation
- Codes and Standards Research
- Codes and Standards Training and Outreach

This report will address codes and standards outreach.

**Codes and Standards Training and Outreach**

NREL has several active training and outreach projects in FY 2010 including the following:

- Codes and standards workshops.
- Update of code official on-line training course.
- Analysis of two emerging fuel cell technology projects (funded through Education).

NREL conducted four Codes and Standards Workshops in FY 2010. These workshops were held in Tampa, FL, New Orleans, LA, San Francisco, CA and Los Angeles, CA. All four were held in collaboration with local fire service departments or organizations. These workshops were targeted at code officials and project developers who would be working on fuel cell or hydrogen technology projects.

The proceedings from these workshops are posted at the Hydrogen Program Safety, Codes and Standards Web page. Generally, the workshops have been effective at getting information to individuals who will be directly involved in hydrogen and fuel cell projects. These individual include plans review officers for fire departments and project managers responsible for getting hydrogen and fuel cell projects built.

The code official training course that was placed on-line in FY 2009 was amended to include material on indoor fueling operations. Indoor fueling is a special concern because of the developing use of hydrogen-fueled forklifts that are typically fueled indoors.

Another key project is two case studies that address emerging fuel cell technologies. The first project is an evaluation of codes and standards and safety issues associated with a fuel cell system used to supply backup power at military base and the second is an evaluation of indoor fueling and forklift operations at a military storage facility. The analysis and findings from these projects will be published as an NREL technical report that would assist code officials and project developers in codes and standards and safety evaluations in similar projects.

Figure 1 shows how the work done in the outreach activities feeds into the research projects and codes and standards development work.

**Conclusions and Future Directions**

NREL will continue to support the development of codes and standards by:

- Working with DOE to implement a national template for vehicle codes and
- 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.
- Performing outreach work to distribute information on hydrogen and fuel cell technologies to code officials, project
- Coordinating domestic codes and standards and International standards to ensure consistent requirements.

**FY 2010 Publications/Presentations**


8. High pressure Hydrogen Storage; Validation Testing of SAE performance Based System Level Requirements, Burgess, R. published in the proceedings of the National Hydrogen Association 2010 Annual Conference.
X.3 Hydrogen and Fuel Cell Education at California State University, Los Angeles

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 (PEM) fuel cell and hydrogen laboratory supporting curriculum and graduate students’ teaching and research experiences.
- Providing engaging capstone projects for multidisciplinary teams of senior undergraduate students.
- Fostering partnerships with automotive manufacturers and energy providers.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Fuel Cell Technologies (FCT) Program Multi-Year Research, Development and Demonstration Plan:

- Lack of Readily Available, Objective, and Technically Accurate Information
- Mixed Messages
- 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 FCT 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 2009-2010 academic year, we continued to offer course modules and hydrogen fuel cell technology dedicated courses: ME 454-Renewable Energy and Sustainability (enrollment 26); ME 554-Fuel Cell Systems (graduate course; enrollment 10); TECH 478-Fuel Cell Applications (enrollment eight technology, seven mechanical); TECH 250-The Impact of Technology on the Individual and Society (detailed in the next section). 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 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: 2008-2009—186 students; 2009-2010—206 students. M:21.

- Work has continued within the Zero Emissions Fuel Cell and Hydrogen Laboratory (ZEFC). Major equipment purchased last year has been integrated into courses: Heliocentris -- Dr. Fuel Cell, Nexa Training System Complete, Nexa Integration Kit; and Proton-Hogen GC600 Electrolyzer. Two graduate and several undergraduate students
worked on educational and research projects in the laboratory. M:21, M:11.

- ECST assembled a multidisciplinary senior design team which is solving the problem of calibrating the amount of hydrogen dispensed at 5,000 psi by building a prototype for the 10,000 psi unit.
- The initial solar installation has grown from 2 kW to 10 kW. The system consists of 56 Sharp and 23 Solec modules. The ECST building is a 3-phase building which requires three inverters per each type of modules. However, SMA has come out with a Tripower inverter which is capable of dual maximum power point tracking and is 10 kW unit. This type is schedule for production in summer 2010 and CSULA is waiting for an available unit. The funds are being provided by Southern California Edison. M:21.
- ECST assembled a multidisciplinary senior design team to design and build a Hydrogen Safety demonstrator. The team consisted of two mechanical engineering and two electrical engineering 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 raised funds and initiated the construction of a hydrogen station with 60 kg/day generation capacity. That will enable further development of educational program. M:21.
- Multidisciplinary team of CSULA faculty, including the principal investigator (PI), received National Science Foundation funding to establish the Center for Energy and Sustainability. One of the projects is to design and evaluate miniature direct-methanol fuel cell. This will contribute to the longevity of the research program. M:21.

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 the ongoing construction of 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. ECST has established ZEFC to support curriculum, undergraduate and graduate students’ teaching and research experiences. Further, enrichment of student experiences is accomplished through projects and fostering partnerships with automotive manufacturers and industry.

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 continued to be offered within 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. TECH 478 continued as flagship of the program. The class hosted the Honda Clarity fuel cell vehicle team that gave a lecture and a demonstration on Honda fuel cell vehicles as well as a visit by a renowned fuel cell researcher Dr. Subbarao Surampudi of the Jet Propulsion Laboratory. As part of the mid-term exam, students attended the 2010 National Hydrogen Association conference which was available locally.

Active work has continued within the ZEFC. The laboratory is designed to provide hands-on activities supporting fuel cell courses offered in the program. One graduate student developed: Lab1 a-b, Characteristic Curve and Efficiency of the Electrolyzer; Lab2 a-b, Characteristic Curve and Efficiency of the Fuel Cell; Lab3, Nexa Training System Complete: Fuel Cell Power Potential; abbreviated operating manuals for Nexa Training System Complete and Hogen Electrolyzer. He also assisted with teaching labs for undergraduate and graduate courses. The same student provided leadership for the “Hydrogen Community” design project sponsored by National Hydrogen Association. The project was called Soaring Eagle and five technology and two mechanical engineering students participated, see Figure 1.

The PI and the graduate student attended an intensive 3-day fuel cell course offered at Los Alamos National Laboratory. The training benefited student’s
graduate research and the PI’s course materials. Later, this student presentation “Root Cause Analysis of Low Fuel Cell Voltage Generation” was awarded the first place oral presentation in Engineering and Computer Science I at the CSULA 18th Annual Symposium on Research, Scholarship and Creative Activity. Among the winners from other disciplines, the student has been invited to the CSU statewide competition in San Jose.

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 fall of 2009, ECST hosted a Boeing open house for middle and high-school students, about 150 of whom toured the ZEFC. ECST is executing its 2010 Research Experience for Undergraduate program in ZEFC through which two students are working on a photolysis shark project and five are building a fuel cell vehicle to demonstrate solar-hydrogen-to-wheel efficiencies. Multiple industry sponsored projects are supported by the PI and ZEFC facility. CSULA hosted 15 East Los Angeles College students for a week-long workshop where a LEGO Mindstorm robot powered by a Horizon 20 W fuel cell was built, see Figure 2.

CSULA has initiated the long awaited $4.5 M hydrogen station on campus, see Figure 3. It will deploy the latest technologies with the capacity of 60 kg/day, sufficient to fuel 15+ vehicles or a bus and five more vehicles. The station will be utilizing a Hydrogenics electrolyzer, first and second stage compressors capable of fast-filling at 5,000 psi and 10,000 psi, 60 kg of hydrogen storage. The station will be grid-tied and powered by 100% renewable power. The station construction has commenced and full operation is expected in January-March 2011.

The PI attended the 2010 Annual Merit Review in Washington DC; 2010 American Society for Engineering Education conference in Louisville, KY; and, 2010 National Hydrogen Assocation conference, Long Beach, CA.

**Conclusions and Future Directions**

CSULA has methodically pursued the stated objectives in executing the grant. The team has offered a comprehensive suite of courses addressing fuel cell and hydrogen technologies. In the second year significant improvements were made integrating experimental experience through ZEFC. The work in ZEFC is continued with the solar installation and student/industry projects far beyond those proposed initially.
Next year efforts will focus on further development of student research and projects to assure the long-term viability of the hydrogen and fuel cell program at CSULA. Significant activities will also be associated with the construction, operation and utilization of the hydrogen station for public outreach and education. Next level of the program development will take place in commissioning the station and raising support for hydrogen infrastructure related curriculum, data collection and research. The team plans to file for project extension beyond September 15, 2010.

**Special Recognitions & Awards/Patents Issued**

1. Best Paper Award (2nd place) in the Energy Conversion Division of American Society for Engineering Education, see below for full reference. The PI was the main co-author.

2. Education Award by Looking Green Magazine at Rose Bowl Green Expo, Pasadena, CA July 2010.

**FY 2010 Publications/Presentations**


X.4 Hydrogen Energy in Engineering Education ($H_2E^3$)

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DOE Project Officer: Gregory Kleen
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Contract Number: DE-FG36-08GO18107

Subcontractor:
University of California, Berkeley (UCB), Berkeley, CA

Project Start Date: September 15, 2008
Project End Date: September 15, 2011

Objectives
The Hydrogen Energy in Engineering Education ($H_2E^3$) 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. $H_2E^3$'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 Fuel Cell 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 Fuel Cell 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
- Successfully introduced $H_2E^3$ curriculum in three engineering courses at HSU and two at UCB.
- Successfully incorporated $H_2E^3$ hardware in lab activities in a total of four engineering courses at the two campuses.
- Continued development of new curriculum materials.
- Performed monitoring and evaluation of the curriculum and lab hardware in use, using feedback.
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 Sponsored Programs Foundation. Our principal partner on the project is the UCB, represented by their Institute of Transportation Studies. The project also began with a number of fuel cell industry partners, but the participation of these manufacturers in the project as hosts for student interns is being reevaluated, as discussed in the following.

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

Having completed development of hardware and begun curriculum development during the first year of the project, in year two we focused on introducing the curriculum and hardware into several engineering courses at UCB and HSU, and refining H₂E³ materials. We also worked on developing relationships that will allow us to reach out to additional campuses, incorporate studies of hydrogen fueling stations into H₂E³ (Figure 1), and establish student internships during year three.

Curriculum Development and Deployment. We introduced our curriculum, in the form of PowerPoint presentations, lab activities, and supporting documentation for lab instructors, into several engineering courses: introduction to environmental resources engineering, introductory thermodynamics, and advanced thermodynamics at HSU; and engineering design and analysis and energy and society at UCB.

Equipment Deployment. The two fuel cell test stations (Figures 2 and 3) and 24 fuel cell/electrolyzer kits (Figure 4) were used in each of the above courses for hands-on lab activities and/or instructor demonstrations. All of the equipment performed satisfactorily.

Monitoring and Evaluation. Project team members used a variety of assessment tools to analyze the effectiveness of the H₂E³ curriculum and lab activities. We had students complete pre- and post-lesson evaluations, we observed and made notes on lectures and lab activities, and we convened focus groups and one-on-one meetings with instructors and teaching assistants to solicit their feedback. Student and instructor feedback has been strongly positive but has also provided useful critique. We are using assessment outcomes to make iterative improvements to the curriculum and equipment.

FIGURE 1. HSU's hydrogen fueling station and fleet of hydrogen vehicles. The fueling station's performance will be analyzed by HSU engineering students as part of the H₂E³ curriculum.
Fuel Cell Industry Internships. Project plans originally called for student internships with a number of fuel cell manufacturer partners during the summers of 2010 and 2011. Due to the economic downturn in general and attrition in the fuel cell industry in particular, we have had difficulty in developing these internships. The only internships we were able to identify for 2010 were existing co-op arrangements, which require students to be available for six months out of the year for full-time work. This is not compatible with the academic schedules of students in the universities we have been working with. We are investigating alternatives, as discussed below.

Conclusions and Future Directions

The main outcome of year two of the project has been the successful introduction of the H₂E³ tools and curriculum into a variety of engineering courses at HSU and UCB. In year three we plan to expand the project by integrating the curriculum into still more engineering courses and reaching out to other California campuses. We have requested and been given tentative approval for an additional $15,000 in funding from DOE, which will permit us to build three additional sets of ten fuel cell/electrolyzer kits. We will distribute these sets to newly participating campuses, allowing current users of kits to keep using them at their campuses for longer periods.

In order to ensure the long-term success of H₂E³, we will follow up with faculty to determine to what extent the use of the H₂E³ materials persists among instructors who have been given access to the curriculum and equipment, and what the learning outcomes are in their courses. We will also continue to develop learning activities that incorporate analysis of operating fueling stations at HSU and elsewhere.

We hope to find or develop summer-season internships for 2011. In addition to making direct contacts with manufacturers, we plan to approach industry groups such as the U.S. Fuel Cell Council and the National Hydrogen Association to solicit their help with this. We are considering alternatives to manufacturer-funded internships, such as “distance internships,” perhaps supported by fixed stipends from a third party.
Special Recognitions & Awards/Patents Issued

1. “National Hydrogen and Fuel Cell Education Program Part I: Curriculum,” selected by Energy Conversion and Conservation Division of the American Society for Engineering Education as 2nd place winner of Best Paper Award at the 2010 ASEE Annual Conference & Exposition, Louisville, KY.

FY 2010 Publications/Presentations


6. Lab handout, blank wiring diagram, and safety guidelines for use in ENGR 115, introduction to environmental resources engineering (HSU).

7. Lab handout, blank wiring diagram, and safety guidelines for use in ENGR 331, introduction to thermodynamics (HSU).

8. PowerPoint presentation for E100, energy and society (UCB).

9. Monitoring and evaluation report on ENGR 331 (HSU) and E100 (UCB).

10. Lab handouts for use in ENGR 471, advanced thermodynamics (HSU):
   - Lab Experiment #1 – Operating the Fuel Cell Test Station
   - Lab Experiment #2 – Evaluating the Performance of a PEM Fuel Cell

11. Spanish translations of PowerPoint presentation originally developed for E100 and document on operation and maintenance of fuel cell/electrolyzer kits, for use at Universidad Don Bosco, El Salvador, by H₂E³ project team member Richard Engel.
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.

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 major accomplishments of this project to date are listed below:

- We have developed and taught one lecture and one laboratory course in hydrogen energy and two courses in fuel cells.
- Effective April 2009, students can receive an “Interdisciplinary Minor in Hydrogen Technology.” The minor includes the elective courses mentioned above and project work in the alternative fuels group enterprise.
- The elective courses are also a component of the “Graduate Certificate in Hybrid and Electric Vehicles” approved May 2010.
- Nearly three dozen modules have been developed to introduce students in core chemical engineering courses to hydrogen and fuel cell technology; similar efforts are underway for mechanical and electrical engineering courses.
- Ninety example problems have been created as supplementary material to be used in the sophomore level introductory chemical engineering course.
- Over the entire project, eight oral presentations have been given and five conference proceedings have been published, with five oral presentations and four conference proceedings during the past year.

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 MTU. 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 (Figure 1). The courses have been taught during the most recent academic year and were well received by students.

Results for Task 2.0, Develop curriculum programs in hydrogen technology:

- The “Interdisciplinary Minor in Hydrogen Technology” was approved by the university effective April 2009.
- The “Graduate Certificate in Hybrid and Electric Vehicles” was approved by the university effective May 2010.
- During the 2009-2010 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 Student Design Contest (Figure 2)
  - Combined Heat and Power from a Fuel Cell
  - Carbon Dioxide Sequestration from a Large-Scale Hydrogen Production Plant

![FIGURE 1. 1.2 kW Hydrogen Fuel Cell used in Hydrogen Measurements Laboratory Course](image-url)
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, nearly three dozen chemical engineering modules and one dozen mechanical engineering modules have been developed. 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 90 examples to supplement the textbook *Elementary Principles of Chemical Processes* authored by R. M. Felder and R. W. Rousseau and published by Wiley. 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.

**Conclusions and Future Directions**

The most significant result of this project to date is the approval of a new minor at MTU 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: Continue to teach hydrogen and fuel cell courses, while improving curriculum material.
- Future work for Task 3.0, Develop modules for core and elective engineering courses: Continue to 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 texts: Test supplementary material for Felder & Rousseau textbook; continue development of supplementary material for Geankoplis textbook (*Transport Processes and Separation Process Principles*, published by Prentice Hall, for junior chemical engineering courses).

**Special Recognitions & Awards/Patents Issued**

1. Jason Keith was named by MTU as the 2010 recipient of the Frederick D. Williams Instructional Innovation Award in recognition of using active learning in his courses and in leadership in the development of modules for hydrogen and fuel cell education.

**FY 2010 Publications/Presentations**

X.6 Bachelor of Science Engineering Technology Hydrogen and Fuel Cell Program Concentration

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DOE Project Officer: Gregory Kleen
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Contract Number: DE-FG36-08GO18109
Subcontractor:
University of North Carolina at Charlotte, Charlotte, NC

Project Start Date: August 1, 2008
Project End Date: March 30, 2011

Objectives

- Develop and implement an accredited baccalaureate level hydrogen and fuel cell technologies (HFCT) university program.
- Prepare students to work as hydrogen and fuel cell technology professionals in government, industry, and academia.
- Prepare program graduates to demonstrate an appropriate mastery of the knowledge, techniques, skills and modern tools related to hydrogen and fuel cell technologies.
- Prepare program graduates to demonstrate an ability to apply current knowledge and adapt to emerging applications of hydrogen and fuel cell technologies.
- Disseminate program information and activities to community colleges, high schools, industrial partners, governmental agencies and universities.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of Readily Available, Objective, and Technically Accurate Information
(B) Mixed Messages

Contribution to Achievement of DOE Education Milestones

- Milestone 21 – Launch new university hydrogen education program. (4Q, 2009)

Accomplishments

- Hydrogen and fuel cell courses have been developed and offered at University of Central Florida (UCF) and at University of North Carolina at Charlotte (UNCC).
- During 2009, program course development and offering was transferred to the UNCC because of academic program reductions at UCF. Administration of program remains at UCF.
- Courses that have been developed and offered are:
  - ETM 4220 Applied Energy Systems – offered in Spring 2009 at UCF.
  - ETGR 3000-002 and MEGR 3090-020 Combined Hydrogen and Production Storage – offered in Summer 2010 at UNCC.
  - Three laboratory experiments (Hydrogen Fuel Cells, Hydrogen as an Energy Carrier and Methanol Fuel Cells) were developed and offered as part of the Combined Hydrogen Production and Storage course.
  - Thermodynamics, Energy Management and Fluid Dynamics Lab courses have been offered at UNCC to complement the HFCT courses.
- Students from all engineering majors and from engineering technology can register for the above courses.
Introduction

The objective of the HFCT program is to develop and implement a baccalaureate level educational program that will supply the need for educating students that will comprise the next generation workforce needed for HFCT research, development, and demonstration activities within government, industry, and academia. The project includes the development and delivery of undergraduate courses at the Engineering Technology Department within an accredited Bachelor of Science in Engineering Technology (BSET). Courses will be offered at UNCC and the laboratory facilities that are developed will be located at UNCC.

Current public knowledge and awareness levels of hydrogen and fuel cells need improvements and have prevalent misunderstandings of hydrogen properties giving negative opinions about the safe use of hydrogen as an energy carrier. The Fuel Cell 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, university faculty, 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 is to develop, offer, and sustain a BSET or BSE program that contains courses for an HFCT concentration. The course offerings were started in Spring 2009 and have continued through the present time. The original courses were offered at UCF and the courses and laboratories are now being offered at UNCC. Efforts to promote the program include advertisement, recruiting students and outreach plans, visits to community colleges and other institutions, publications and presentations in professional meetings.

Future efforts will include the evaluation of the HFCT program offerings using 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 technologies? Is faculty using project-developed content to replace some of their standard lessons?

Results

This project is comprised of completing three major tasks – developing courses, offering the developed courses, and promoting the program through advertisement, recruiting students and outreach plans. The results for these tasks follow.

Developing Courses

The courses that have been developed are:

- Hydrogen Production and Handling 3 Credit Hours
- System Analysis of Renewable Energy Systems 3 Credit Hours
- Analysis of Renewable Energy Systems 3 Credit Hours
- Combined Hydrogen Production and Storage 3 Credit Hours
- Fuel Cell Technologies I 3 Credit Hours

Other course development activities that will be offered in the Fall 2010 semester are:

- Hydrogen Laboratory Schedule
  - Introduction and Hydrogen Laboratory Safety
  - Gas Cylinder and Safety Handling
  - Instrumentation I
  - Instrumentation II
  - Material Balance
  - Characterization of Chemical Hydride Materials
  - Hydrogen Liquefaction Experiments
  - Student Project

- Fuel Cell Laboratory Schedule
  - Introduction and Laboratory Safety
  - Fuel Cell Chemistry and Efficiency
  - Electrochemistry
  - Fuel Cell Components and Assembly
  - Operating Conditions I
  - Operating Conditions II
  - Fuel Cell Diagnostics
  - Student Project

Work has also begun on development of two one credit hour courses called hydrogen lab and fuel cell lab. These will be offered at a time to be determined in the future. The course outlines for the two labs are:

- Hydrogen Laboratory Schedule
  - Introduction and Hydrogen Laboratory Safety
  - Gas Cylinder and Safety Handling
  - Instrumentation I
  - Instrumentation II
  - Material Balance
  - Characterization of Chemical Hydride Materials
  - Hydrogen Liquefaction Experiments
  - Student Project

- Fuel Cell Laboratory Schedule
  - Introduction and Laboratory Safety
  - Fuel Cell Chemistry and Efficiency
  - Electrochemistry
  - Fuel Cell Components and Assembly
  - Operating Conditions I
  - Operating Conditions II
  - Fuel Cell Diagnostics
  - Student Project

In addition, development has begun on a new senior design course.
Offering the Developed Courses

The course ETM 4220 Applied Energy Systems was offered in Spring 2009 at UCF. The course was taught by Dr. Sleiti as part of the HFCT program. Thirty-seven students took the course.

The course ETGR 3000-Analysis of Renewable Energy Systems was offered to UNCC students in the Spring Semester 2010. This course was taught by Dr. Sleiti. The course included lectures, field visits to energy related sites and power plants and a semester-long student project. Examples of the student projects are: Fuel Cell Applications in Transportation, Applying Geothermal to Recreation Facility, Solar Panels for UNCC Charlotte, and Wind Generation Plant Feasibility Study. The course was offered to all students in the College of Engineering with 22 students originally registered for the class – 20 are seniors and two are juniors. Two students withdrew from the course and 20 students successfully completed the course.

The syllabus and course analysis forms for Analysis of Renewable Energy Systems course are available, but not presented here. The syllabus includes the course title, name of the instructor, textbook used for the class, prerequisites and co-requisites, goals/objectives, course outcomes, term project description, course grading policy, course website, course policies, and a 16-week schedule of topics that are covered. The Course Analysis Form includes course assessment, program outcome assessment, recommendations and overall course observations and comments and student grades.

The course ETGR3000-002 and MEGR3090-020 — Combined Hydrogen Production and Storage was offered in the Summer Semester of 2010 to both Engineering Technology Students and Mechanical Engineering students. Five students completed the course. The syllabus and course analysis forms for the course are available. The experimental labs that were taken by the students as part of the courses are:

- Experiment 1 – Hydrogen Fuel Cells
- Experiment 2 – Hydrogen as an Energy Carrier
- Experiment 3 – Methanol Fuel Cells

Each experiment was designed to be completed within 2.5 hours and the students are required to submit a report including description, procedure, results, discussion and conclusion.

Other existing courses in the engineering technology program that complement the HFCT courses and that are being offered at UNCC are Thermodynamics, Energy Management and Fluid Dynamics Lab. Outlines for those three courses are available. Note is made that these courses are taught jointly by several instructors and they have more than one section. These courses and instructors are as follows:

<table>
<thead>
<tr>
<th>Course</th>
<th>Section</th>
<th>Instructor</th>
<th>Semester</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETME 3143-002 Thermodynamics</td>
<td>002</td>
<td>Patty Tolly</td>
<td>SP 2010</td>
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<td>ETGR 4245: Energy Management</td>
<td>001</td>
<td>Nan Byars</td>
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<td>ETGR 4245: Energy Management</td>
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<td>Dan Hoch</td>
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<tr>
<td>ETME3151: Fluid Mechanics Lab L01</td>
<td>A. Sleiti</td>
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<td>ETME3151: Fluid Mechanics Lab L02</td>
<td>R. Priebe</td>
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<td>ETME3151: Fluid Mechanics Lab L03</td>
<td>T. Jarrell</td>
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<td>ETME3151: Fluid Mechanics Lab L04</td>
<td>Dan Hoch</td>
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</table>

These courses will be repeated during subsequent semesters and will be available to students from all engineering and engineering technology majors.

Promoting the Program through Advertisement, Recruiting Students and Outreach Plans

During the past year, the following activities have been completed:

A. Visits to community colleges:

The team has been following up with and scheduling meetings with community colleges that currently have technology programs with potential to transfer students from those community colleges with associate of science degrees to the HFCT program. Visits to Central Piedmont Community College and participation in the Wake Tech Spring Fling have been done.

B. Visits to local industry:

The team established collaboration with Savannah River National Laboratory (SRNL) during a SRNL visit to UNCC on February 18, 2010 and have had collaborations with the following companies/organizations:

- North Carolina Hydrogen Economy and Advancement Team
- North Carolina Fuel Cell Alliance
- The Advanced Vehicle Research Center of North Carolina
- Duke Energy
- AREVA
- Electric Power Research Institute
- Shaw Group
- Siemens

C. Contacting Universities:

The team is continuing to contact universities around the country through e-mails to make the academic community aware of the HFCT program.
D. Other Activities:
The UNCC team is participating in high school competition and coordinating program information sessions each semester.

Project Management and Reporting

The major activity in the project management area was the termination, because of financial problems, of the Bachelor of Engineering Technology program at UCF and the changing of employment of the project Co-PI, Dr. Ahmad Sleiti, to the BET program at University of North Carolina at Charlotte. Following this change, the decision was made for UCF to retain project management and to subcontract project implementation to UNCC. A subcontract was issued to UNCC to be the provider for the HFCT courses beginning on January 4, 2010 and ending on March 30, 2011.

Conclusions and Future Directions

At the present time, course development and offering are 65% complete, and promotion is 80% complete. The overall project is estimated at 75% complete and there are no problems or issues that will delay completion.

The plans for finishing the program activities are:

- Continue offering the developed courses at UNCC for the HFCT concentration.
- Continue evaluation of courses offered.
- Continue development of HFCT courses and labs.
- Continue working on promoting the program and recruiting students.
- Attend seminars and meetings to disseminate program results.

FY 2010 Publications/Presentations


Special Recognitions & Awards/Patents Issued

It is noted that paper #1 was recognized by the American Society for Engineering Education Energy Conversion and Conservation Division as recipients of “Best Paper Award”.
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 a “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.

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 Fuel Cell 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

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 21: Launch new university hydrogen education program. (4Q, 2009)

Accomplishments

- Case studies targeting 1) freshman introductory engineering courses, 2) chemical engineering mass and energy balances, and 3) chemical engineering thermodynamics have been implemented into the undergraduate curriculum.

- The course content in EE 522-Renewable Energy Systems was modified to increase the content related to fuel cells and electrolysis. A new course, Hydrogen Production and Storage was developed and taught. Approximately 60 students per semester enroll in these two courses.

Two undergraduate students have been placed for internships as the Energy & Environmental Research Center’s (EERC’s) National Center for Hydrogen Technology. One intern from last year is now employed there. Two interns have been placed at Oak Ridge National Laboratory.
Three new experimental setups were designed and implemented into chemical and electrical engineering undergraduate laboratories.

Two senior design projects were completed focused on various aspects of hydrogen production.

The student organization, PowerOn developed experiments that will be incorporated into a mobile laboratory that are being presented to middle schools as a part of a program to stimulate interest in science, technology, engineering, and mathematics 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 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 though the National Center for Case Studies in 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 though 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 (formerly the Accreditation Board for Engineering and Technology) 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 UND 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

The first in a series of case studies developed for this program were implemented in the freshman Introduction to Chemical Engineering course this spring. The intent is to introduce students to the basics of a fuel cell and its importance and relative place in helping the U.S. meet its future energy needs. This case study will also be used to demonstrate the interactions between electrochemistry and chemical, electrical, and mechanical engineering required to fully develop and deploy fuel cell technology. Other case studies developed for courses such as Chemical Engineering Fundamentals, and Thermodynamics will focus on technical aspects of hydrogen production and use.

A course entitled Hydrogen Production and Storage was developed was taught during the fall semester. The course was being recorded and can be uploaded at a later date in the UND or DOE Web site.

Two new series of laboratory experiments have been developed and implemented into the undergraduate
curriculum using new experimental setups purchased from Heliocentris though the support of the DOE. The HP 600 includes a 600 watt water-cooled PEM fuel cell stack, a direct current (DC)/DC and DC/alternating current (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 Masters student developed the set of laboratories that are being implemented into the undergraduate curriculum during the 2009-2010 academic year.

In addition to performing the basic experiments to generate current-voltage (IV) and power curves, an experiment was added to record individual cell responses to increases in load current. Ambient temperature (approximately 26°C versus stack temperature of approximately 40 degrees) impacts the performance of the outer cells, and therefore, the overall performance of the stack. However, it is assumed that the effect is minimal. Examining the performance of individual cells can help explain the overall behavior of the stack and is a good introduction for student investigation into the more complex reactions occurring in each cell (see Figure 1).

A second set of experiments was developed to demonstrate the effectiveness of the fuel cell as a power source under varying load conditions. Students begin by generating the typical IV curve and power curve to develop an understanding of efficiency as a function of load. Dynamic load tests show the students the lag time between a change in load and the response of the fuel cell. For electrical engineering labs, this can be further utilized to develop equivalent circuits and to study the time constants related to a dynamic system. Typical results are shown in Figure 2.

ABET requires institutions of higher education to demonstrate that their students achieve a number of program outcomes. Several of these outcomes and objectives address the need for engineers who can apply knowledge from the classroom to real-world problems. The use of hands-on experiments designed to encourage student exploration is one of the ways UND prepares students to be successful engineers. Hands-on experiential learning allows students to supplement their classroom background with actual results and to improve critical thinking skills by developing and solving research problems of their own design. Details of these student laboratories were presented at the 2010 summer meeting of the American Society of Engineering Education.

Two senior design projects were completed. One senior design group from chemical engineering chose to design a process that utilizes a waste gas stream from a biomass to fuel processing plant to produce hydrogen. The waste stream contained small amounts of hydrogen, methane, ethane, propane, with a larger amount of CO and the balance of nitrogen and CO₂. Using a steam reforming and high and low shift reactors followed by a Benfield separation plant, the group demonstrated that the process is technically and economically feasible. The group showed that this utilizing this waste stream as a source of hydrogen was technically feasible, and economically feasible (depending upon the assumptions made for the price of hydrogen). A senior design project in Electrical Engineering involved developing a lab-scale electrolyzer system that can be used as a teaching tool, or in applications requiring small hydrogen flows.

**Conclusions and Future Directions**

To date this project has impacted approximately 120 students, primarily through the classroom and 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 10 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. 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.

**Special Recognitions & Awards**


**FY 2010 Publications/Presentations**


Objectives

Through both segments of the project: 1) education and 2) deployment, the objective has been focused on increasing hydrogen awareness through:

- Continued education of an ever-broadening group of stakeholders to the benefits of fuel cell and hydrogen technologies in material handling applications to include: facility management, operators, maintenance personnel, safety groups, first responders, authorities having jurisdiction, technical/community colleges.

- Demonstration of fuel cell and hydrogen technology through the continuing demonstration schedule of two hydrogen fuel cell-powered lift trucks in real-world applications at large prominent companies.

- Demonstration of these fuel cell-powered trucks at high profile public events.

- Assisting in the further commercialization of fuel cell and hydrogen technology by establishing a series of cost value propositions to interested companies.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.95) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Mixed Messages

- Product Performance
- Limited Model Availability
- Infrastructure/Cost Justification

Contribution to Achievement of DOE Technology Validation Education Milestones

This project has and will continue to contribute to achievement of the following DOE milestones from the Education section of the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan:

- **Milestone 1:** Developed “Awareness- Level” information for first responders (4Q, 2009). Accomplished by LiftOne’s on-site presentation to the Kannapolis, NC, Fire Department of the Hydrogen 101 seminar, with specific emphasis on hydrogen properties, safety items and general hydrogen awareness geared toward fuel cell applications for material handling applications. Included was a live demonstration of the fuel cell-powered lift truck (10/09). More are planned for September and October - 2010.

- **Milestone 14:** Hold community seminars to introduce local segments of the community to hydrogen (3Q, 2009, 4Q 2009, 1Q 2010). Accomplished through participation and “live” demonstrations at regional business events such as the “Green Is Good For Business Expo” (Columbia, SC - 9/2009); North Carolina Trucking Association Maintenance Council Chapter Meetings (Charlotte -10/09 and Asheville -1/10); BMW’s H2 Expo (Greer, SC 11/2009) (see Figure 1); “Upstate Green Business Summit”, (Spartanburg, SC - 4/10).

- **Milestone 18:** Develop end-user workshop materials for use at events. (3Q, 2009 through 4Q 2010). The LiftOne hydrogen fuel cell-powered lift trucks continue to be shown in conjunction with both the projects’ deployments and at the Hydrogen 101 Sessions conducted with end-users at the LiftOne branch locations in NC, SC and VA. Moreover, the education sessions were updated to include real-world performance data from the deployments and the evolving cost models for group discussions.
**Milestone 19**: Develop short courses for end-users at technical colleges (3Q, 2010 through 2Q, 2011). The LiftOne Hydrogen 101 Seminar has been condensed for presentations at local technical and community colleges, and includes the live demonstration of the fuel cell power pack. Two additional sessions are planned for the upcoming year.

**Milestone 29**: Evaluate knowledge and opinion of hydrogen technology of key target audiences and progress toward meeting objectives. (4Q, 2009 through 4Q, 2010). Each Hydrogen education session includes an introduction segment where the hydrogen awareness level of each attendee is assessed. Again, these sessions have primarily included attendees that manage material handling fleets at large companies.

**Accomplishments**

- Within the past 12 months, LiftOne has successfully executed and concluded five deployments of two CAT® electric sit-down rider lift trucks powered by the Hydrogenics Fuel Cell Power Packs. The data from these deployments were compiled and sent to the National Renewable Energy Laboratory for analysis.
- The final of the project’s six deployments commenced in early July and will continue through mid-August. Through these deployments, end-users are introduced to the benefits of fuel cell power with the hands-on experience of operation and refueling.
- LiftOne’s participation at one of the five sites (in conjunction with two other providers), led to an agreement for the eventual acquisition of over 100 fuel cells for a large corporation. The collective effort was a major triumph for the fuel cell industry.
- LiftOne’s continued participation at several regional city “Green Business” expos and forums, with live demonstrations of the working fuel cell-powered lift trucks, has provided a large cross-section of businesses with the opportunity to witness this alternative and clean source of fuel cell power. As a result, the general awareness level of hydrogen has been increased in regional areas including Charlotte, North Carolina, and the cities of Greenville, Columbia and Spartanburg in South Carolina.

**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 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 proton exchange membrane (PEM) fuel cells in 2007, and was able to gain early field trial experience, while recognizing the acute need for overall hydrogen education.

To assist in facilitating the integration of hydrogen fuel cells into real-world material handling application, LiftOne developed a Hydrogen education and awareness presentation for lift truck users. These sessions have been conducted at each of the LiftOne branches on a rotational basis. Additional sessions have been tailored for presentations at selected technical colleges, professional organization meetings, industrial shows and to large companies in a Web format. These Hydrogen awareness classes began in early 2009, and will continue through August of 2011. The Deployment Segment of the LiftOne project, where the two fuel cell-powered lift trucks are put into real-world applications at six strategically selected major companies’ facilities for one-month long trials, provide an excellent method for demonstrating the viability of fuel cell power. The deployments began in May of 2009 and will conclude in August of 2010.

**Approach**

Recognizing the need to help increase hydrogen awareness among material handling users, LiftOne’s approach for Hydrogen education has been focused on the identification of key target audiences. This strategy has been employed for both the education and deployment segments. For the education segment, the seminar content has been designed for the layman’s introduction to hydrogen and included in the 4-5 hour-long sessions are a thorough review of hydrogen uses, its properties, infrastructure review as well as

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**FIGURE 1.** LiftOne’s Display Booth at the BMW H2 Expo, Greer, SC, November, 2009
acquisition cost models and a live demonstration. The target audience for the education segment includes representatives from companies operating medium to large electric material handling fleets, with a secondary audience being those operating fossil fuel-powered fleets. Smaller fleet operators also have participated.

For the LiftOne deployment segment, high profile companies with sizable fleets and multiple locations were selected for the trial sites, in order to gain the best opportunities with potential for effective regional exposure. For each site, presentations and proposals for the trials were made, detailing the equipment, fueler location/regulations, on-site monitoring arrangements and data gathering. At the conclusion of each deployment, comprehensive review meetings are held, in which all performance data presented, feedback from operators reviewed, and a cost justification evaluations presented with full proposals for fuel cell and infrastructure acquisition for more involved “pilot” type programs.

Results

Over the past year, LiftOne has seen positive results in both the education and deployment segments associated with the project. Close to 20 hydrogen education sessions have been conducted at the LiftOne branches, at customer locations, at community colleges and at the regional “Green” type business expos attended. At each session or event, LiftOne has included a live demonstration of the working fuel cell-powered lift truck, an essential element necessary to satisfy the interest present and maximize awareness. A positive development has been LiftOne’s tailoring of the hydrogen education session content to cater to the specific participating groups. In some cases, the session length has been shortened to encourage optimum participation. LiftOne also conducted a special session on hydrogen safety at the Kannapolis, NC, Fire Department that was transmitted simultaneously to multiple fire stations, and resulted from the fire department’s participation at the Deployment #1 Orientation.

For the deployment segment of the project there have generally been medium to excellent results. The deployments were conducted at: 1) Stanley Tools, 2) ABC Company (name withheld by request), 3) Bausch & Lomb, 4) BMW, 5) Electrolux and 6) AGI - In Store (underway presently). There were good results at all sites with regard to run time, truck performance, power, and ease of refueling. At site # 2, there was some component failure on the fuel cell power packs that were corrected with parts replacements. There was never any danger as the system detectors in the packs worked to detect and shut down, while the input gathered allowed the manufacturer to make corrections. All sites were able to experience fuel cell power, with well over 200 employees at each site made aware of the hydrogen power. Site # 4 had particularly good results, and the trial among three fuel cell companies resulted in a large-scale fuel cell adoption by that company (see Table 1). LiftOne was able to self-grade each of the five completed deployments (Table 2).

<table>
<thead>
<tr>
<th>TABLE 1. Site # 4 - LiftOne Fuel Cell Deployment Summary</th>
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<tbody>
<tr>
<td><strong>LiftOne’s Site # 4 - 23 days operated</strong></td>
</tr>
<tr>
<td>* Lift Truck / Cell #1 ran 165 hrs</td>
</tr>
<tr>
<td>* Lift Truck / Cell #2 ran 190 hrs</td>
</tr>
<tr>
<td>* 71 kg of H₂ used / 62 fuelings</td>
</tr>
<tr>
<td>* 2.6 minutes average fuel time</td>
</tr>
<tr>
<td>* 8.0 hrs avg run time per tank (1.6 kg)</td>
</tr>
<tr>
<td>Notes: Best deployment of all five</td>
</tr>
<tr>
<td>Straight forks - sideshifter application</td>
</tr>
<tr>
<td>Trucks ran great. Fantastic run time.</td>
</tr>
<tr>
<td>Trial went well…moving forward.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE 2. Self Grading each of the Five Completed LiftOne Fuel Cell Deployments</th>
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</thead>
<tbody>
<tr>
<td><strong>Fuel Cell Deployments</strong></td>
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<tr>
<td><strong>Self Grades - Sites 1 - 5</strong></td>
</tr>
<tr>
<td>Site #</td>
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</tr>
<tr>
<td>1</td>
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Conclusions and Future Directions

For the second year of the LiftOne hydrogen education project, the following conclusions have been determined:

- The intrigue concerning fuel cells was addressed, as a wide variety of users were able to learn and see the hydrogen fuel cells powering lift trucks in real-world applications.
- The fuel cell power option is a viable method of accomplishing the work in most lift truck applications – however not all applications are ideal, for a variety of reasons.
The cost justification is not there for every facility; larger fleets are still a requirement.

Infrastructure cost remains a major concern for companies considering eventual fuel cell adoption.

Future plans for year three of the project involve:

- The hydrogen education sessions will continue at the LiftOne branches, at company sites and in some cases in Web-based formats for larger companies with multiple locations.
- Continued participation at material handling events, seminars and area business expos.
- Continued follow up with completed deployment sites to encourage fuel cell acquisition.

**FY 2010 Publications/Presentations**

X.9 Hydrogen Education in Texas

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


Accomplishments

- Developed Texas e-mail hydrogen/fuel cell contact list to reach target audiences.
- Initiated discussions with regional contacts, including Clean Cities’ coordinators, to assist and participate in organizing and conducting metro area workshops.
- Conducted outreach and education activities including four Texas Hydrogen 101 education workshops in four target metro areas; eight outreach events featuring Hydrogen 101 education material and displays in the Dallas/Ft. Worth, Austin, San Antonio, and Houston metro areas and three briefings in Austin and Houston.
- Organized display and demonstration of hydrogen fuel cell transit bus at three outreach events; two in Austin and one in the Dallas/Ft. Worth area.
- Presented project at the DOE 2009 and 2010 Annual Merit Review events.
- Completed and deployed Web site design.
- Assembled basic educational materials, including information on Texas and hydrogen.
- Compiled baseline awareness information of workshop participants.
- Co-sponsored student participation in hydrogen fuel cell vehicle competition: University of Houston School of Technology; Shell Eco-Marathon.
- Organized tour of Houston food warehouse with new fuel cell fork trucks.

Introduction

Between 2000 and 2004, Texas demonstrated considerable interest and activity related to hydrogen and fuel cell technology. During that time, the HARC organized a fuel cell consortium and created a fuel cell testing lab. Interest and activities have declined in the State 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 adoption, 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 cell efforts by Texas 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 decision makers 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 identified for this project included 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 have been 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, (2) scheduling and implementing hydrogen education workshops, and (3) conducting outreach events in target metro areas. Based on discussions with other state hydrogen education programs, it was important to coordinate workshops with key organizations in the Texas metropolitan areas to best reach 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, and participation at related conferences and workshops.

Educational materials developed by DOE and other organizations were reviewed by project staff to determine how they could be utilized. One-page flyers on each topical areas have been provided to participants, and incorporated in the project’s Web site. A limited number of links to key educational materials and sites was included in the Web site design 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 were incorporated in presentation materials. In addition, HARC identified recent hydrogen fuel cell applications in Texas, including a fuel cell bus and fueling station at the University of Texas at Austin, over 130 new fuel cell fork trucks, and deployment of fuel cells for cell phone tower back-up power. These have been used in the project as real world examples for outreach and education. This included having the fuel cell bus at two workshops and speakers on the fuel cell fork truck deployments.

As an example of coordinative activities, HARC identified a joint opportunity with the National Renewable Energy Laboratory’s (NREL’s) hydrogen code training workshop in San Antonio. HARC worked with NREL staff and contractors to establish a date and meeting place for these two events. This enabled local government staff to 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. The
The San Antonio 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 will serve as a real world example for further outreach and education.

Following discussions with various organizations, workshop dates and venues were identified for the Houston, Austin, San Antonio, and Dallas/Ft. Worth areas. The Houston event occurred as part of two related events that reached the target audience, a conference on air quality and another on energy. In all target cities, HARC has worked 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 have been posed as part ofbriefings and outreach to roughly assess the current level of knowledge of the target audience. Topic areas from the DOE’s hydrogen education surveys have been used for this purpose to help establish a baseline. Follow-up assessments will be used with workshop participants to gauge progress. This has not been intended as 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 website.

Finally, various incentives were used to help ensure active participation in Texas workshops and briefings. For example solar flashlights, fuel cell kits and a fuel cell remote control car were used as part of workshops and conference displays, and awarded to participants.

**Summary and Future Directions**

- The final Hydrogen 101 workshop will be held in the Austin area to follow up on contacts with key state and local leaders.
- Project staff will help inform target audiences in Texas of the Fuel Cell Seminar to be held in San Antonio, October 18-21, 2010.
- Additional opportunities for briefings to target audience will be identified.
- Target audience contacts will continue to be expanded.
- Follow-up assessments will be distributed to participants and the target email list.
- The major conclusions to date are: (1) the key role that Clean Cities programs can play as a conduit to target audiences, and (2) the importance of having real-world applications, such as fuel cell buses, fuel cell fork trucks, and associated hydrogen fueling, for gaining interest.

**FY 2010 Publications/Presentations**


**Hydrogen 101 Workshop Presentations**

3. There is a Hydrogen Fuel Cell Bus Operating in Texas, R. Thompson, University of Texas Center for Electromechanics, Austin Workshop presentation, February 24, 2010.
X.10 Development of Hydrogen Education Programs for Government Officials

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Contract Number: DE-FG36-08GO18113
Subcontractor: 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 Fuel Cell 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 Fuel Cell 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 29: Evaluate knowledge and opinion of hydrogen technology of key target audiences and progress toward meeting objectives. (4Q, 2009)

Accomplishments

- Conducted in-person presentations to over 20 groups of targeted South Carolina decision makers.
- Held eight Webinars to provide information to stakeholders throughout South Carolina.
- Reached 1,446 targeted additional state and local government officials and decision makers.
- Created a SlideShare channel through which webinar presentations can be viewed.
- Placed hydrogen education videos on the SCHFCA YouTube channel.
- Developed over 20 topic specific slides that included value proposition for telecommunications, permitting of fuel cells, etc.
- Produced a tri-fold handout that summarizes key messages with a fun quiz.
- Maintain a Web site that keeps a running log of industry news and allows access to fact sheets at www.schydrogen.org.
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. The Hydrogen 101 program led by the SCHFCA seeks to raise awareness about hydrogen and fuel cells to community leaders within South Carolina and the Southeast.

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. The state has been recognized as one of the top five fuel cell states by Fuel Cells 2000 in 2010 but a lack of information regarding the hydrogen and fuel cell industry still exists among state and local leaders. 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.

During the legislative process to pass the South Carolina Hydrogen and Fuel Cell Permitting Act into law, a need for additional educational efforts within the South Carolina legislature was identified. We learned that there was very little opposition to hydrogen and fuel cells in state government but quite a bit of ambivalence. The ambivalence grew from a lack of exposure and understanding to the potential for a hydrogen and fuel cell industry in South Carolina.

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 local 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 program 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 were conducted.

Results

A major achievement of the SCHFCA was the creation of a support base among community leaders to champion hydrogen related initiatives at the state level. The support base was built through the DOE Hydrogen 101 program by delivering presentations and webinars to groups of leaders throughout the state. A good example of the progress achieve through the Hydrogen 101 program was the passage of the South Carolina Hydrogen and Fuel Cell Permitting Act that had support from project partners such as the South Carolina Municipal Association, the State Fire Marshal’s Office, local stakeholders and SCHFCA members.

After focusing mostly on maximizing the messaging to state leaders from the National Hydrogen Association meeting in Columbia in 2009, the Hydrogen 101 program in 2010 expanded its audience to include state and local government officials from a wide variety of groups impacting the adoption of hydrogen and fuel cells. The program performed outreach to these groups through group presentations, Webinars, and focused small group and individual meetings. Presentation materials and fact sheets were updated and expanded depending on the audience and tri-fold brochures were printed to summarize key messages.

The SCHFCA Hydrogen 101 program far exceeded the original goal of three Webinars and eight in-person presentations with eight Webinars and over 20 presentations. The direct number of targeted, high-quality stakeholders reached was 1,446 and the wider educational efforts that leveraged Hydrogen 101 materials reached over 1 million people. In addition to
education of leadership groups, the SCHFCA has started reaching out to candidates for political offices who will be filling vacated offices in 2010. This includes talking with candidates to replace the current term-limited governor and candidates running for three Congressional seats without an incumbent.

Groups have been overwhelmingly supportive of hydrogen and fuel cell technologies as a result of the presentations and view the technologies as having the potential to foster economic development within the state. There was significant interest in the value proposition for the fuel cell technologies and additional information regarding the economics of these technologies was of interest to the audiences.

Conclusions and Future Directions

The SCHFCA Hydrogen 101 program has met all of the yearly goals and our efforts are having an impact in creating wider support for hydrogen. A concrete goal that was assisted by Hydrogen 101 was the passage of the South Carolina Hydrogen and Fuel Cell Permitting Act. In 2011, our efforts will focus on:

- Finalizing the market value proposition case studies for cell tower backup power, material handling equipment and combined heat and power units.
- Using the case studies as an educational tool with government leaders and business decision-makers within industries that can utilize fuel cells (i.e. forklifts).
- Work with the South Carolina Department of Health and Environmental Control to investigate the streamlining of air permits for hydrogen and fuel cell technologies.
X.11 VA-MD-DC Hydrogen Education for Decision Makers

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Contract Number: DE-FG36-08GO18115

Subcontractors:
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  Los Alamos National Laboratory, Los Alamos, NM
- Greg Jackson and Peter B. Sunderland
  University of Maryland, College Park, MD

Project Start Date: September 1, 2008
Project End Date: September 30, 2011

Objectives
The goal of the three-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 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 Fuel Cell 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 in Measuring Success

Contribution to Achievement of DOE Education Milestones
This project will contribute to achievement of the following DOE milestones from the Education Technical Plan (3.9) section of the Fuel Cell 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 July 2009 – June 2010 by Virginia Clean Cities and project partners:

- Developed key partnerships with over 30 different public and private organizations in Virginia/Washington D.C./Maryland to promote the Hydrogen Program and message.
- Conducted two “Hydrogen 101” seminars in Virginia and Washington D.C.
- Finished shooting for and wrapping up production of second year MotorWeek video.
- Completed four of four articles.
- Developed and updated Web site and social media tools (Facebook, YouTube, Twitter).
- Produced two versions of seminar curriculum.
- Held ride-n-drives of Equinox fuel cell electric vehicle and coordinated tour at Shell Hydrogen station in Washington D.C. for local decision makers.
- Published quarterly newsletters.
- Implemented surveys at each workshop.
- Developed draft for 3-part, 5-hour Web-based curriculum to be live Webcast and recorded for archiving.
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.

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 and Web-cast seminars for our target market, state and local governments. Messaging ties to the hydrogen knowledge survey, on which the subprogram objectives and targets are based. Under DOE guidance, existing Hydrogen Education subprogram 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. Demonstrations and tours such as of the Shell Hydrogen station in the District of Columbia have been well received.

Results

The major achievements over the last year include designing curriculum for and hosting two successful, and highly received seminars to date, completing a shooting schedule and beginning production of a second seven-minute video for seminar use and broadcasting on the Public Broadcasting Service (PBS), developing Webinar curriculum and identifying ways to provide continuing education credit, and developing a university student senior thesis deployment project. Additionally, individuals were interviewed to gather information for four electronic technology demonstration articles, which are now completed and available online for download.

Seminar Results

The curriculum prepared and presented by Dr. Catherine E. Grégoire Padró of Los Alamos National Laboratory at the November 13, 2009 and December 3, 2009 seminars covered the following content:

- Our current energy system
- What is hydrogen and what is a fuel cell?
- Why hydrogen?
- Hydrogen production, storage, distribution, and use
- Environmental, energy and economic implications
- Safety
- The future of hydrogen and fuel cells

At both seminars, 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 [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.

MotorWeek “Hydrogen Update” Video

Virginia Clean Cities worked with MotorWeek to shoot footage for the second year video. In addition to footage of many of the manufacturer-prepared vehicles, and early market applications at the 2010 National Hydrogen Association conference, footage also included interviews with leaders of hydrogen and fuel cell focused organizations. The video will likely run around seven minutes, and cover the theme of hydrogen as part of a portfolio of options and discuss early market opportunities.

The video will be completed by September 2010 and is scheduled to air on MotorWeek in the fall of 2010. MotorWeek is available on PBS and the SPEED channel. The first year video is available for viewing on the Virginia Clean Cities YouTube Channel at http://www.youtube.com/virginiacleancities.
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 and increasing attendance through creative dissemination means.

Future Project Outputs

Over the next year, Virginia Clean Cities and partners will:

• Host up to five in-person seminars and Webinars and work with National Education Energy Development to co-host teacher training seminars.
• Complete more “technology profiles”/articles.
• Finish production of a second MotorWeek video.
• Conduct follow-up surveys of participants from past seminars.
• Record and archive several of the seminars to be linked from the Website.
• Continue to update Twitter, Facebook and YouTube.
• Attend events to discuss and promote project and project outputs.

Planning and Improvements

After surveying several targeted individuals, it was confirmed that travel restrictions and time constraints have affected our ability to attract participants at in-person workshops. It is our hope that the Webinars will address this issue. A preliminary outline has been developed and is undergoing review by several experts. Scheduling is being worked on to accommodate main instructors’ schedules.

Virginia Clean Cities worked to facilitate the development of a student thesis project at James Madison University. Seniors will begin designing and building a hydrogen fuel cell motorcycle beginning fall semester of 2010. Additionally, the students will develop an education and outreach program to compliment their thesis project.

Key Issues

The main issue relates to extra demands falling on current project participants as well as target audiences over the last year.

FY 2010 Publications/Presentations


References

X.12  State and Local Partnership Building

<table>
<thead>
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<th>Joel Rinebold (Primary Contact), Paul Aresta</th>
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</thead>
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<td>Project Start Date: September 1, 2008</td>
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<tr>
<td>Project End Date: August 30, 2010</td>
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**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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Lack of Readily Available, Objective, and Technically Accurate Information
- Mixed Messages
- Disconnect Between Hydrogen Information and Dissemination Networks
- Lack of Educated Trainers and Training Opportunities
- Difficulty of Measuring Success

This project will contribute to achievement of the following DOE milestones from the Education section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- 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 identify criteria for the deployment of technologies for transportation and stationary 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.
- Presented at nine regional planning agencies/regional councils of government.
- Exhibited at the Connecticut Conference of Municipalities Conference.
- Presented on a Bi-Monthly State and Regional Initiatives Call.
- Developed and held a workshop for municipalities.
- Developed and held a legislative briefing/forum.
- Provided information to municipal decision makers including hydrogen and fuel cell benefits and project analysis.
- Monitored state energy studies/plans for accurate information regarding hydrogen and fuel cells.
- Developing a plan with the Connecticut Department of Transportation for hydrogen fueling infrastructure and vehicles.
- Identified financial and investment opportunities for local, state and federal stakeholders.
Planned a regional briefing for outreach and establishment of dialogue between New England hydrogen and fuel cell stakeholders and decision makers.

- CCAT developed two hydrogen and fuel cell educational videos available online for dissemination.

Introduction

This project assists with the building of partnerships between the DOE, states and municipalities. CCAT is implementing this 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 has been 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 also coordinates 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

- CCAT has developed 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 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 completed a preliminary assessment of 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 resources have been developed including criteria for target locations (i.e. supermarkets, institutions, industrial facilities) for the deployment of hydrogen and fuel cell technologies and educational videos that serve to increase the awareness levels of local and state stakeholders.

Through the development of models and associated outreach activities, CCAT has provided analytical services and project development assistance. Table 1 below depicts notable results from outreach efforts. In addition, CCAT has provided assistance to over 24 additional end-users including municipalities, state government, and commercial and industrial facilities.

**TABLE 1. Results of Notable Analysis/Modeling**

<table>
<thead>
<tr>
<th>Organization</th>
<th>Potential Fuel Cell</th>
<th>Notes</th>
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<tbody>
<tr>
<td>Town of Weston</td>
<td>UTC 400</td>
<td>Project Modeling and Interconnection Assistance</td>
</tr>
<tr>
<td>Town of Killingly</td>
<td>FCE 300</td>
<td>Project Modeling</td>
</tr>
<tr>
<td>University of Bridgeport</td>
<td>FCE 300 or UTC 400</td>
<td>Project Modeling and RFP Development Assistance</td>
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<td>United States Postal Service</td>
<td>FCE 300 or UTC 401</td>
<td>Project Modeling and ESCO Assistance for Distribution Centers</td>
</tr>
<tr>
<td>Greater Hartford Transit District</td>
<td>FCE EHS 300</td>
<td>Tigger/Tiger Grant Application Assistance for Vehicles and Refueling</td>
</tr>
<tr>
<td>Department of Veteran Affairs</td>
<td>Fuel Cell of other CHP</td>
<td>Project Modeling and Verification</td>
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</table>


**Conclusions and Future Directions**

This partnership effort has successfully created criteria, models and tools that 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 the execution of a regional briefing to be held on July 22, 2010 which will discuss federal, regional and state efforts, partnership opportunities, planning efforts and tools to facilitate project identification and development. CCAT will also undertake a concluding project survey to assess the effectiveness of the current outreach program.

Finally, CCAT seeks to leverage additional DOE funding to continue education and outreach efforts on the regional scale to encourage and support the development of state roadmaps. Through past project success, CCAT can effectively encourage and support the successful development and deployment of hydrogen and fuel cell projects in the New England region.

**FY 2010 Publications/Presentations**

X.13 Raising $H_2$ and Fuel Cell Awareness in Ohio*

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Contract Number: DE-FC36-08GO18117

Subcontractor:  
Edison Material Technology Center (EMTEC),  
Dayton, OH

Project Start Date: March 2009  
Project End Date: June 30, 2011  
*Congressionally directed project

**Objectives:**

- Increase understanding of hydrogen and fuel cell technologies among state and local governments by 10% 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 Fuel Cell Technology Program Multiyear Research Development and Demonstration Plan:

(A) Lack of Readily Available, Objective and Technical 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 the following milestones from the Education section of the Fuel Cell 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 (ongoing)
- **Milestone 16**: Develop database of state activities (ongoing)
- **Milestone 17**: Hold “Hydrogen 101” seminars (3Q, 2009 through 2Q, 2011)

**Accomplishments**

- August 21, 2009 – ADA – Ohio Northern University – 50 people
- September 2, 2009 – Youngstown University – 50 people
- September 14, 2009 – Dayton, Ohio – 25 people
- October 19, 2009 – AFRL
- October 20, 2009 - Akron Sierra Club
- November 12, 2009 - Wayne County Sustainability Forum
- November 16, 2009 - US Fuel Cell Council Seminar
- December 12, 2009 - State House of Representatives Hearing
- January 13, 2010 – Ohio Board of Regents – Green Pathways Inaugural Meeting, Columbus, Ohio - 25 people
- February 4, 2010 – Presentation at Great Lakes Educational Partnership at Stark State College - 20 people
- February 23, 2010 – Ohio Economic Education Summit III - 50 people
- March 2, 2010 – STEM Education Panel at COSI in Columbus, Ohio - 40 people.
- April 9, 2010 – Dublin, Ohio - 75 people – Fuel Cells Opportunity for Growth in Central Ohio
- April 16, 2010 – Aurora, Ohio – 20 people – Industrial Advisory Board for the College of Technology of Kent State University
- May 4, 2010 – Columbus, Ohio – 40 people – 2010 Ohio State University Sustainability Conference
- May 6 and 7, 2010 – Cleveland, Ohio – 180 people – 2010 Symposium
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 held 19 community leaders forums. A community leaders forum was held in conjunction with the 2010 Ohio Fuel Cell Symposium. On May 6 and 7 over 200 people gathered at the Great Lakes Science Center for the 2010 Ohio Fuel Cell Symposium. The Symposium presented by the Ohio Fuel Cell Coalition began with two community leaders forums where participants had an opportunity to learn about fuel cells and the hydrogen economy. Day 2 of the symposium opened with the focus in the morning on the theme of “Ten Years of Success and Beyond” and in the afternoon “Fuel Cells in the Commercial Market.” In the morning of the first day we honored Governor Bob Taft and Chairman Emeritus of the Ohio Fuel Cell Coalition, Trevor Jones for their lifetime achievements in advancing the fuel cell initiative in the State of Ohio. A panel discussion followed were Rodger McKain of Rolls-Royce, Lionel Batty of GrafTech, Bill Dawson of NexTech and Frank Svet of EMTEC discussed their successes over the last 10 years. In the afternoon, we started out with a panel discussion on the proposed Great Lakes Science Center Electrolysis Project. On that panel were Valerie Lyons of the National Aeronautics and Space Administration (NASA), Pete Buca of Parker Hannifin and George Shaw of NASA. They were followed by Bill Whittenberger of Catacel, Bob Rose of the US Fuel Cell Council and Mike McKay of the Ohio Department of Development. This event allowed the Coalition to educate over 200 individuals on fuel cells and the hydrogen economy which exceeded our expectations.

Approach

The approach we used and will be using for all the 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 answers periods followed up by informal discussions on fuel cells and the hydrogen economy.

Results

In summary, as you see the community leaders forums have been very successful in the last year with over 800 people being drawn to them. As always we followed up the forums 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 additional input on the community leaders forums and we continued to add input to future events. The following community leader forums will be held in the next three months:
- Cincinnati, Ohio
- Toledo, Ohio
- Athens, Ohio
- Dayton, Ohio
- Akron, Ohio
- Canton, Ohio
Objectives

- Create presentation materials tailored to effectively communicate with state and local government leaders...relate hydrogen to their interests and spheres of responsibility.
- Establish pathways for working with national associations of state and local officials as a route for disseminating information about hydrogen...set pattern for on-going information flow.
- Launch learning sessions by conducting initial workshops for local and state officials at national gatherings...achieve nationwide reach.
- Create the following report: Infrastructure for Fuel Cells Market Analysis. This report will establish improved understanding of the current state of production, distribution, storage, and the use of hydrogen, which is a critical fuel for the fuel cell industry and the backbone of fuel cell infrastructure. The data gathering and analysis will focus on the following main topics related to infrastructure for fuel cells.

Technical Barriers

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

- Lack of Readily Available, Objective, and Technically Accurate Information
- Mixed Messages
- Disconnect Between Hydrogen Information and Dissemination Networks
- Lack of Educated Trainers and Training Opportunities

Contribution to Achievement of DOE Education Milestones

The H2L3 project will directly address the following milestones of the Education sub-program:

- 17: Hold “Hydrogen 101” seminars. (4Q, 2008 through 4Q, 2012)
- 18: Develop end-user workshop materials for use at events. (4Q, 2009)
- 30: Evaluate knowledge and opinion of hydrogen technology of key target audiences and progress toward meeting objectives. (4Q, 2012)

The H2L3 project directly contributes to achieving these milestones by conducting education workshops with hundreds of local and state officials from across the country and, further, by training motivated local officials to replicate the workshops in their own communities. By fostering and using the H2L3 team’s existing dissemination network of national associations of local and state government officials, the reach and the credibility of the outreach will be substantially and uniquely strengthened. This dissemination network will continue to pay dividends to DOE beyond the three-year life of this project by establishing institutional relationships that will enable on-going and expanding opportunities for hydrogen outreach through the national associations representing local and state officials.

Accomplishments

- Core Curriculum
  - Comprehensive, basic presentation developed to communicate with audiences of state and local officials.
  - Curriculum trimmed or modified to tailor further for specific audiences as needed.
- Advisory Committee of Local and State Officials
  - Established an advisory committee comprised of Public Technology Institute members (local),
Introduction

Increasing education about hydrogen and fuel cells is a key need to enable widespread commercialization and in many cases the introduction of the related technologies. This project began with a focus on educating local leaders and has developed to include other ways to reach new audiences with educational and information tools that increase knowledge about hydrogen and fuel cells.

Approach

Activities include Hydrogen 101 in-person presentations, Webinars, the creation of a market report that features industry data not published before, the creation of a business solution forum for existing and potential hydrogen customers and a student contest to engage university students to design a hydrogen community in southern California.

Results

For brevity’s sake here is a summary of select results:

For the Hydrogen 101 presentations, through several different venues connected with the Public Technology Institute and the National Association of State Energy Officials, local leaders have been engaged from the following areas:

- Cincinnati Health Department
- City of Boston Environment Dept.
- City of Carlsbad, CA
- City of Cincinnati, OH
- City of Culver, CA
- City of Dayton, OH
- City of Des Moines, IA
- City of Fort Wayne IN
- City of Fort Worth, TX
- City of North Kingstown, RI
- City of Orlando, FL
- City of Phoenix, AZ
- City of San Diego, CA
- City of Santa Monica, CA
- City of South Sioux City, NE
- City of Wilmington, NC
- City of Winston-Salem, NC
- District of Washington, D.C.
- Fairfax County Dept. of Vehicle Services, VA
- Los Angeles County, CA
- Regional Governmental Services of CA
- San Diego County, CA
Feedback from attendees Hydrogen 101:

- “Very understandable”
- “For the first time, I understood what hydrogen is.”
- “Personally, I’m not that interested in this [topic] but my boss needed me to learn about it and now I won’t be totally lost.”
- “This was really good.”
- “Really informative.”
- “Showing the number of fueling stations made it real. I thought hydrogen was more of an impossibility before.”

Regarding the U.S. Market Report: Hydrogen and Fuel Cells, the report includes dozens of pages of results covering 57 different research areas. The full report and 8-point brief (see Figure 1) can be viewed and downloaded from: http://hydrogenassociation.org/marketreport. As of July 2010, the report has become the most popular download on the NHA Web site (see Table 1).


- “It’s outstanding and will be a very useful resource for the community. NHA should be proud to put our logo on your work..... Thanks for the chance to review this impressive document.” – Ken Schultz, Operations Director, Energy Group, General Atomics.
- “Lot of great data. I had no idea that there are so many renewable projects.” – Sandy Thomas, former President, H2Gen Innovations.
- “A really good report. I think the front sections will make a great reference tool on the hydrogen industry generally and I already learned a few things!” – Lisa Calaghan Jerram, Fuel Cell Today.
- “This is an excellent report. I think it is very useful.” – Dr. Finis H. Southworth, Chief Technology Officer, AREVA NP Inc.
- “I am working on a hydrogen study for the University of Colorado and the Reliability and Sustainability Energy Institute (RASEI). Your US Market report on Hydrogen is great.”
- “Excellent reports - some of the most salient data & information out there, and very well presented.” – Randy Cole, CEO at Renewable Opportunities, Inc, via LinkedIn.
- “Love the 8-point brief. Succinct and direct. Thanks for drawing our attention to it.” – Tom Sperrey, CEO, UPS Systems plc, via LinkedIn.
- “The brief version is my kind of report! The full version looks very useful; many thanks for sharing the link.” – Graham Cooley, CEO at ITM Power Plc, via LinkedIn.
- “Very well done and very much needed!” – Bay Elliott, EVP, Partner, Executive Recruiter, The Farwell Group, via LinkedIn.

![Figure 1](image-url)


<table>
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<th>Month</th>
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<th>Downloads - Executive Summary</th>
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</table>

**TOTAL DOWNLOADS (15July10)** 45,686
“Is it possible to obtain a copy of your report in a non-pdf format? I would like to utilize some of the graphs and figures regarding H2 Energy in an internal slide presentation. If not the whole study, specifically pages 26-37” – from an industrial gas supplier (obviously a significant compliment if they’re happy using this information internally).

“These are very nice reports. I circulated them within Proton.” – Mark Schiller, VP Business Development, Proton Energy Systems.

“You and your team did an excellent job. Congratulations!” – Patricia Irving, Ph.D., President & CEO, InnovaTek, Inc.

“This looks really, really nice. Thank you. I’ve stared teaching the graduate course at Wayne State University in alternative energy, and I plan to share this report with my class, as well as working it into my thinking about price and market position. Thank you again, and good luck with your work.” – Robert Buxbaum, President, REB Research & Consulting.

The 2010 Hydrogen Student Design Contest challenged teams of university students from around the world to plan and design the basic elements of a hydrogen community in Santa Monica, CA. They were asked to design one scalable hydrogen fueling station; identify renewable hydrogen sources in the community; and identify customers for early market hydrogen applications.

University teams from the United States, Canada, Bangladesh and Ukraine submitted contest entries. These entries were evaluated across ten different categories by a team of judges from government and industry.

The team from Missouri University of Science and Technology was declared the Grand Prize winner (see team photo, Figure 2). Teams from the University of Waterloo and the National University of Kyiv received Honorable Mention awards.

Conclusions and Future Directions
The feedback we have received through this project has been overwhelmingly positive. Where improvements have been suggested, adjustments have been made to improve the experience for any audience being education. Going forward, we recommend continuation of the Hydrogen 101 presentations, an expansion of the Market Report to include the next year’s data to show trends and future Hydrogen Student Design Contests.

FY 2010 Publications/Presentations

FIGURE 2. The Hydrogen Student Design Contest’s 2009-10 grand-prize winning team: Missouri University of Science and Technology, http://www.hydrogencontest.org/
Objectives

- To build greater familiarity and understanding of stationary fuel cell technologies and applications among state policymakers.
- To disseminate and encourage the adoption of best practice policies which accelerate the adoption and reduce barriers to fuel cell installations.

Technical Barriers

This project addresses the following technical barriers from the Education section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of Readily Available, Objective, and Technically Accurate Informationn
(B) Mixed Messages
(C) Disconnect Between Hydrogen Information and Dissemination Networks

Contribution to Achievement of DOE Hydrogen Education and Outreach Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Education and Outreach section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

16. Develop database of state activities. (2Q, 2007)

Accomplishments

- Completed survey of state hydrogen and fuel cell programs and policies.
- Developed case studies of exemplary state programs.
- Developed series of four briefing guides for state policymakers on fuel cell technologies, policies and programs, critical power applications and hydrogen production, transport and storage.
- Established and maintained fuel cell listserv and Web pages providing current news on state policies and programs.
- Co-organized series of Webinars on fuel-cell related topics.
- Established sub-contractor relationship with National Council of State Legislators to assist in outreach to their members.

Introduction

While stationary fuel cell installations have been growing at a rapid rate in the United States, this growth has been concentrated in just a few states that have provided strong financial incentives to encourage their use. This project addresses the need for more supportive state policies and programs to further accelerate the adoption of stationary fuel cells. In this project, Clean Energy States Alliance (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 is using its membership network of state clean energy funds to educate state clean energy policy makers and program managers about fuel cell and hydrogen technology developments and the efforts by states to advance these technologies. With the outreach assistance provided by NCSL, CESA will have increased access to state legislators from all 50 states to provide information on hydrogen/fuel cell issues and policies.

This project is emphasizing efforts to develop stationary fuel cell industries and markets without directly advancing transportation technologies (with the
understanding that advancing stationary and portable fuel cell applications could facilitate the development and deployment of transportation fuel cells).

**Approach**

The basic approach to the project involves three stages:

First, CESA gathered baseline information on state programs and policies to advance fuel cell industries and deployment including the development of case studies to identify exemplary programs (Connecticut, Ohio, California, New York, Hawaii). This research was conducted to identify policies that appear to be most effective as well as the barriers which states have erected or failed to remove that impede the deployment of hydrogen infrastructure and stationary fuel cell deployment.

Second, CESA developed a series of briefing reports providing background on fuel cell technologies and best state programs and policies. These are targeted at both state policymakers and state renewable energy program fund managers. CESA also continues to enhance its hydrogen and fuel cell Web pages by posting current information on new program and policy development at both the state and federal levels.

CESA is currently in the third stage of this project which focuses on direct outreach to state legislators, policy managers, and renewable energy program managers. CESA is organizing a workshop on stationary fuel cell deployment for its fall CESA member national meeting in Washington, DC. Working with our partner, the NCSL, CESA will also be organizing a Webinar for state legislators and a presentation at NCSSL’s fall legislative summit. CESA will also be seeking selective opportunities to present at both the state and regional level to targeted audiences such as building code officials, and state and higher education facilities managers (emphasizing the value proposition of fuel cells for critical power).

**Results**

CESA has now developed a comprehensive set of best practice programs and policies supporting hydrogen and fuel cell industrial development and project deployment. We have produced educational materials which should prove effective in engaging state policymakers and others on the value of supporting fuel cell technologies. We are beginning to reach out directly to policymakers to further explain the technologies and how they fit within the overall framework of clean energy development within their states. It is difficult, however, to measure the results of these educational and outreach efforts against either the project’s or DOE’s objectives. State-level policy changes can take several years to occur. In addition, while we can track state renewable energy program spending on fuel cells, near-term spending increases are most likely to occur in those states with existing fuel cell programs.

**Conclusions and Future Directions**

- There is little state-level engagement on fuel cell deployment beyond the handful of states with active programs and funding (CA, CT, HI, MA, NY).
- Other states (OH, SC) have active fuel cell industry development programs but little in the way of project deployment support.
- More effort is needed to build policymaker knowledge of and engagement in hydrogen and fuel cell technologies and policies (beyond vehicles). In particular, states which have been supportive of distributed, non-dispatchable renewable energy technologies (solar and wind) need to recognize the benefits of a clean (though not necessarily renewable) distributed energy technology which can provide baseload power while also meeting thermal energy loads.
- The future direction of this project will be focused on communicating this “value proposition” to the states.

**FY 2010 Publications/Presentations**


X.16 Hydrogen Technology and Energy Curriculum (HyTEC)

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Contract Number: DE-FG36-04-GO14277

Subcontractor:  
Schatz Energy Research Center (SERC),  
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 Lawrence Hall of Science (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 Fuel Cell 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

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Fuel Cell 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

- Eleven new teachers piloted the module in their classrooms and provided feedback.
- The curriculum module manuscript was submitted to the publisher, LAB-AIDS, Inc. and professional editing is in progress.
- LAB-AIDS produced prototype electrolyzers for the student curriculum kit. These have been tested by LHS and SERC, and are undergoing further modification for the commercial kit.
- The materials were disseminated via 10 presentations to secondary science educators and hydrogen and fuel cell professionals.

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.

The past year focused on expanding implementation of the curriculum into new sites and preparing the curriculum and materials kit for commercial distribution.

Approach

The curriculum materials are developed and revised through a close collaboration between curriculum developers at LHS, scientists and engineers at 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 local 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 two to three days of 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 assist with dissemination and implementation of the published curriculum.

Dissemination is conducted by presentations at science teacher education conferences and through the extensive networks of both LHS and LAB-AIDS, Inc.

Results

The curriculum module addresses Education Technical Barrier 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 curriculum is developed by the Science Education for Public Understanding Program (SEPUP), a curriculum development group that produces issue-oriented science materials that avoid advocacy. The module is extensively reviewed for technical accuracy by scientists and engineers at SERC.

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. Teachers receive professional development in the unit content, teaching approaches, science of hydrogen and fuel cells, and fuel cell applications.

The expanded implementation during the past year addressed Barrier E (Regional Differences), by testing the curriculum in new locations and Barrier D (Lack of Educated Trainers) by providing professional development and implementation experience to teachers from school districts in these new locations. New teacher participants taught the curriculum to over 860 students in new sites in Connecticut, Georgia, New York, South Carolina, and Southern California. The classrooms using the materials in the past year included chemistry, physical science, physics, and environmental chemistry classrooms in public comprehensive, magnet, and alternative high schools in urban and suburban settings. In this final year of testing, most participating teachers had not previously worked with the SEPUP curriculum development group or SEPUP products, to ensure usability of the materials by a variety of teachers. Figure 1 shows two of the new teachers, from Georgia and Connecticut, who implemented the curriculum during the 2009–2010 school year.

An online survey was used to collect feedback on the curriculum and kit from the new participating teachers. Eleven teachers completed the survey, which includes questions about the curriculum module as a whole and about each of the six curriculum activities.

FIGURE 1. Teachers Trained in June 2009 Implemented the Module during the 2009–2010 School Year
Feedback was generally positive about the module, with many constructive suggestions for improving specific activities. Figure 2 summarizes feedback on teachers' interest in using the module again. All teachers indicated that they would teach the core activities of the module again either as is or with minor changes. One teacher responded: “Using this kit is an excellent way to bring in the concepts of science and social responsibility. The concepts were challenging and thought provoking, but obtainable and relevant.” Another wrote, “I really enjoyed the approach that was used to teach this unit.” Several included in their written comments their hopes that their school will purchase the curriculum when commercially available.

Presentations at science teacher conferences reached over 240 teachers during the past year. In these one to two-hour presentations, teachers were introduced to the module, given background on fuel cells, and conducted an activity on the fuel cell reaction (Activity 4 from the module) that they were then given to take back to their classrooms and try out.

Commercialization of the module and accompanying kit is expected to take place this fall. The curriculum kit includes a student electrolyzer produced specifically for this project. LAB-AIDS has produced and modified prototype electrolyzers for the kit based on original prototypes developed by SERC, and LHS and SERC have tested these prototypes. Final modifications are currently being made to produce the commercial student electrolyzers. The manuscript for the module has been submitted to LAB-AIDS and professional editing is in progress.

![Figure 2. Teacher Survey Responses: “Would you use this unit again?”](image)

**FIGURE 2.** Teacher Survey Responses: “Would you use this unit again?”

**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), in diverse settings, and with diverse student populations. Students and teachers continue to react positively to these materials. Over 860 students participated in the module in the past year.
- Presentations at nine national, state, and regional teacher workshops reached over 240 teachers. Reactions to these workshops were positive.

**Future work will focus on:**

- Publishing and distributing the HyTEC module print and kit materials.
- Expanding work with new school districts, and strengthening collaborations with current districts.
- Reaching greater numbers of teachers by presenting the project at science teacher conventions and working with the publisher to disseminate the module. So far, sessions have been accepted or submitted for Fall 2010 teacher conferences in California, Connecticut, North Carolina, South Carolina, Texas, and the National Science Teachers Association Northeastern Regional Conference in Baltimore. The project will also be presented at the Spring 2011 National Science Teachers Association National Convention in San Francisco.
- Expanding professional development for teachers and implementation of the curriculum at existing and new sites. A conference to prepare a new group of teachers is planned for early 2011.
- Preparing additional student materials and teacher support materials for the project website.

**FY 2010 Publications/Presentations**


X.17 $H_2$ Educate – Middle School Hydrogen Education Program

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DOE Project Officer:  Reg Tyler  
Phone: (503) 275-4929  
E-mail: Reginald.Tyler@go.doe.gov  

Contract Number: DE-FG36-04GO14278  

Subcontractors:  
- Senterch, Inc., Bethesda, MD  
- Los Alamos National Laboratory, Los Alamos, NM  

Start Date: August 1, 2004  
Projected End Date: July 30, 2010, extension to July 30, 2011  

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 Fuel Cell 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 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 $H_2$ 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 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan – Task Six: Facilitate Development and Expansion Hydrogen Technology Education for Middle and High Schools

- Milestone 6.22: Develop curriculum for middle schools (2Q, 2006)
- Milestone 6.26 and 27: Materials developed are in use in high schools and training provided to high school educators.

G. 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 8,000 teachers trained.
  - Training programs completed in 35 states with additional training in 2011 due to extension of DOE funding.
  - Pre-survey scores were 5 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 30-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 DOE’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 DOE, 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 5 out of 15 correct successful response and a post-training survey result showing a 15 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 8,000 teachers trained by 2010. 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 DOE 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 DOE 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. NEED continues to provide hydrogen materials through the National Energy Conference for Educators, the National Science Teachers Association annual conference and a number of state science conferences throughout the country.

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 two National Energy Conferences for Educators in July and August 2010.
- 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. Hydrogen curriculum will be redesigned as part of the redesign of NEED curriculum for the 2010 – 2011 school year.
- 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. AMERICAN RECOVERY AND REINVESTMENT ACT ACTIVITIES
XI.0 American Recovery and Reinvestment Act Activities

Introduction

In April 2009, the DOE announced the investment of $41.9 million in American Recovery and Reinvestment Act (ARRA) funding for fuel cell technologies to accelerate the commercialization and deployment of fuel cells and to build a robust fuel cell manufacturing industry in the United States, with accompanying jobs in fuel cell manufacturing, installation, maintenance, and support services. Twelve grants were awarded to develop and deploy a variety of fuel cell technologies including polymer electrolyte membrane, solid oxide, and direct-methanol fuel cells in auxiliary power, backup power, combined heat and power (CHP), lift truck, and portable applications. The cost share provided by the project teams is about $54 million, over 56% of the total cost of the projects.

These projects are addressing the objectives stated above as well as the overall ARRA goals to create new jobs and save existing ones; spur economic activity; and invest in long-term economic growth. Deployment of nearly 1,000 fuel cells is planned in these applications. These efforts have required the DOE and ARRA project teams to identify and address key challenges in technology innovation and deployment, and also in reporting requirements, performance measurement and tracking, and safety and environmental management.

Reports addressing technology and deployment status and jobs and costing data are submitted quarterly by the project teams and are available to the public through the Recovery.gov Web site. Collection and analysis of operational and performance data from the fuel cell deployments are being performed by the National Renewable Energy Laboratory (NREL) Hydrogen Secure Data Center (HSDC) to assess the performance and commercial readiness of the fuel cell technologies. Data are aggregated across multiple systems, sites and teams, and are made available quarterly through composite data products (CDPs) available on the NREL Web site. In addition, detailed data products (DDPs), shared only with the project partner, are produced twice annually for each fuel cell system and site. Safety plans are being developed by all project teams and will be reviewed by the Hydrogen Safety Panel.

The Safety, Codes and Standards sub-program is facilitating market entry for fuel cell-powered lift trucks, through tank testing and analysis, which it initiated at Sandia National Laboratories in Fiscal Year (FY) 2010. This effort addresses fatigue crack initiation and growth in steel tanks used in high-cycle applications. The test tanks were obtained from two ARRA project fuel cell partner companies and from tank manufacturers. Hydrogen pressure-cycle testing and engineering analysis of commercial Type-1 hydrogen pressure vessels are being performed under conditions similar to in-service environments for lift truck storage tanks. Results will be used to help inform design methodologies and code development processes for high-frequency refueling applications, and to provide the technical basis for Canadian Standards Association HPIT1.

ARRA Project Summaries

Auxiliary Power

Delphi Automotive (Troy, Michigan and Rochester, New York): Delphi will develop a 3- to 5-kW solid oxide fuel cell (SOFC) auxiliary power unit (APU) for heavy-duty commercial Class 8 trucks at their laboratory in Rochester, New York. Delphi will test and demonstrate the diesel APU in a high visibility fleet vehicle that will provide power for vehicle hotel loads and other vehicle needs under real-world operating conditions. There will also be a series of in-house tests, including on-vehicle testing, to validate the “road worthiness” of the diesel APU, prior to installation on the demonstration truck. Delphi will provide a comprehensive system specification and—with heavy-duty truck manufacturer partner PACCAR—will define commercial requirements. System development efforts will improve Delphi’s current generation SOFC technology by increasing net output power and fuel processing efficiency, decreasing heat loss and parasitic power loss, and establishing diesel fuel compatibility. The primary focus will be accelerating the development and acceptance of the APU by the Class-8 heavy-duty truck market. Partners include Electricore Inc., PACCAR Inc., and TDA Research Inc.

1“Hydrogen Safety, Codes and Standards R&D—Materials and Components Compatibility,” Daniel Dedrick et al., this volume.
Backup Power

**ReliOn, Inc. (Spokane, Washington):** ReliOn is deploying over 150 fuel cell systems into the telecommunications and utility networks at AT&T and PG&E for backup power, across nine states, combined with the deployment of a refillable stationary hydrogen storage module unit and accompanying refueling logistics platform for AT&T sites. This effort will add reliability to communications networks where no backup power was previously available. ReliOn will provide DOE with installation, fueling logistics, and operating data for fuel cells in voice and data communications networks in mountain, desert, and urban locations. Partners include Air Products & Chemicals, Inc., AT&T, and PG&E.

**Sprint Nextel Corp. (Reston, Virginia):** Sprint Nextel is planning to demonstrate the technical and economic viability of deploying 1-kW to 10-kW polymer electrolyte membrane (PEM) hydrogen fuel cells with 72 hours of on-site fuel storage (using a new Medium Pressure Hydrogen Storage Solution [MPHSS] with on-site refueling) to provide backup power for critical code division multiple access cell sites on the Sprint Wireless network. Over 200 new hydrogen fuel cell systems will be deployed to sites in California, Connecticut, New Jersey, and New York. In addition, 70 already in-service fuel cell systems at cell sites in Louisiana and/or Texas will be converted from a low-pressure storage solution (bottle swap) to the new MPHSS. Partners include Air Products & Chemicals, Inc., Altergy Systems, Black & Veatch Corporation, Burns & McDonnell Engineering Co. Inc., Ericsson Services Inc., and ReliOn, Inc.

**Plug Power Inc. (Latham, New York):** This project will demonstrate the market viability of low-temperature, 6-kW PEM GenCore® fuel cells fueled by liquid petroleum gas (LPG) to provide clean and reliable primary power and emergency backup power (72 hours or more). Plug Power will install and operate 20 fuel cell systems at Fort Irwin in Barstow, California, and Warner Robins Air Force Base in Warner Robins, Georgia. These units will run continuously on LPG, providing power to the grid and will switch to emergency backup power during a grid failure. A small battery pack will be used for spikes in power demand. Partners include the Army Corp of Engineers' Construction Engineering Research Laboratory (CERL), Warner Robins Air Force Base, and Fort Irwin.

Combined Heat and Power

**Plug Power Inc. (Latham, New York):** Plug Power is evaluating the performance of 12 high temperature, natural gas-fueled, 5-kW micro-CHP fuel cell units (GenSys Blue®). The objective of the project is to validate the durability of the fuel cell system and verify its commercial readiness. Six units will undergo an internal Plug Power test regime to estimate failure rates, and six units will be installed and tested in real-world residential and light commercial end-user locations in California. Partners include Sempra Energy and the National Fuel Cell Research Center at the University of California, Irvine.

Fuel-Cell Powered Lift Trucks

**FedEx Freight East (Harrison, Arkansas):** FedEx is deploying 35 fuel cell systems as battery replacements for a complete fleet of electric lift trucks at FedEx's service center in Springfield, Missouri. Success at this service center may lead to further fleet conversions at some or all of FedEx's other 470 service centers. Partners include Air Products & Chemicals, Inc. and Plug Power Inc.

**GENCO (Pittsburgh, Pennsylvania):** Over 350 fuel cell systems are being deployed as battery replacements for fleets of electric lift trucks at five existing distribution centers (Coca-Cola in Charlotte, North Carolina; Kimberly Clark in Graniteville, South Carolina; Sysco Foods in Philadelphia, Pennsylvania; Wegmans in Pottsville, Pennsylvania; and Whole Foods in Landover, Maryland). Success at these distribution centers may lead to further fleet conversions at some or all of GENCO’s other 109 distribution centers. Partners include Air Products & Chemicals, Inc., Linde North America, and Plug Power Inc.

**Nuvera Fuel Cells (Billerica, Massachusetts):** Nuvera is deploying 14 fuel cell forklifts in H-E-B Grocery Company's distribution facility in San Antonio, Texas. Fuel will be supplied by Nuvera's natural gas reformer and its storage and dispensing system. Partners include H-E-B Grocery Co.
Sysco of Houston (West Houston, Texas): Sysco is deploying 98 fuel cell systems as battery replacements for a fleet of lift trucks at Sysco’s new distribution center in Houston, Texas, opened in March 2010. This installation is the first-ever greenfield installation without battery infrastructure for a pallet truck fleet. Success at this distribution center may lead to further fleet conversions at some or all of Sysco’s other 169 distribution centers. Partners include Air Products & Chemicals, Inc. and Plug Power Inc.

Portable Power

Jadoo Power (Folsom, California): Jadoo Power is developing portable, propane-fueled SOFC generators and an electro-mechanical propane fuel interface, as a potential replacement for traditional gas/diesel generators and lead-acid battery power sources. Two portable fuel cell generators will be deployed in this project. One of them will be used in a demonstration with police and fire first-responders in the City of Folsom, California, to power equipment in emergency and off-grid situations; both units will then be used to power media production equipment at automobile racing events at multiple locations throughout the United States. Partners include Delphi Inc., NASCAR Media Group, and the City of Folsom, California.

MTI MicroFuel Cells (Albany, New York): MTI is demonstrating a 1-watt consumer electronics power pack. The project is focused on improving reliability to meet the standards required by the electronics market and includes testing of individual components, subsystems, and complete direct methanol fuel cell (DMFC) systems. MTI is also developing manufacturing processes to improve product yields and reduce overall costs.

University of North Florida (Jacksonville, Florida): The University of North Florida is further integrating and miniaturizing the components of a portable power system for use in mobile computing, and analyzing failure modes to increase durability. The power system would be a DMFC that meets the requirements for power density, energy density, and operating lifetime. The university will also conduct a design for manufacturability and assembly review to ensure that the systems meet the cost targets for commercialization. Partners include the University of Florida, Gainesville.

FY 2010 Status and Accomplishments

As of the end of September 2010, 276 fuel cell lift trucks and 24 fuel cell backup systems for communication cell towers had been deployed and 51% of the ARRA project funds had been spent by the projects. A total of 36 direct jobs have been created or retained as a result of the Fuel Cell Technologies ARRA projects (excluding supply chain and other indirect jobs). NREL’s HSDC has set up data reporting protocols with each of the project teams. CDPs and DDPs showing progress to-date have been prepared. The CDPs are available on the NREL HSDC Web site, www.nrel.gov/hydrogen/news/2010/807.html.

Auxiliary Power

Delphi Automotive Systems has completed initial system specifications and system design and layout for their SOFC APU, and they have identified its commercial requirements. Initial system and subsystem vibration testing and analysis have been completed, as has initial on-vehicle testing and demonstration; component fabrication is underway. Over the next year, Delphi will complete and test the APU system/subsystem build. Delphi will also complete the integration and characterization of the system and begin their full-scale demonstration.

Backup Power

Plug Power is working with CERL to identify deployment sites at Warner Robins Air Force Base in Warner Robins, Georgia, and Fort Irwin in Barstow, California, for 20 GenCore® fuel cells. It was determined that a system that starts quickly with hydrogen and runs for extended periods with LPG or natural gas is more favorable, economically, than a pure hydrogen system. The first fleet is currently being built and module testing and qualification are being performed.
ReliOn, Inc. has completed the site qualification stage for over 150 communications sites. They have fabricated, integrated, and delivered fuel cell equipment to AT&T for 132 sites, and hydrogen storage modules for 69 sites. Fuel cell equipment has been fabricated and integrated for all nine PG&E sites. ReliOn had installed fuel cells at 24 sites as of the end of September 2010. Technology and methodology for remote monitoring and collection of operational data have been developed.

Sprint Nextel is addressing siting and permitting requirements necessary for the deployment of hydrogen fuel cell systems at their communications sites. Design of the MPHSS is being completed. The project team plans to benchmark the life-cycle costs, performance, and operational characteristics of the hydrogen fuel cell systems against incumbent technologies (batteries and diesel generators).

**Combined Heat and Power**

Plug Power has built and commissioned an internal GenSys Blue® micro-CHP test fleet and is conducting durability tests. Control and efficiency of the units have been improved, resulting in faster start-ups and thermal response time, improved heat modulation, and increased total efficiency. Manufacturability improvements have reduced build time by over 55%, and material costs for low-volume production of the fuel cell units have been reduced. Site selection has been initiated for external customer testing in California.

**Fuel Cell-Powered Lift Trucks**

FedEx Freight East deployed 35 fuel cell-powered lift trucks in June 2010 at their distribution center in Springfield, Missouri. These fuel cell systems will serve as battery replacements for the complete fleet of Class-I electric lift trucks in their 53,000-square-foot facility. A permanent hydrogen fueling infrastructure has been built and installed by Air Products & Chemicals, Inc., including liquid hydrogen handling and gaseous compression, storage, and dispensing (for two indoor dispenser stations) equipment. Success in this project may lead to additional fleet conversions at some or all of FedEx's other 470 centers.

Sysco of Houston has deployed 98 hydrogen fuel cell-powered pallet trucks and forklifts at Sysco Corporation's new 585,000-square-foot food distribution facility in Houston, Texas, and a permanent hydrogen fueling infrastructure has been built and installed by Air Products & Chemicals Inc. In the first quarter of 2010, 2,664 fills were logged. On June 17, 2010, business leaders and government representatives attended an official ribbon cutting and media event at this facility.

GENCO has deployed 59 GenDrive® fuel cell lift trucks at a Wegman’s distribution facility in Pottsville, Pennsylvania. The units logged over 24,000 operating hours during the first quarter of 2010. The Wegman’s fueling station completed almost 2,000 hydrogen fills during the first quarter of 2010. By the end of September 2010, 61 GenDrive® fuel cell lift trucks were delivered to Whole Foods in Landover, Maryland, and nine fuel cell lift trucks were delivered to Kimberly Clark in Graniteville, South Carolina. Deployment of an additional 228 fuel cell lift trucks is planned for four different distribution facilities.

Nuvera has installed 14 PowerEdge™ fuel cells in lift trucks and completed installation of their PowerTap™ hydrogen infrastructure technology at the H-E-B Grocery Co. distribution center in San Antonio, Texas. At this site, fuel cell forklifts and battery forklifts are operating in parallel to allow direct comparison. An initial productivity gain of 10% from the use of fuel cells instead of lead-acid batteries has been reported.

**Portable Power**

Jadoo has developed preliminary requirements for the portable generator and fuel interface. Desulfurizer hardware has been delivered from Delphi and reformer testing has been initiated. Existing technologies and methodologies applicable to a portable SOFC propane fueling system have been compared and evaluated. Site specific baseline load data on media equipment power requirements have been collected.
MTI MicroFuel Cells has demonstrated reduced cost, manufacturability, and assembly for a redesigned one-watt DMFC charger for consumer electronics. System level testing has verified that the charger is capable of operating well during transients such as start-up and shut-down and at all specified temperatures, humidity, and orientations. High power density, high fuel efficiency, and low stack degradation rates exceeding product requirements have also been demonstrated. Seventy-five fuel cell charger systems are being deployed to organizations and individuals for evaluation and feedback.

The University of North Florida has completed component design requirements for the DMFC portable power system and started analysis of design failure modes. The university will continue component development and testing and will demonstrate that component performance meets system requirements. Subsequently, they will integrate components and subsystems into a packaged unit and conduct extensive system tests to evaluate performance, robustness, and durability.

### Budget

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>AWARD</th>
<th>APPLICATION</th>
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<tbody>
<tr>
<td>Delphi Automotive</td>
<td>$2.4 M</td>
<td>Auxiliary Power</td>
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<tr>
<td>FedEx Freight East</td>
<td>$1.3 M</td>
<td>Lift Truck</td>
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<td>GENCO</td>
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<td>Jadoo Power</td>
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<td>MTI MicroFuel Cells</td>
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<td>Nuvera Fuel Cells</td>
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<td>Plug Power, Inc. (1)</td>
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<tr>
<td>Sysco of Houston</td>
<td>$1.2 M</td>
<td>Lift Truck</td>
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FY 2011 Plans

Completion of all project safety plans and National Environmental Policy Act compliance reviews are priorities for early FY 2011. The Fuel Cell Technologies Safety Panel will review the project safety plans and submit formal written assessments to DOE and the project teams. In addition, safety panel members will visit at least four project sites to discuss project-specific safety issues, as well as findings that may have broader impact on the fuel cell community.

In FY 2011, deployment of over 500 additional fuel cell systems for backup power, CHP, and lift truck applications is planned. It is anticipated that the NREL HSDC will be able to report performance and productivity data in FY 2011, beginning with the first-quarter FY 2011 CDP.
Finally, in FY 2011, DOE will begin documentation of lessons-learned associated with the ARRA projects, including the strategies developed for risk management with respect to safety, environmental and siting requirements, and market entry. Planning for business case analysis and case studies will be initiated.

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XI.1 Commercialization Effort for 1 W Consumer Electronics Power Pack

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Contract Number: EE0000477  
Project Start Date: January 8, 2009  
Project End Date: December 31, 2010

Objectives

Demonstrate and field test a commercially viable 1 Watt direct methanol fuel cell (DMFC) charger for consumer electronic devices:

- Design for low-cost, high-volume manufacturing processes and ease of assembly.
- Demonstrate performance across temperature and humidity range of consumer electronic devices.
- Deploy 75 units into the field to obtain real world usage feedback.

Relevance to the American Recovery and Reinvestment Act (ARRA) goals of saving and creating jobs:

- Project funding created/retained 14 full-time equivalent jobs in Albany, NY.
- The leverage DOE funds offered enabled MTI to obtain private investment.

Relevance to the U.S. DOE Fuel Cell Technologies (FCT) ARRA goals of accelerating the commercialization and deployment of fuel cells:

- Fuel cell charger will be ready for commercialization at the end of this project.
- Components have been redesigned for low-cost, high-volume manufacturing.
- Seventy-five fuel cell systems will be deployed in 2010 during the field test.

Technical Barriers

Progress against the barriers listed below is discussed in the following sections:

- Cost and manufacturability
- Performance and degradation
- Market acceptance

Accomplishments

- Reduced cost and improved manufacturability and assembly:
  - Previously machined components are now being produced using injection molding for plastic parts and metal stamping for metallic parts.
  - Over 50% reduction in labor content achieved in system assembly.

- Achieved over 6,000 hours of stack operation with less than 5% decay per 1,000 hours.
- Demonstrated high performance, high fuel efficiency, and low degradation.
- Demonstrated system temperature and humidity latitude (0-40°C, 0-90% relative humidity, RH).
- Achieved all technical metrics and passed the Go/No-Go phase gate on-schedule.

Introduction

The objective of this project is to demonstrate and field test a commercially viable 1 Watt DMFC charger for consumer electronic devices. The fuel cell system and replaceable methanol cartridge will meet all requirements for commercialization. The system will achieve targets of cost, performance, and design reliability at a level compatible to the standards and requirements of the consumer electronics market.

Approach

The project’s environmental and safety plans had been developed and submitted during 2009. The project has been organized into three phases. Phase 1 demonstrates alpha level of capability and readiness for a consumer product, Phase 2 demonstrates beta level of capability and readiness for a consumer product,
and Phase 3 demonstrates usability in the hands of the customer by conducting a field test with 75 units.

The tasks in Phase 1 include component cost reduction, redesign for manufacturability, performance and reliability testing, and system integration. Phase 2 tasks include tool fabrication, debugging, and tooling component prove-out in working systems. Phase 3 tasks include demonstrating the DMFC charger’s functionality in the hands of real users while also providing feedback for potential design improvements. This field test will be the first time a significant number of MTI units will be put into the field to test usability and functionality. This field test will generate user feedback on product viability as well as identify potential improvements. The fuel cell charger will be ready for commercialization at the completion of this project.

Results

A major focus of this project was to reduce the cost of MTI’s DMFC-powered charger to attain a competitively priced product when in production. To achieve a low-cost system many of the components had to be redesigned so that they could be produced using low-cost, high-volume, manufacturing processes. The system also had to be redesigned for ease of assembly to increase build yield and reduce the amount of labor content needed. In addition, the assembly process had to be simplified so that technicians and assemblers could perform the assembly rather than engineers and scientists.

During Phase 1 of this project many parts and process steps were completely eliminated or were significantly simplified. In one instance a complete subassembly, with all associated cost and reliability issues, was eliminated. Phase 1 of the project was completed during the fall of 2009 and there was a successful Go/No-Go review meeting that occurred on November 5, 2009 at MTI’s facility in Albany, NY. At the completion of Phase 1 almost all components were redesigned for reduced cost and high-volume manufacturing. The following are examples of component redesigns implemented to reduce cost and make the components capable of being manufactured using common, low-cost, high-volume manufacturing processes:

- Plastic components previously machined were designed to be injection moldable.
- Sheet metal components previously machined were redesigned to be stamped and coined.
- Laser cut free-standing gaskets were redesigned to be profiled gaskets, either over-molded onto components they seal or otherwise easily placed.
- Many adhesives and small bridge plates were completely eliminated by integrating their function in other interfacing components.

There were several performance improvements achieved at the engine/stack subsystem level. Figure 1 demonstrates an engine/stack completing over 6,000 hours of operation with a decay rate of only 5% per 1,000 hours. This decay rate was achieved on multiple engine/stack subsystems.

The engine stack subsystem also demonstrated increased performance for membrane electrode assembly (MEA) power density. Figure 2 shows the power density of 85 mw/cm² and 100 mw/cm² corresponding to two different fuel feed rates. Part of this achievement was due to engine/stack design changes that enable the engine to efficiently consume methanol at higher fuel feed rates. In past engine/stack designs there was a substantial efficiency fall off at higher fuel feed rates. Figure 3 shows the stack/engine life test obtaining both high power density and relatively high fuel efficiency at increased fuel feed rates.

During Phase 2 of the project, tools were fabricated and parts were produced for evaluation of the design intent. This required several iterations of part, tool and process changes until the parts produced off of the tooling met the design requirements. Comprehensive
subsystem level testing was carried out to quantify the impact the redesigned subsystems had on durability and performance. There was also a significant amount of system integration work done to bring the new lower cost subsystems together. Testing at the system level was used to verify that the system is capable of operating well during transients such as start-up and shut-down and at all specified temperatures, humidity, and orientations.

At the system level there were several configuration changes that required system integration activities followed by complete system characterization testing. Testing at the system level included:

- Algorithm development
- Performance and qualification testing:
  - Sound testing
  - Cold and hot ambient start-up
  - Surface temperature measurement
  - Drop testing
  - Temperature and humidity latitude (0-40°C, 0-90% RH)
- Life testing
  - Steady-state decay rate
  - Start-stop decay rate

**Conclusions and Future Directions**

- High power density and high fuel efficiency has been achieved simultaneously.
- Low stack degradation rate exceeding product requirements has been demonstrated.
- Performance of system at temperature and humidity latitude (C-40°C, 0-90% RH) has been demonstrated.
- Phase 3 field test underway:
  - First units shipped in June.
  - Participants identified for the field trail.
  - Field trial feedback forms designed.

The main area of future work for this project is to complete the field test successfully. Support for the fuel cell units in the field with additional cartridges and quickly addressing any issues that arise is important to obtaining the maximum amount of useful information from the field test. Areas of particular interest in the evaluation are the user interface, field reliability and performance, and determining new user preferences.

**FY 2010 Publications/Presentations**

XI.2 Solid Oxide Fuel Cell Diesel Auxiliary Power Unit Demonstration

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Contract Number: DE-EE0000478

Subcontractors:
• PACCAR, Inc., Bellevue, WA
• TDA Research, Inc., Wheat Ridge, CO
• Electricore, Inc., Suite 105, Valencia, CA

Project Start Date: August 1, 2009
Project End Date: January 31, 2012

Objectives

• Design, develop and demonstrate a 3-5 kW solid oxide fuel cell (SOFC) auxiliary power unit (APU) for heavy-duty commercial Class 8 trucks.
• Utilize Delphi’s next generation SOFC system as the core power plant and prove the viability of the market opportunity for a 3-5 kW diesel SOFC system.

• Test and demonstrate the diesel APU system in a high visibility fleet customer vehicle application that will support hotel loads and other real-world operating conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) Durability
(B) Cost
(C) Performance
(G) Start-up and Shut-down Time and Energy/Transient Operation

This project also is key to the development of the SOFC technology specific to the transportation industry which will have the opportunity to create new high tech jobs while maintaining and growing existing technical and non-technical jobs. The long-term economic impact can be very significant and will enable America’s dominance in this area.

This project in conjunction with other efforts is assisting in enabling the acceleration of Delphi’s commercialization goals for SOFCs which are in line with the DOE Fuel Cell Team’s ARRA project goals of accelerating the commercialization and deployment of fuel cells and fuel cell manufacturing, installation, maintenance, and support services.

<table>
<thead>
<tr>
<th>TABLE 1. APU (3-5 kW rated, 5-10 kW peak) Actuals</th>
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<td><strong>Technical Targets : 1-10 kW SOFC Auxiliary Power Units (1)</strong></td>
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<td>Cycle Capability (from cold start) over operating lifetime</td>
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<tr>
<td>Operating Life</td>
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<tr>
<td>Start-up time</td>
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</table>

1 Operating on Standard Ultra-Low Sulfur Diesel
2 Initial targets for program as defined in 2003 SOPO
3 Regulated DC Net/Lower heating value of fuel
4 Heavy duty truck market is highly price sensitive.
5 < 50 System Cycles but >200 stack Cycles
Accomplishments

- Completion and submission of Delphi’s Hydrogen Safety Plan and National Environmental Policy Act documentation.
- Completed initial system specifications and commercial requirements.
- Completed system design and layout.
- Initiated component fabrication.
- Completed initial on-vehicle testing/demonstration.
- Completed initial system (Level A) and subsystem vibration testing and analysis.
- Onsite project review with DOE.

Introduction

Based on previous APU work with DOE Topic 2 contract DE-FC56-04GO14319, Delphi has teamed with heavy-duty truck manufacturer PACCAR Incorporated (PACCAR), and catalysts and advanced materials firm TDA Research, Inc. to develop, test and demonstrate a diesel APU that will meet or exceed the 2010 development targets for APUs.

In addition, Delphi has identified the following barriers that must be addressed:
- System Vibration Robustness
- Packaging/Size (Form factor)
- System Weight
- System Cost
- System Manufacturability
- System Durability/Reliability

The project will test and demonstrate the diesel APU in a high visibility fleet vehicle that will provide power for vehicle hotel loads and other needs under “real world” operating conditions. There will also be a series of in-house tests, including on-vehicle testing, to validate the “road worthiness” of the diesel APU prior to installation on the demonstration truck. The primary focus will be the acceleration of the development and acceptance of the diesel APU by the Class 8 heavy-duty truck market. The project will also focus on meeting the 2015 technical targets specified within this project. Delphi will demonstrate an integrated SOFC APU system on an in-service long-haul Class 8 commercial truck. The project will include:
- Operating data from at least one field unit at a customer site.
- Degradation analysis including failure mode analysis.
- Projection of system lifetime.

Approach

Based on manufacturer, market and DOE requirements, Delphi will develop, test and demonstrate a next generation diesel APU (Gen5 APU) that will meet or exceed current development targets. Working with PACCAR, Delphi will create a detailed application and commercial requirements list for the diesel Gen5 APU for on-board auxiliary power. These along with DOE requirements will become part of a comprehensive system specification. The specifications include:
- Application requirements and metrics formalization;
- Defining of real-world, on-road operating conditions for the APU;
- Defining electrical load duty cycles for testing the APU; and
- Obtaining load cycles from PACCAR for system electrical testing.

Delphi will focus on several key enabling developments in order to implement the new APU. The new Gen5 APU that will be developed as part of this project will then be deployed as the demonstration unit. Data from this unit will be collected, analyzed, and reported in the final report.

Results

Delphi has updated the customer requirements using Peterbilt as the primary point of contact. The document was updated for size; mass; forecast thermal cycles; and reliability. With that information, Delphi modified the existing APU to the Gen5 APU configuration (see Figure 1 for the basic outline).

FIGURE 1. DPS3000D Design Level A Layout
Conclusions and Future Directions

The project is on target and will meet the budget and timing requirements. During this next year Delphi will complete the following:

- System/Subsystem Build and Test
- System Integration
- System Characterization
- Demonstration Initiation

FY 2010 Publications/Presentations:

XI.3 Highly Efficient, 5 kW CHP Fuel Cells Demonstrating Durability and Economic Value in Residential and Light Commercial Applications

Introduction

The high-temperature proton exchange membrane (PEM) fuel cell system is the culmination of a nine-year technology development effort that has produced numerous technical innovations. Plug Power began exploring the application and feasibility of high-temperature PEM technology in 1999 with the creation of an “Alpha” system to demonstrate technical feasibility. It was quickly evident that the high-quality heat produced and the resulting system simplification would make this a preferred technology for micro-CHP applications—one that held the promise of a commercial, grid-connected, stationary fuel cell product that provided a cost benefit to the end user. Indeed, high-temperature PEM technology offers a unique value proposition over low-temperature PEM systems in applications where heat utilization is required. In a low-temperature system, the quality of the heat supplied is insufficient to meet consumer needs and comfort requirements, so peak heaters or supplemental boilers are required. Low temperature systems operate between 55 and 75°C and after capturing the heat and delivering it to an end use the resultant temperature is a maximum of around 50°C preventing it from being used as a stand-alone heating device. By contrast, the higher operating temperature of the polybenzimidazole (PBI) membrane technology allows the fuel cell to operate at temperatures that can produce heat sufficient to meet the comfort demand without the additional equipment.

GenSys Blue is a pre-commercial, 5 kW, natural gas-fueled product technically ready to be demonstrated in real-world residential and light commercial installations. There are no major technical risk areas to be described. Further refinements in the areas of PBI technology, stacks, advanced controls, and fuel reforming will be made from the standpoint of design hardening or design for manufacturing criteria, as Plug Power begins to separate technology development from product development with this fuel cell system.

Objectives

- Demonstrate the durability and economic value of GenSys Blue.
- Verify its technology and commercial readiness for the marketplace.

Relevance to ARRA and DOE-FCT Goals

- Deploy 12 GenSys Blue, natural gas-fueled, micro-combined heat and power (CHP) fuel cell units that provide economic savings and environmental benefits for residential and light commercial users.
- Maintain five U.S., high-tech jobs in New York State and provides work for U.S. suppliers and field service contractors.

Accomplishments

- Controls and efficiency improvements resulting in faster start-ups, thermal response time, heat modulation and increased total efficiency from 89 to 94%.
- Manufacturability improvements to enclosure, piping, insulation and wiring which has reduced build time from over 120 hours to below 50.
- Reduction in material cost from $90k to $58k in volumes less than 20 units.
- Steady-state system model was developed and much progress made on the dynamic model.
- Long-term reliability testing established in Plug Power labs with over 3,500 run hours demonstrating, increasing reliability and decreasing failure rates.

Introduction

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GenSys Blue is a pre-commercial, 5 kW, natural gas-fueled product technically ready to be demonstrated in real-world residential and light commercial installations. There are no major technical risk areas to be described. Further refinements in the areas of PBI technology, stacks, advanced controls, and fuel reforming will be made from the standpoint of design hardening or design for manufacturing criteria, as Plug Power begins to separate technology development from product development with this fuel cell system.
**Approach**

Plug Power is executing a demonstration project that will test multiple units of its high-temperature, PEM fuel cell system in residential and light commercial micro-CHP applications in California. The specific objective of the proposed demonstration project is to substantiate the durability of GenSys Blue, and, thereby, verify its technology and commercial readiness for the marketplace. In the proposed demonstration project, Plug Power, in partnership with the National Fuel Cell Research Center (NFCRC) at the University of California, Irvine (UCI), and Sempra, will execute two major tasks:

- **Task 1**: Internal durability/reliability fleet testing. Six GenSys Blue units will be built and will undergo an internal test regimen consisting of typical residential load profiles to estimate failure rates.

- **Task 2**: External customer testing. Six GenSys Blue units will be installed and tested in real-world residential and light commercial end user locations in California.

**Results**

Five percent of Plug Power’s employees are supporting this effort maintaining an internal and external reliability fleet of 12 GenSys Blue natural gas power systems. Automotive suppliers are delivering stack, reformer and balance of plant components.

The NFCRC at UCI began its dynamic modeling efforts of the GenSys Blue system this year. The team began with the modification of an older SU-1 based model to a high-temperature PBI model. SU-1 was Plug's attempt to penetrate the residential market with low-temperature PEM technology. After achieving reasonable correlation with a simplified system model, the team’s focus became the integration of the system components, including autothermal reformer, anode tail-gas oxidizer, cathode recirculation and the burner model.

Sempra Energy and members of the Plug Power team have begun to finalize the list of sites for the California fleet and have begun preliminary planning and design. In evaluating homes as installation candidates, the criteria for selection consists of the owner being a Sempra Energy employee with an understanding of the technology, a home with a persistent need for the generated heat (presence of a heated pool or equivalent), a home with close proximity to UCI and with upper-half California population electrical requirements. Sempra received a robust response to their polling for volunteers and three leading candidates have been down selected. The final selection process should be complete by the end of July.

With the “go ahead” from DOE to begin work on this project after its award but prior to contract signing, the team ordered the parts and began building the systems to the upgraded design. To date, Plug Power has received in roughly $740,000 in materials. This material has enabled the assembly of the first six systems which have been installed and are currently in test within our labs. Additionally, 70% of all critical components and long lead items have been received for the next three systems.

The team commenced long-term reliability testing on the internal fleet installed in Plug Power labs (Figure 1). Each system is being tested according to a predetermined test plan with the goal of generating preliminary fleet reliability statistics which we can use to make engineering improvements and programmatic decisions. It is this information that will allow us to gauge our readiness for the commercial market.

The project is experiencing a high number of facility, test equipment and program issues causing uncharged downtime. While we do not count facility related shutdowns against reliability statistics, there is a strong likelihood that these failures, which would rarely be seen in the field, cause damage to systems. We have attempted to add hardware and software provisions against these accidents (such as loss of natural gas supply) but their impact (fuel starvation, for example) must be evaluated in reviewing long term test results. Raw reliability numbers and system degradation rates should be considered conservative when viewed against these disturbances (Table 1).

A noted noise factor in our test plan is our inability to closely control the ambient temperatures in which the systems operate. This makes cabinet temperature and heat loss vary from system to system as they are commissioned between January and May. Three systems began operation in January with an ambient temperature...
of ~10°C. The remaining systems are seeing ambient temperature ranges of 20-30°C for their first 1,000 hrs.

Another noise factor is the introduction of control upgrades as the team learns about the long-term operation of the system. These will allow newer systems to operate more robustly as control upgrades are implemented. This process is inevitable but must be considered when evaluating overall fleet reliability trends.

The statistical significance of the current data is moderate with relatively high confidence intervals since collected run hours per system average below 1,000 hrs. The team's confidence in the data set will improve dramatically over the next quarter when average run times per system should be well over 2,000 hours with a fleet total of over 10,000 hours. At this point the team will feel more comfortable using conclusions from the fleet to guide program decision making and investment.

The failure and maintenance call rate has a decreasing trend. March 2010 data is mostly an accumulation of three systems worth of data for three months of operation. April 2010 data is the cumulative reliability statistics of four months of operation with four systems (Fox Trot3 is commissioned in March).

Controls, thermal management and air delivery module problems dominate as the cause of unscheduled shutdown events. Failure modes unique to 2010 hardware improvements have been discovered and highlighted. Controller lockups due to software bugs and stepper motor position losses were the major contributors to downtime. Coolant leaks did not cause a downtime but counted as failures. All failures were contained and controls provisions are added to resolve the issues.

The fleet has experienced one stack failure in system EpsilonPlus9 after just less than 1,600 hours of operation (~1,000 hours debug and 580 hours reliability test). This stack was suspect upon commissioning and was useful in debugging the system and collecting runtime hours until a replacement could be built. The team believes the stack failed due to an internal coolant leak and it is scheduled for autopsy and analysis (Figure 2).

In the past year the team participated in community events designed to increase the public’s awareness and education level regarding renewable energy in general and micro-CHP technology in particular. The first event was showcasing a GenSys Blue system at Union College in Schenectady, New York for their alumni day. Members of the team explained the system and its economic benefits to over 50 Union College alumni, members of the faculty and their families. The second event was also a showcase at Ballston Spa High School in Ballston Spa, NY for the annual New York State Science, Technology, Engineering and Mathematics Educational Collaborative where team members introduced the system and its benefits to New York State educators from all over the state.

### Conclusions and Future Directions

The internal test fleet is built and commissioned. A reliability activity complete with metrics has been established. Sites have begun to be selected for the external customer testing in California. Future milestones include:

- First Go/No-Go decision.
- Completion of the system model by NFCRC.
- Ship six systems to California.
- Maintain the reliability fleet, capturing requirements from the California market.

---

**TABLE 1. GenSys Blue Reliability Fleet Statistics**

<table>
<thead>
<tr>
<th>System</th>
<th>Commissioned Date</th>
<th>System Runtime (hours)</th>
<th>Current Stack Runtime</th>
<th>Blame Runtime</th>
<th>Electrical kWh</th>
<th>Thermal kWh</th>
<th>Startup Reliability</th>
<th>Heat Operational AQI</th>
<th>CHP Operational AQI</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epsilon Plus9</td>
<td>1/8/2010 14:46</td>
<td>720</td>
<td>898</td>
<td>3686</td>
<td>5624</td>
<td>0.96</td>
<td>1.00</td>
<td>1.06</td>
<td>Stock in Union system since mid Feb</td>
<td></td>
</tr>
<tr>
<td>Epsilon Plus9</td>
<td>1/11/2010 15:14</td>
<td>589</td>
<td>791</td>
<td>6925</td>
<td>5921</td>
<td>0.84</td>
<td>0.93</td>
<td>0.32</td>
<td>Needs new stack, original stack did not run since 1/7/200</td>
<td></td>
</tr>
<tr>
<td>Fox Trot2</td>
<td>1/8/2010 14:46</td>
<td>1403</td>
<td>1064</td>
<td>2086</td>
<td>1403</td>
<td>0.94</td>
<td>0.94</td>
<td>0.65</td>
<td>Running on high demand load</td>
<td></td>
</tr>
<tr>
<td>Fox Trot3</td>
<td>3/2/2010 10:47</td>
<td>657</td>
<td>1193</td>
<td>4217</td>
<td>0.95</td>
<td>0.93</td>
<td>0.93</td>
<td>0.98</td>
<td>Running at demand load profile</td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

**FIGURE 2. Fleet Failure Mode Allocation**

The failure and maintenance call rate has a decreasing trend. March 2010 data is mostly an accumulation of three systems worth of data for three months of operation. April 2010 data is the cumulative reliability statistics of four months of operation with four systems (Fox Trot3 is commissioned in March).

Controls, thermal management and air delivery module problems dominate as the cause of unscheduled shutdown events. Failure modes unique to 2010 hardware improvements have been discovered and highlighted. Controller lockups due to software bugs and stepper motor position losses were the major contributors to downtime. Coolant leaks did not cause a downtime but counted as failures. All failures were contained and controls provisions are added to resolve the issues.

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XI.4 Advanced Direct Methanol Fuel Cell for Mobile Computing

Objectives

- The project objective is to develop a direct methanol fuel cell (DMFC) power supply for mobile computing using the novel passive water recycling technology acquired by UNF from PolyFuel, Inc., which enables significant simplification of DMFC systems.

- The objective of the 2010 effort to date is to define the system concept and develop the required design requirements (system, sub-system, and component) in order to achieve the 2010 technical targets. Initial component development effort, based on the component design requirements (CDRs), is nearly completed.

Technical Barriers

- Storage Degradation - The prototype stack technology developed previously by PolyFuel displays a moderate level of degradation during storage, which needs to be understood and possibly mitigated before such technology can progress into commercialization. Extensive testing continues to refine hypotheses and zero in on root causes for such degradation. Recent testing has identified at least one factor and has also shown some degree of reduction is such degradation with extended time. As there are no qualified accelerated tests for this important barrier, such testing will continue in parallel with other activities for the duration of the project.

- Integration of Component Subsystems - Engineering efforts to create integrated subsystems which meet functional and power density targets and are also on the design path toward volume production is the near term technical barrier to be overcome. New components are being designed and evaluated to meet aggressive technical targets and brassboard testing is planned in the coming quarter.

Technical Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>UNF 15 W DP3 2008 Status</th>
<th>DOE 2010 Target</th>
<th>UNF Proposed 20 W System Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Powera</td>
<td>W/kg</td>
<td>35</td>
<td>100</td>
<td>54</td>
</tr>
<tr>
<td>Power Densitya</td>
<td>W/L</td>
<td>48</td>
<td>100</td>
<td>63</td>
</tr>
<tr>
<td>Energy Density</td>
<td>W-hr/L</td>
<td>250 (1 x 100 ml)(^b)</td>
<td>1,000</td>
<td>198 (1 x 100 ml)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>396 (1 x 200 ml)(^b)</td>
<td></td>
<td>313 (1 x 200 ml)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>507 (3 x 200 ml)</td>
</tr>
<tr>
<td></td>
<td>W-hr/kg</td>
<td>155 (1 x 100 ml)(^b)</td>
<td>N/A</td>
<td>180 (1 x 100 ml)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>247 (1 x 200 ml)(^b)</td>
<td></td>
<td>302 (1 x 200 ml)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>532 (3 x 200 ml)</td>
</tr>
<tr>
<td>Lifetimec Operating</td>
<td>Hours</td>
<td>1,000 hrs in single cell</td>
<td>5,000</td>
<td>2,500 Integrated System</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11 (est. in volume)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost</td>
<td>$/Watt</td>
<td>&lt;3</td>
<td>&lt;10</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Beginning of life, 30°C, sea level, 50% relative humidity, excluding hybrid battery, power module alone.

\(^b\) Normalized from DP3 data from 150 ml cartridge to either 100 ml or 200 ml for comparison purposes.

\(^c\) Lifetime measured to 80% of rated power.

N/A – not applicable

This project will contribute to the relevance of DOE’s objectives for ARRA projects in general and the DMFC projects in particular.

- Create direct and supporting jobs nationwide as the UNF fuel cell technology becomes commercially available.

- Reduce the necessity and use of the power grid as fuel cells power increasing numbers of portable electronic devices, thereby creating more “green” jobs.

- Create more business activity in the fuel cell supply industry.
• Expand the user base of new alternative power technologies.
• Increase the level of competition among producers of alternative energy technologies.

While this project is recently funded (January 1, 2010), significant milestones to date are:
• CDRs – 90% complete
• Design failure mode effects and analysis (FMEA) – 25% complete
• Key subsystems prototypes – 25% complete
• Fuel cartridge prototype – 25% complete
• Numerous other tasks at least 20% complete

Approach

The approach of the project is to develop a revised set of CDRs based on concept design that integrates revised component packaging and integration of key sub-systems. The focus of the approach is to both miniaturize balance-of-plant components and integrate them into sub-systems such as the fuel recirculation pump, the carbon dioxide separator and the retained liquid reservoir. These components will be rigorously tested individually, as sub-systems, and ultimately at the system level. Initially, existing components will be evaluated for durability and failure modes, and the results will be used to help further define component requirements. Once available, the new design prototype components will be evaluated for durability and robustness. As functional performance data from component and integrated sub-system testing become available, the system model will be refined to reflect the optimized performance characteristics. Sub-systems will be integrated for testing, first onto a brassboard enabling detailed instrumentation of the system and verification of sub-system design, and then into an integrated package with auxiliary instrumentation. Control system development will optimize the key operational protocols for start-up, rest/rejuvenation, and shut-down to optimize operating lifetime and minimize both operational and storage degradation rates. A test plan driven by the consumer electronics performance requirements for operational and storage degradation rates and nominal and extreme operating conditions will establish a benchmark for a statistically significant sample of systems for a thorough evaluation of durability and robustness of the system.

Accomplishments

The project was initiated in January 2010. Major accomplishments are:
• Submitted a hydrogen safety plan.
• CDRs completed.
• System design review with project members.
• Membrane electrode assembly prototype production facility online.

Future Directions

• Complete FMEA.
• Complete component development and rigorous testing.
• Assemble brassboard system for system testing.
• Key Milestone: Demonstrate component performance meets requirements.
• Complete development of advanced control strategies.
• Integrate components and sub-systems into packaged unit.
• Test the system extensively to evaluate performance, robustness, and durability.
XI.5 Jadoo Power Fuel Cell Demonstration

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E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Gregory Kleen
Phone: (503) 275-4875
E-mail: Greg.Kleen@go.doe.gov

Contract Number: DE-36-09GO0000479
Subcontractor:
Delphi Corporation, Troy, MI

Project Start Date: January 1, 2010
Project End Date: January 31, 2012

Objectives

- The development of two portable electrical generators in the 1,000 watt range utilizing solid oxide fuel cells (SOFCs) as the power element and propane as the fuel.
- The development and demonstration of a proof-of-concept electro-mechanical propane fuel interface that provides a user-friendly capability for managing propane fuel in a manner that supports the widespread adoption of fuel cells.
- The deployment and use of the fuel cell portable generators to power media production equipment over the course of several months at multiple high profile automobile racing events staged in multiple locations throughout the United States.
- The deployment and use of the fuel cell portable generators at scheduled events by first responders (police, fire) of the City of Folsom, California to power equipment in emergency and/or off-grid situations.
- Capturing data with regard to the systems’ ability to meet DOE technical targets and evaluating the ease of use and potential barriers to further adoption of the systems.

Technical Barriers

- Reducing stack and balance of system to size allowing portability.
- Reliability of SOFC system under rough field conditions.
- User factors related to start-up times and refueling.
- Effectiveness/complexity of processing propane to remove sulfur.
- Potential constraints on type or source of propane.

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

(A) Durability
(C) Performance
(E) System Thermal and Water Management
(G) Start-up and Shut-down Time and Energy/Transient Operation

Relevance to ARRA

The Jadoo project will result in the saving of five to six jobs at Jadoo Power and Delphi Automotive. Longer term, the project will provide data in a high-profile environment to potential users of fuel cell generators, and hence will ultimately spur economic activity by promoting the procurement of more fuel cell generators for similar applications.

The project also is relevant to the DOE-FCT’s ARRA project goals by accelerating the commercialization and deployment of fuel cells and fuel cell manufacturing, installation, maintenance and support services for these fuel cells.

Technical Targets

<table>
<thead>
<tr>
<th>TABLE 1. Generator Performance Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metric</strong></td>
</tr>
<tr>
<td>Power (Continuous)</td>
</tr>
<tr>
<td>Efficiency (Peak)</td>
</tr>
<tr>
<td>Noise</td>
</tr>
<tr>
<td>Start-Ups &amp; Cycles</td>
</tr>
<tr>
<td>Operating Hours</td>
</tr>
</tbody>
</table>

- Propane desulfurizer to reduce the level of sulfur in propane to less than 10 ppb for eight continuous hours.
• Propane fuel interface that can indicate the amount of propane within ± 10% of the actual amount for the entire range from full to empty.

Approach

This project will develop and install two SOFC systems in "real world" portable generator applications in order to ascertain that applicability of fuel cell solutions with respect to operational requirements and constraints, portability, and ease of use. Data capture will be done with regard to the systems’ ability to meet DOE technical targets and potential barriers to further adoption of the systems.

Two portable generators will be developed by leveraging parallel work by Delphi related to the use of SOFCs in truck auxiliary power unit applications. Delphi SOFC technology will be modified and packaged for portable application with alternating current power capability. Delphi will develop a desulfurizer to allow use of commonly available propane as the fuel source. Delphi will also develop a reformer for commonly available propane fuel. Jadoo Power will develop an electromechanical fuel interface by leveraging prior learning from development of an interface between proton exchange membrane fuel cells and metal hydride canisters, used in both government and commercial applications. Both SOFC systems will have final validation at the Jadoo facility prior to initial deployment at the City of Folsom. The systems will then be deployed and transported between multiple National Association of Stock Car Racing events to evaluate ruggedness, portability and suitability for “real world” applications.

This project’s environmental and safety plans for both hydrogen and propane for both the Delphi site and the Jadoo site, in addition to the test sites, are presently under development and will be based on prior environmental and safety plans of both Delphi and Jadoo.

Accomplishments

• Analyzed drawbacks for police and fire agencies of utilization of gasoline-powered generators.
• Conducted site survey of National Association of Stock Car Racing event and gathered site-specific baseline load data on media equipment power requirements.
• Researched propane industry standards and practices for storage, transport, safety and measurement of propane fuel, including methods of propane fuel level measurement, tank designs and sizes.
• Compared various current industry technologies and methodologies for measurement of propane levels.
• Evaluated potential of applying existing technologies and methodologies to a portable SOFC propane fueling system.
• Determined potential factors that may relate to application requirements for portable fuel cell propane tank fuel level determination, operation and safety.
• Surveyed current fueling and fill status monitoring techniques, evaluated capabilities and drawbacks, and developed set of potential solutions for this application.
• Developed preliminary requirements for fuel interface.
• Developed generic requirements for a portable generator.
• Facility support of propane complete.
• Reformer testing has begun.
• Blue Rhino propane characterization test complete. Data currently being analyzed.
• Desulfurizer hardware for performance testing has been delivered and on schedule for test start.
• System start-up requirements have been evaluated.
• Fuel delivery system design 75% complete.
• An environmental and safety plan has been developed in its basic form, and will be expanded to provide coverage to all manufacturing and test sites.

Future Directions

• Requirements definition complete
• Applications specifications design review
• System design – generator
• System design – desulfurizer
• Demonstrate sulfur removal – less than 10 ppb for eight hours
• System design – propane fuel canister interface
• Build and test generators
• Build and test propane fuel canister interface
• Demonstrate state-of-fill performance at ± 10%
• Demonstrate generation of 1 kW for eight hours
• Deployment, demonstrations and field tests
• Follow up tests, analysis and report generation

FY 2010 Publications/Presentations


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DOE Technology Development Manager: Ned Stetson
Phone: (202) 586-9995
E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: James Alkire
Phone: (303) 275-4795
E-mail: James.Alkire@go.doe.gov

Contract Number: DE-EE0000487

Subcontractors:
• Fortune Wireless, Indianapolis, IN
• Betacom, Inc., Pompano Beach, FL
• United Commercial Real Estate Services, Inc., Lake Mary, FL
• Peek Site-Com, Inc., Auburn, CA
• Jeffrey Rome and Associates, Newport Beach, CA
• Vertical Horizons Contracting, Lincoln, NE
• Telecom, Tower and Power, LLC, Romulus, MI
• Front Range Wireless, Centennial, CO
• Air Products and Chemicals, Inc. (APCI), Allentown, PA

Project Start Date: August 1, 2009
Project End Date: July 31, 2011

Objectives

• Install 189 fuel cell systems with 72-hour capacity as back-up power equipment for communications sites in use by Pacific Gas and Electric (PG&E), a California utility, and as critical emergency reserve power for cell sites operated by AT&T.
• Demonstrate that fuel cells are a reliable source of clean back-up power for key communications facilities.
• Transform the market within PG&E and AT&T by moving beyond limited demonstration sites to wider deployments.

Market Transformation Barriers

This project addresses the barriers to market transformation for stationary fuel cell equipment:

• Site Selection: myriad considerations in site selection factor into the adoption of fuel cells for backup equipment.
• Permitting: multiple stakeholders, including authorities having jurisdiction, fire officials, building officials, and landlords, all have varying perspectives and reference a variety of non-harmonized standards for permitting.
• Fueling infrastructure: this program deploys a new model for stationary hydrogen fuel cells, relying on a refillable storage module, in place of the historically used cylinder exchange model. This requires the development of a fueling infrastructure that can deliver bulk compressed hydrogen to small, geographically diverse, remote sites.

Relevance to the goals of the American Recovery and Reinvestment Act (ARRA) of 2009, and to the goals of U.S. DOE Fuel Cell Technologies’ (FCT) ARRA project for accelerating the commercialization and deployment of fuel cells and fuel cell manufacturing, installation, maintenance, and support services.

This project will contribute to achievement of the DOE’s objectives for ARRA projects in general, and the FCT projects in particular:
• Create direct and indirect jobs in seven regions across the continental U.S., throughout the supply chain.
• Train and deploy installers of fuel cell systems.
• Increase the number of commercially available fuel cell systems.
• Generate volume for fuel cell supply chain.
• Create and deploy new refillable hydrogen storage for stationary hydrogen fuel cells.
• Create and deploy new hydrogen delivery model for stationary hydrogen fuel cells.
• Expand practical user operating experiences.
• Validate performance.

This project includes milestones to measure progress:
• Survey candidate sites to identify 189 sites for installation.
• Secure all permitting, site acquisition, lease amendments, etc. to proceed with installations.
• Manufacture, ship, install, and commission 189 stationary fuel cell sites.
• Collect data on operation, fuel service, and maintenance.
Accomplishments

- Submitted required documentation for National Environmental Policy Act (NEPA) clearance, and received a categorical exclusion.
- Submitted a hydrogen safety plan.
- Reviewed database records of 654 candidate AT&T sites to down-select sites based on the feasibility of fuel cell installation and on-site refueling accessibility.
- Performed physical site surveys at 460 candidate AT&T sites to further down-select sites based on the feasibility of fuel cell installation and refueling accessibility.
- Generated and delivered 380 unique quotes for the 180 AT&T sites to be constructed.
- Processed 509 unique purchase orders from AT&T Procurement for equipment, site acquisition (SAC) services, fuel cell installation services, and supplemental shelter direct air cooling equipment and installation services.
- Initiated the SAC process (leasing, zoning/planning, permits, etc.) on 188 AT&T sites.
- Completed the SAC process for 16 AT&T sites.
- Fabricated, integrated, and delivered fuel cell equipment for 132 sites, and hydrogen storage modules (HSMs) for 69 sites.
- Constructed and commissioned eight sites and provided hand-off to the customer.
- Performed physical site surveys at 36 PG&E candidate sites to evaluate the feasibility of fuel cell installation.
- Generated 25 unique scopes of work for PG&E sites to be constructed (customer subsequently selected nine of these viable sites).
- Completed all contract negotiations with PG&E and processed the final purchase order for the installation of fuel cells at nine sites in the PG&E network.
- Fabricated and integrated nine sets of fuel cell equipment for all nine PG&E sites.
- Developed the methodology, and validated the equipment and network architecture required to remotely obtain operational data from the sites in order to satisfy the National Renewable Energy Laboratory (NREL) data gathering obligation.

Introduction

Market transformation is best achieved by reaching a critical mass in the market that significantly raises awareness and direct experience of the value proposition. With the assistance of this project, ReliOn is installing 189 fuel cell systems into the telecommunications and utility networks at AT&T and PG&E for back-up power, across nine states, combined with the deployment of a refillable stationary HSM unit and the accompanying refueling logistics platform for 180 AT&T sites. These are real-world, tangible changes to the market resulting in the use of hydrogen-based systems to harden critical communications networks.

Approach

ReliOn’s approach begins with the basic research needed to identify viable candidate sites and then narrow down the list in order to focus efforts on the most viable and critical sites that can be installed and refueled successfully, ensuring that these assets will remain viable for decades. This work is primarily performed by ReliOn personnel. The next task is to secure rights to perform the construction through the use of SAC vendors who structure the leasing and permitting packages to prepare the sites for construction. ReliOn utilizes third parties who are skilled in this profession and will remain part of the project until all SAC activities have been completed.

As a site clears the SAC process, it is then constructed (typically within 15 business days) and brought on-line as a fully functional back-up power system. Installation construction is performed only after the SAC vendor has secured the installation and operating rights for each site. ReliOn utilizes third parties to perform installation construction, yet retains the roles of project management and supervision. ReliOn partnered with an established hydrogen provider, APCI, an industry expert in hydrogen storage and delivery for the development and production of the HSM. Once the sites are installed, fueled and operational, they are monitored remotely for data collection. ReliOn personnel collect and report fuel cell operational data to NREL. The use of both ReliOn and third party resources maximizes the effectiveness of the project, creates or retains jobs across a breadth of companies and regions, and delivers the maximum amount of infrastructure for the given financial investment.

Results

To date, ReliOn has completed the site qualification stage for the entire project. This has allowed for the successful initiation of SAC activities on all target sites, plus a few reserve sites as contingencies for sites that may fail to complete the SAC process due to unforeseen circumstances. SAC has been completed on the first 16 AT&T sites. ReliOn has installed fuel cells at eight sites to date with eight more sites pending construction. Of the eight sites installed, three systems are installed in Colorado and five systems installed in Utah. This ongoing process of SAC approval and site construction
has resulted in the continuous need for labor and has secured multiple jobs. PG&E performed the SAC of their nine sites using their internal real estate and legal department resources, and PG&E construction will commence in August of 2010.

Figure 1 shows the first site completed within the project. This is an AT&T site located in Arvada, CO. This fuel cell system is on-line and fully operational. The leftmost cabinet is the fuel cell equipment enclosure with an adjacent 6-cylinder hydrogen storage cabinet. The larger cabinet to the right is the HSM. The HSM is connected to the system in parallel with the 6-cylinder hydrogen storage cabinet, and contains the majority of the fuel capacity.

Figure 2 shows the second site completed within the project. This is an AT&T site located in Byers, CO. The photograph shows the HSM cabinet receiving its initial fueling from the bulk hydrogen refueling vehicle.

This project deploys fuel cell systems into eight states as shown in Figure 3, though it promotes jobs and supports business in other states which are the home bases of various subcontractors. AT&T will have systems operating in all eight states. As a California utility, all of PG&E’s systems are located within California. As discussed earlier, the SAC activity is a primary task which must be completed before fuel cell system installation construction can commence. Figure 4 shows the original schedule for the AT&T SAC activity, and progress made towards this goal. Delays in ‘SAC Initiation’ during the months of February and March were the result of end-user corporate approval processes which were completed at the beginning of the second quarter of 2010. Once ReliOn received approval to proceed, sites were released to begin the SAC process, and the schedule was recovered.

Conclusions and Future Directions

During the past year of effort, ReliOn has learned that the initial site identification process is much more
involved than originally anticipated. Many sites that the ReliOn field survey engineer qualified as serviceable based on an acceptance rubric provided by APCI for refueling vehicle access were subsequently rejected during secondary surveys by APCI drivers who provide the refueling service. This required the refueling vendor to be much more involved in the site selection and qualification process from the beginning. It was also discovered that the SAC process takes longer on average than original estimated by subcontractors. Where originally two months was considered an adequate gestation period for the process, in reality it was discovered that three to four months is more typical.

Tasks planned for the next year include:

- Complete the SAC process for all remaining sites within the project.
  - This activity includes working with the local authorities having jurisdiction to educate them on hydrogen safety, fuel cells, and codes and standards to resolve any questions/issues that arise during SAC.
- Construct all remaining sites and commission the equipment for hand-off to the customer/end-user.
- Obtain and report operational data to fulfill the DOE/NREL data reporting requirement.

**FY 2010 Publications/Presentations**

XI.7 Accelerating Acceptance of Fuel Cell Backup Power Systems

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Contract Number: DE-EE0000448
Project Start Date: June 1, 2009
Project End Date: December 31, 2011

Objectives
- Increase distributed power generation.
- Improve reliability and efficiency of mission critical backup power.
- Decrease fossil fuel dependencies for power generation.

Relevance to ARRA and DOE-Fuel Cell Technologies
Goals
- Demonstrates market viability and increase pull of hydrogen and fuel cell systems within our government customers/partners.
- Deploys 20 GenSys hybrid, hydrogen start/liquefied petroleum gas (LPG) or natural gas run units that provide economically viable backup power in excess of 72 hours.
- Maintains seven U.S., high-tech jobs in New York State and provides work for U.S. suppliers and field service contractors.

Accomplishments
- Warner Robins Air Force Base in Georgia and Fort Irwin in California have expressed interest in being site hosts for extended backup GenSys and Plug Power conducted a site review at Warner Robins in March 2010.
- An economically viable path to 72 hours worth of backup power with a pure hydrogen solution was not determined and the focus of the project has shifted to a successful hydrogen start with an LPG/natural gas run.

Introduction
Since 2001, Plug Power has installed more than 800 fuel cell systems worldwide. Plug Power’s prime power systems have produced approximately 6.5 million kilowatt hours of electricity and have accumulated more than 2.5 million operating hours. Intermittent or backup power products have been deployed with telecommunications carriers, government and utility customers in North and South America, Europe, the United Kingdom, Japan and South Africa. Some of the largest material handling operations in North America are currently using the company’s motive power units in fuel cell-powered forklifts for their warehouses, distribution centers and manufacturing facilities. The low-temperature GenSys fuel cell system provides remote, off-grid and primary power where grid power is unreliable or nonexistent. Built reliable and designed rugged, low-temperature GenSys delivers continuous or backup power through even the most extreme conditions. Coupled with high-efficiency ratings, low-temperature GenSys reduces operating costs making it an economical solution for prime power requirements. Currently, field trials at telecommunication and industrial sites across the globe are proving the advantages of fuel cells—lower maintenance, fuel costs and emissions, as well as longer life—compared with traditional internal combustion engines.

Plug Power has determined that extended backup power requirements of 72 hours and beyond can be best met with a hybrid GenSys solution. This system can both meet the demands of Department of Defense customers, and a broad global commercial market. At this time Plug Power was unable to determine an economically viable path to 72 hours worth of backup power with a pure hydrogen solution and has therefore stopped development of a pure hydrogen solution. The hybrid hydrogen/LPG or natural gas solution provides the economics needed for a flexible backup power solution.

Approach
This project will leverage technology from Plug Power’s two existing product lines to create a reliable power source that starts fast and runs as long as fuel is available. The project tasks and status are shown in Table 1:
TABLE 1. Project Tasks and Status

<table>
<thead>
<tr>
<th>Task</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost Analysis and Commercialization Study</td>
<td>85% complete</td>
</tr>
<tr>
<td>Site Planning and Applications Engineering</td>
<td>30% complete</td>
</tr>
<tr>
<td>Site Specific Engineering Development</td>
<td>Not started</td>
</tr>
<tr>
<td>System Builds and Factory Testing</td>
<td>20% complete</td>
</tr>
<tr>
<td>Field Deployment Go/No-Go</td>
<td>Not started</td>
</tr>
<tr>
<td>Fleet Operation and Managed Services</td>
<td>Not started</td>
</tr>
<tr>
<td>Project Closeout</td>
<td>Not started</td>
</tr>
<tr>
<td>Program Management</td>
<td>38% complete</td>
</tr>
</tbody>
</table>

TABLE 2. Telecom Cell Tower Application Comparison

<table>
<thead>
<tr>
<th>GENSYS</th>
<th>Features</th>
<th>Diesel Generator</th>
</tr>
</thead>
<tbody>
<tr>
<td>42,800 hours (5 years)</td>
<td>System Life</td>
<td>15,000 hours (1.71 years)</td>
</tr>
<tr>
<td>System, inverter, batteries</td>
<td>5 Year Capital Costs</td>
<td>3 generators, AMF panel, PIU, SMPS, batteries 2.4% more</td>
</tr>
<tr>
<td>2.4% less</td>
<td>Efficiency</td>
<td>Range: 7-21%</td>
</tr>
<tr>
<td>4.5kW point: 29.1% (Beginning of Life)</td>
<td></td>
<td>4.5 kW point: 18.5% (Beginning of Life)</td>
</tr>
<tr>
<td>LPG, potential to run on a range of hydrocarbons</td>
<td>Fuel Type</td>
<td>Diesel</td>
</tr>
<tr>
<td>&gt; 99%</td>
<td>Reliability/Availability</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>7.0 metric tons of Carbon, 0.04 g of NO₂, 0.06 g of SO₂, 0.051g of CO annually</td>
<td>Emissions</td>
<td>14.4 metric tons of Carbon, 743 g of NO₂, 49 g of SO₂, 160 g of CO annually</td>
</tr>
<tr>
<td>65 dBA at 3 m</td>
<td>Noise Level</td>
<td>75 dBA sheltered</td>
</tr>
<tr>
<td></td>
<td></td>
<td>92 dBA unsheltered</td>
</tr>
</tbody>
</table>

For the past year Plug Power has collaborated with partners the Army Construction Engineering Research Laboratory and Warner Robins Air Force Base to demonstrate market viability and increase market pull of hydrogen fuel cell systems. To date, 38 percent of the project has been completed and barriers are actively being addressed, including: cost, system reliability and market volume.

Results

Fifteen percent of Plug Power’s employees are supporting this effort to deploy 20 GenSys hybrid hydrogen start/LPG or natural gas run units. Automotive suppliers are delivering stack, reformer and balance-of-plant components.

Eighty-five percent of the cost analysis and commercialization study has been completed. The GenSys offers economic and environmental benefits over the incumbent diesel generator technology. It has a nearly threefold advantage in system life with only 20-25 percent higher maintenance cost and offers the customer a 20-30 percent decrease in power generation expense (Table 2).

An economically viable path to 72 hours worth of backup power with a pure hydrogen solution was not determined, shifting focus to the success of a hydrogen start with LPG/natural gas run. This solution provides for a more flexible backup power solution.

In March 2010 Plug Power visited Warner Robins Air Force Base in Warner Robins, Georgia to discuss its viability as a site. Warner Robins Air Force Base requires extended backup power to enable base service operations, including a server room and heating, ventilation and air conditioning. Although hydrogen is available on site its proximity to potential unit placement and logistics may be difficult and costly.
XI.8 H-E-B Grocery Total Power Solution for Fuel Cell-Powered Material Handling Equipment

Objectives

- Validate DOE market transformation activities by demonstrating fuel cell forklifts operating in highly transient environments and demonstrating a distributed natural gas-based hydrogen refilling system as a precursor to future automotive fuel cell refilling stations.
- Install one PowerTap™ hydrogen generation system and 14 PowerEdge™ fuel cell power pack units for use in the dry goods and produce sections of the H-E-B Grocery, Inc. (H-E-B), San Antonio, Texas distribution center.

Expected Outcomes

- One PowerTap™ and 14 PowerEdge™ fuel cell systems delivered, installed in forklifts and operated at the H-E-B distribution center.
- Periodic performance reports documenting results from operating systems including any safety or performance data and issues identified during the operation of the units.
- Widespread adoption of hydrogen and fuel cell technology by employing this as a best practice across the H-E-B fleet of 1,000 forklifts upon verification of the value proposition.

Relevance to ARRA and U.S. DOE Fuel Cell Technologies Goals

The project, per the methodology in quarterly reporting via grants.gov, has preserved 2.05 full-time equivalent jobs annualized. In addition, this project facilitates the fuel cell market transformation initiative by deploying 14 fuel cell power pack units and one on-site hydrogen generation system into a strategic early market application for this industry.

Other Accomplishments

- Conducted site planning and secured all required permits and insurance coverage.
- Created a site-specific service plan for both the PowerEdge™ and PowerTap™ products.
- Completed the installation of PowerTap™ hydrogen infrastructure.
- Completed the installation of 14 PowerEdge™ fuel cells in forklift trucks.
- Verified an initial productivity gain of 10% versus operation on standard lead acid batteries.

Introduction

H-E-B is a privately-held, San Antonio, Texas-based supermarket chain with 310 stores throughout Texas and northern Mexico. H-E-B management believes that fuel cell forklifts can help alleviate several issues in their distribution centers including truck operator downtime associated with battery changing (labor savings), truck and battery maintenance costs (expense savings), and reduction of grid electricity usage (environmental savings).

Currently, the H-E-B distribution center operates a total of approximately 300 Class II reach trucks and 700 Class III pallet jacks over two work shifts, for a total of 20 hours per day. There are three temperature zones in the facility, ranging from dry goods at ambient temperature, to refrigerated goods at 34°F (1°C), to freezer goods at -13°F (-25°C). The PowerEdge™ units provided will fit into Class II fork lift trucks designed for use with 1,000 Ah lead acid batteries, and are capable of operation in both the ambient and refrigerated goods temperature zones of the San Antonio facility.
Approach

The approach taken for this installation was to develop a site-specific installation plan that detailed where all hydrogen generation, compression, storage, and dispensing equipment would be placed. As the site plan was being developed, the PowerTap™ and PowerEdge™ equipment was manufactured and delivered to the H-E-B facility, where it was installed in accordance with all required codes and standards. Upon final sign-off from both the local authorities having jurisdiction and the insurance carrier, the forklift fleet was deployed for operation in the grocery and perishable sections of the distribution center alongside forklifts operating with standard lead-acid batteries. The fuel cell forklifts and the battery forklifts will operate in parallel to allow direct comparison between the two, allowing H-E-B and DOE to validate the value proposition associated with the PowerEdge™ and PowerTap™ products.

Market Transformation Barriers

As presented at the Annual Merit Review meeting on June 10th, 2010, the market transformation barriers and risks included “fuel cell operation and maintenance” and “hydrogen station operation and maintenance.”

Fuel Cell Operation and Maintenance

Nuvera conducted an engineering trial at H-E-B in early December 2009 to tune the RL25 (PowerEdge™, motive power unit) field configurable parameters for optimal performance in H-E-B’s produce warehouse. Discovered that the RL25 was not able to consistently satisfy all of the requirements of the customer's forklift duty cycle, which was considerably more intensive than any duty cycles previously measured. During the peak season demands of November-December, the duty cycle began to approach and exceed the 5 kW sustained maximum power rating of the RL25. As a high productivity warehouse, H-E-B has continually sought to move more pallets, of heavier weight, and be able to store them on higher racks. While the RL25 could effectively keep up with most of the needs of H-E-B’s produce warehouse, it could not do so over multiple shifts without requiring a change in H-E-B’s fleet operation. After extensive testing of performance and sustainable capability, as of January, 2010, 12 of the 14 trucks were transferred to the grocery warehouse for continuing operation.

Hydrogen Station Operation and Maintenance

For the infrastructure, several challenges specific to project location have been identified:

- **Environment**: High ambient temperatures required design modifications for improved cooling of both the PowerTap™ generation and compression modules. San Antonio averages 111 days per year >90°F. The hydrogen infrastructure also needed to be upgraded to withstand 120 mph winds as tropical storms are prone to come in from the Gulf Coast.

- **Electrical Power Quality**: The San Antonio grid is susceptible to frequent brown-outs and instability of the local 480 V 3-phase power. This required design modifications to reduce sensitivity to momentary disruptions or fluctuations in power.

- **Natural Gas Quality**: The San Antonio region has unusually high levels of mercaptan in the natural gas composition. This has required tailoring of the PowerTap™ desulfurizing media and the replacement schedule in order ensure high fuel processor lifetime and hydrogen purity for the fuel cell vehicles.

- **City Water Quality**: The San Antonio region also suffers from very high water hardness levels. This has required more frequent replacement of membranes in the reverse osmosis water treatment system in order to prevent scaling in the steam generation subsystem.

Results

As presented in Table 1, the build of all 14 PowerEdge™ systems and the PowerTap™ hydrogen refueling equipment was complete as of October 30, 2009. In parallel, Nuvera application engineers, working with H-E-B facility engineers, created site-specific service and installation plans. As part of the process, Nuvera conducted a survey of H-E-B’s site to identify potential locations for the on-site hydrogen generation and refueling infrastructure, and applied our knowledge of H-E-B’s fleet operation in order to minimize the travel time to the dispensing locations.

Based on the agreed site plan, Nuvera identified and provided basic training to H-E-B service personnel. The role of these service personnel is to keep the PowerEdge™ systems operational by providing a fast response to diagnosing and repairing system faults. This type of service includes scheduled preventive maintenance, basic troubleshooting, and the repair or replacement of non-safety critical items. Nuvera’s Customer Care group provided spare parts, training, data analysis, and more complex field support, including troubleshooting and repairs of safety-critical items (high pressure, high voltage).

During this process, all relevant codes and standards were identified, and working with the local authorities having jurisdiction and the H-E-B insurance carrier, all permits were obtained for site construction, installation, and operation.
The deployment process began upon establishing the final site plan, shown pictorially in Figure 1, and was completed on February 28, 2010. During this process the following tasks were performed:

**Hazards and Operability Analysis**: Ensure safe design, installation, and operation of the equipment by rigorously identifying all potential hazards, and quantifying the resulting risks.

**Site Layout**: Apply knowledge of the applicable national and local codes to ensure proper offset distances between the hydrogen generation and refueling equipment, structures, and potential hazards.

**Permitting and Approvals**: Submit the site plan to qualified professional engineer for approval.

Review the approved site plan with local authorities having jurisdiction with regard to applicable permits and approvals. Obtain applicable permits to allow commencement of site construction activities.

**Site Construction**: Prepare final site drawings for use by mechanical, electrical, and civil contractors. Source and select appropriate contractors and construct site.

**Wireless Data Collection Infrastructure**: Deploy a wireless infrastructure that collects operational and fault data from the fuel cell fleet and hydrogen generation and refueling equipment.

**Installation, Commissioning, and Training**: Deploy the fuel cell fleet and hydrogen generation and refueling equipment and complete the site acceptance test for each. Provide training to the forklift operators regarding safety, operation, refueling procedures, and appropriate responses to system faults.

The resulting deployment of PowerEdge™ fuel cell forklifts and PowerTap™ hydrogen generation, compression, storage, and dispensing products are shown in Figures 2 and 3, respectively.

Since the commencement of full fuel cell fleet operations in March 2010, H-E-B has operated the equipment in normal daily service, and continues to compare the productivity and life cycle costs of operation on a side-by-side basis with standard lead acid battery powered forklifts. Over the first three months of operation, H-E-B reported an increase in productivity of 10% for the PowerEdge™ systems compared to forklifts running on batteries, as shown in Figure 4.

As part of the ongoing project, Nuvera provides data to the National Renewable Energy Laboratory (NREL) using jointly agreed data templates. Information collected during the course of daily operations includes the following:

- Power pack fault code indication
- Service notifications

### TABLE 1. Work Breakdown Schedule

<table>
<thead>
<tr>
<th>Task #</th>
<th>Project Milestones</th>
<th>Original Planned</th>
<th>Revised Planned</th>
<th>Actual</th>
<th>Percent Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Build</td>
<td>10/30/09</td>
<td>10/30/09</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Site Plan</td>
<td>10/30/09</td>
<td>10/30/09</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Deployment</td>
<td>11/30/09</td>
<td>2/28/10</td>
<td>2/28/10</td>
<td>100%</td>
</tr>
<tr>
<td>4</td>
<td>Go/No-Go: 2 PowerEdges Productivity Trial; certify passing of FAT*: permitting and approvals</td>
<td>11/30/09</td>
<td>12/30/09</td>
<td>12/30/09</td>
<td>100%</td>
</tr>
<tr>
<td>5</td>
<td>Confirm Value Proposition</td>
<td>5/31/11</td>
<td>5/31/11</td>
<td>5/31/11</td>
<td>7%</td>
</tr>
<tr>
<td>6</td>
<td>Final Testing</td>
<td>7/31/11</td>
<td>7/31/11</td>
<td>7/31/11</td>
<td>0%</td>
</tr>
<tr>
<td>7</td>
<td>Project Management and Reporting</td>
<td>7/31/11</td>
<td>7/31/11</td>
<td>7/31/11</td>
<td>25%</td>
</tr>
</tbody>
</table>

* FAT - factory acceptance test. For the PowerEdges, this consisted of a two-week trial with two trucks versus electric stockpickers to verify productivity. For PowerTap, the FAT verified 50 kg daily production and purity.

**FIGURE 1. Location of Hydrogen Infrastructure at H-E-B Grocery Site**
XI. ARRA

Mitchell – Nuvera Fuel Cells, Inc.

Currently, the PowerTap™ hydrogen generation, compression, storage, and dispensing system, as well as all 14 PowerEdge™ hybrid fuel cell power systems, are fully operational and are being used in normal daily operations. Over the next 12 months, H-E-B will:

- Continue to operate fleet in normal operations to gain durability and life cycle cost information on the fuel cell systems.
- Monitor and record the long-term operation cost of on-site hydrogen generation.
- Compile performance data of PowerEdge™ and PowerTap™ systems and send to NREL for analysis.
- Continue to assess the increase in productivity associated with the fuel cell solution in comparison with the lead acid battery forklift.
- Assess whether to increase the size of the fleet as expansion opportunities arise.
- Nuvera completed revisions to safety plan and submitted final version on July 3, 2010.

Conclusions and Future Directions

FY 2010 Publications/Presentations

Objective

- Safe and reliable operations of hydrogen material handling equipment (MHE).
- Convert an entire MHE fleet at FedEx Springfield, MO facility with fuel cell-powered forklifts (class-1).
- Demonstrate economic benefits of conversion.
- Provide cost effective and reliable hydrogen.
- Spur further lift truck fleet conversions.
- Establish proving ground for hydrogen MHE.

Technical Barriers

- Interim forklifts at new facility until fuel cells come online.
  - Because it was not possible to have the fuel cells operational at the time the new center opened, propane forklifts were used until the fuel cells could come online. The forklifts were pulled from other centers that at the time were not being used. However freight levels are beginning to rise and there is a need for the forklifts to be moved back to their original center. That is why it was imperative to get the fuel cell up and running.

- Permits for indoor dispensing.
  - There was an issue with the permitting of the dispensers because the city of Springfield went by a different set of codes for putting in hydrogen than what Air Products was used to and these codes did not match up in all areas. An example of this was that it was required from the city that the indoor dispensers required labeling that it was rated for dispensing indoors. This was new to Air Products so they had to go back to the dispensers' manufacturers and have the dispensers tested by a 3rd party and labeled that they were rated for indoor dispensing.

- Introducing hydrogen into the everyday world of FedEx Freight.
  - Working with hydrogen is very new to FedEx Freight. This created some challenges on how to address uninformed and inaccurate perceptions regarding hydrogen safety risks, to having to know how to work with new equipment, to how to do accounting for the project. Despite these challenges FedEx Freight has work to learn more about fuel cells and how they work to overcome these challenges.

American Recovery and Reinvestment Act

The purchase or these fuel cells from Plug Power resulted in approximately five jobs created at Plug Power to build the fuel cells. In addition, the success of this project could contribute to accelerating commercialization and deployment of fuel cells and hydrogen technologies, with an accompanying increase in jobs for fuel cell manufacturers, hydrogen providers, and associated maintenance and support services.

Accomplishments

- Plug Power built and delivered 35 GenDrive class-1 power units two months ahead of schedule.
- Air Products installed the liquid hydrogen handling and gaseous compression, storage and dispensing equipment.
- This includes all interconnecting piping, civil, electrical and mechanical connections, and safety systems:
  - Two indoor dispensers
  - 6,000 US gallon liquid hydrogen horizontal tank
  - Refuel time 3-6 minutes
  - ~91 kg/day usage
Introduction

This project addresses the DOE’s priorities related to acquiring data from real-world fuel cell operation, eliminating non-technical barriers, and increasing opportunities for market expansion of hydrogen fuel cell technologies.

Approach

The project involves replacing the batteries in a complete fleet of class-1 electric lift trucks at FedEx Freight’s Springfield, MO service center with 35 Plug Power GenDrive fuel cell power units. Fuel for the power units involves on-site hydrogen handling and dispensing equipment and liquid hydrogen delivery by Air Products.

The project builds on FedEx Freight’s previous field trial experience with a handful of Plug Power’s GenDrive power units. Those trials demonstrated productivity gains and improved performance compared to battery-powered lift trucks. Full lift truck conversion at our Springfield location allows improved competitiveness of operations and helps the environment by reducing greenhouse gas emissions and toxic battery material use. Success at this service center may lead to further fleet conversions at some of the other larger FedEx Freight service centers and possible conversion of other fleets in the Less-than-Truckload market.

Results

<table>
<thead>
<tr>
<th>Milestones</th>
<th>Progress</th>
<th>% Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fueling Station Installation</td>
<td>Air Products’ completed construction and installation of the fueling equipment. FedEx to finish system integration.</td>
<td>100%</td>
</tr>
<tr>
<td>Hydrogen Safety Plan</td>
<td>Working with Air Products and Plug Power to complete the hydrogen safety plan.</td>
<td>90%</td>
</tr>
<tr>
<td>Go/No Go</td>
<td>Fueling station tested and operational.</td>
<td>100%</td>
</tr>
<tr>
<td>GenDrive Power Unit Build</td>
<td>Plug Power completed build of 35 class-1 units in December 2009.</td>
<td>100%</td>
</tr>
<tr>
<td>Start-up and Training</td>
<td>Start-up and training completed.</td>
<td>100%</td>
</tr>
<tr>
<td>Lift Truck Operation and Evaluation</td>
<td>Operation and evaluation will begin after commissioning.</td>
<td>1%</td>
</tr>
</tbody>
</table>

Conclusions and Future Directions

FedEx Freight’s project is well under way. The GenDrive units have been delivered, hydrogen infrastructure is completed and approved and is in use. Now that the units and infrastructure are in use the remainder of the project will require regular monitoring and evaluation. This includes:

- Data collection from the power units and evaluation of performance, operability and safety.
- Data collection from the liquid and gaseous hydrogen fueling equipment and evaluation of performance, operability and safety.

FY 2010 Publications/Presentations

XI.10 Fuel Cell-Powered Lift Truck Sysco Houston Fleet Deployment

Accomplishments

- Converted the entire class-2 and class-3 lift truck fleet to fuel cell use.
- Built permanent hydrogen fueling infrastructure.
- Trained over 100 employees on operation and safety of hydrogen use.
- Improved operator productivity due to elimination of battery degradation and charging time.
- Through life of project 5.5 jobs have been created.
- Completed 2,664 fills in first quarter 2010.

Introduction

This project addresses the DOE’s priorities related to acquiring data from real-world fuel cell operation, eliminating non-technical barriers, and increasing opportunities for market expansion of hydrogen fuel cell technologies.

Sysco Houston’s objectives are to support the American Recovery and Reinvestment Act goals of long-term economic growth by successfully demonstrating this new technology. Establishing a proving ground for expanded use of hydrogen fueling technology at Sysco promotes future adoption of fuel cells in other applications thereby driving their use in the U.S. Sysco also hopes to promote the economic and environmental benefits of hydrogen fuel cell technology.

To see these objectives to fruition, Sysco Houston has and is:

- Converted the entire class-2 and class-3 lift truck fleet to fuel cell use.
- Demonstrating the economic benefits of large fleet conversions of lift trucks from lead-acid batteries to fuel cell power units by measuring, analyzing and reporting on the performance, operability and safety of the systems.
- Demonstrating freezer operability.
- Spurring further fuel cell lift truck fleet conversions.
- Establishing a proving ground for hydrogen fueling technology that will promote the future adoption of fuel cells in other applications and help drive the use of fuel cell technology in the United States.

Technical Barriers and Goals

This project addresses the following technical barriers:

- Safe hydrogen use in high throughput distribution center.
- Full fleet conversion to Greenfield center.
- Operator productivity improvements.
- Fuel cell use in freezer setting.
- GenDrive fuel cell lifetime and reliability.

Approach

The project involves replacing the batteries in a complete fleet of class-3 electric lift trucks at Sysco’s new Houston, TX distribution center with 72 Plug Power GenDrive fuel cell power units (plus the rental of seven additional class-3 power units for 6-month use in rented lift trucks). Fuel for the power units involves on-

Objectives

- Convert the entire class-3 lift truck fleet at a Greenfield distribution center in Houston, Texas to fuel cell use.
- Demonstrate the economic benefits of large fleet conversions of lift trucks from lead-acid batteries to fuel cell power units by measuring, analyzing and reporting on the performance, operability and safety of the systems.
- Demonstrate freezer operability.
- Provide affordable and reliable hydrogen.
- Spur further fuel cell lift truck fleet conversions.
- Establish a proving ground for hydrogen fueling technology that will promote the future adoption of fuel cells in other applications and help drive the use of fuel cell technology in the United States.
site hydrogen handling and dispensing equipment and liquid hydrogen delivery by Air Products.

The project builds on Sysco’s previous field trial experience with more than 40 of Plug Power’s GenDrive power units. Those trials demonstrated productivity gains and improved performance compared to battery-powered lift trucks. Full lift truck conversion at the Houston location allows improved competitiveness of operations and helps the environment by reducing greenhouse gas emissions and toxic battery material use. Success at this distribution center may lead to further fleet conversions at some or all of Sysco’s 170 distribution centers.

Sysco Houston’s hydrogen safety plan has been fully implemented and all National Environmental Policy Act forms have been submitted for review and approval.

## Results

<table>
<thead>
<tr>
<th>Milestones</th>
<th>Progress</th>
<th>% Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fueling Station Installation</td>
<td>Big-D construction company completed preparatory work for hydrogen infrastructure installation. Air Products completed installation of hydrogen fueling system.</td>
<td>100%</td>
</tr>
<tr>
<td>GenDrive Build</td>
<td>Plug Power completed build of 26 class-2 and 79 class-3 power units.</td>
<td>100%</td>
</tr>
<tr>
<td>► Go/No-Go</td>
<td>1. Fuel station was fully tested and deemed operational. 2. Fuel cells passed factory acceptance testing.</td>
<td>100%</td>
</tr>
<tr>
<td>Annual Assessments</td>
<td>Assess reliability of the fuel cells by measuring the time between failures and examining the cause of failure. Assess cost to maintain and operate the fuel cells, as well as overall operator experience.</td>
<td>0%</td>
</tr>
</tbody>
</table>

The liquid tank operates with a maximum allowable working pressure of 150 psig and the bulk high-pressure storage tanks operate at 6,000 psig. The indoor dispensers are 250 bar and capable of over 700kg/day. A pin code and badge scan is required for dispenser operation. Hydrogen gas detectors alarm at 25 percent of the lower explosive level and will shut down the system automatically.

Sysco Houston is successfully using hydrogen fuel cell technology for the first time in a fleet environment and the facility has proper safety, backup and operational procedures in place. Close monitoring and return on investment calculations have increased Sysco’s involvement in fuel cell-powered lift truck operations.

### Conclusions and Future Directions

Sysco Houston is successfully using hydrogen fuel cell technology for the first time in a fleet environment. The facility has proper safety, backup and operational procedures in place and a fully implemented hydrogen safety plan. Close monitoring and return on investment calculations have increased Sysco’s involvement in fuel cell-powered lift truck operations. One hundred and five of Plug Power’s GenDrive units are currently in use and hydrogen fueling is occurring regularly, Air Products providing the hydrogen support.

The majority of the project tasks have been completed at the front end of the project. The balance of the demonstration period will include:

- Monitoring GenDrive power units project performance, operability and safety.
- Monitoring liquid and gaseous hydrogen fueling equipment project performance, operability and safety.
- Monitoring and providing project performance, operability and safety reports to the DOE, including any safety and performance data and issues identified during operation of the power units. This encompasses maintenance and operation of the GenDrive units.
- Supporting DOE communication efforts.

### FY 2010 Publications/Presentations

2. Kickoff Event, Houston, TX, May 2010.
XI.11 Fuel Cell-Powered Lift Truck GENCO Fleet Deployment

Jim Klingler  
GENCO  
100 Papercraft Park  
Pittsburgh, PA  15238  
Phone: (412) 820-3718  
E-mail: klinglej@genco.com  

DOE Technology Development Manager:  
Jason Marcinkoski  
Phone: (202) 586-7466  
E-mail: Jason.Marcinkoski@ee.doe.gov

DOE Project Officer:  Jim Alkire  
Phone: (303) 275-4795  
E-mail: James.Alkire@go.doe.gov

Contract Number:  DE-EE0000483

Subcontractors:
• Plug Power Inc., Latham, NY
• Air Products and Chemicals, Inc., Allentown, PA
• Linde North America, Murray Hill, NJ

Project Start Date:  October 1, 2009  
Project End Date:  September 30, 2013

Objectives

• Convert electric-drive fork lift truck fleets to fuel cell use in a variety of large distribution centers and manufacturing facilities.
• Demonstrate the economic benefits of large fleet conversions of lift trucks from batteries to fuel cell power units by measuring, analyzing and reporting on the performance, operability and safety of the systems.
• Provide affordable and reliable hydrogen.
• Spur further fuel cell lift truck fleet conversions.
• Establish a proving ground for hydrogen fueling technology that will promote the future adoption of fuel cells in other applications, such as cars, and help drive the use of fuel cell technology in the United States.

Accomplishments

General

• Nine jobs were maintained through the third quarter of 2010 in New York.

Wegmans

• National Environmental Policy Act (NEPA) environmental forms have been approved and the fueling station is operational, logging almost 2,000 hydrogen fills during first quarter 2010.
• Fifty-nine GenDrive power units are running and have logged 24,375 operating hours during the first quarter of 2010.
• Nine of the GenDrive power units were delivered two months ahead of schedule.
• Wegmans has achieved all project milestones and is pleased with performance of GenDrive power units.

Sysco Philadelphia

• Sysco contractors have completed concrete pad for the hydrogen fueling station.
• The remainder of the fueling station will be completed concurrent with building construction.
• NEPA environmental forms are nearing completion.

Coca-Cola

• NEPA environmental forms have been approved.
• Linde fueling station contracts are under final negotiation.

Kimberly-Clark

• Lease arrangement has been completed.
• Air Products fueling station contracts are under final negotiation.
• Nine GenDrive power units have been delivered to date.
• NEPA environmental forms have been approved.
• Permits have been secured.
• Site contractor has poured pad.
• Air Products to set equipment for the fuel station the week of October 19.

Whole Foods

• Linde fueling station contracts are under final negotiation.
• Permit application is ready for submission.
• All sixty-one GenDrive power units have been delivered.
• NEPA environmental forms have been approved.
Introduction

This project addresses the DOE’s priorities related to acquiring data from real-world fuel cell operation, eliminating non-technical barriers, and increasing opportunities for market expansion of hydrogen fuel cell technologies.

Approach

The project involves replacing the batteries in 357 electric lift trucks with 110 class-1, 61 class-2, 14 stock picker (modified class-2) and 172 class-3 Plug Power GenDrive fuel cell power units at five distribution centers. These distribution centers handle goods for Wegmans (Pottsville, PA), Coca-Cola (Charlotte, NC), Sysco Foods (Philadelphia, PA), Whole Foods (Landover, MD) and Kimberly-Clark (Graniteville, SC). Fuel for the power units involves on-site hydrogen handling and dispensing equipment and liquid hydrogen delivery by Air Products or Linde, depending on location.

The project builds on GENCO’s previous field trial experience with a handful of Plug Power’s GenDrive power units. Those trials demonstrated productivity gains and improved performance compared to battery-powered lift trucks. Full lift truck conversion at the five distribution center locations allows improved competitiveness of operations and helps the environment by reducing greenhouse gas emissions and toxic battery material use. Success at these distribution centers may lead to further fleet conversions at some or all of GENCO’s 110 distribution centers.

Results

<table>
<thead>
<tr>
<th>Class 1 GenDrive</th>
<th>Wegmans</th>
<th>Whole Foods</th>
<th>Coca-Cola</th>
<th>Sysco Phil.</th>
<th>Kimberly-Clark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>45</td>
<td>40</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Class 2 GenDrive</td>
<td>36</td>
<td>14</td>
<td>0</td>
<td>25</td>
<td>0</td>
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<tr>
<td>Class 3 GenDrive</td>
<td>100</td>
<td>2</td>
<td>0</td>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>136</strong></td>
<td><strong>61</strong></td>
<td><strong>40</strong></td>
<td><strong>95</strong></td>
<td><strong>25</strong></td>
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</table>

<table>
<thead>
<tr>
<th>Hydrogen Supplier</th>
<th>Wegmans</th>
<th>Whole Foods</th>
<th>Coca-Cola</th>
<th>Sysco Phil.</th>
<th>Kimberly-Clark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Fueling Station Operational</th>
<th>Wegmans</th>
<th>Whole Foods</th>
<th>Coca-Cola</th>
<th>Sysco Phil.</th>
<th>Kimberly-Clark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Go/No-Go</td>
<td>59 of 136</td>
<td>61 of 61</td>
<td>10/31/2010</td>
<td>9/30/2011</td>
<td>9 of 25</td>
</tr>
<tr>
<td>Project Complete</td>
<td>9/30/2013</td>
<td>9/30/2013</td>
<td>9/30/2013</td>
<td>9/30/2013</td>
<td>9/30/2013</td>
</tr>
</tbody>
</table>

Conclusions and Future Directions

GENCO has made great strides facilitating hydrogen fuel cell usage at the Wegmans site and progress is being made to bring the four remaining sites online. Successful integration of Plug Power’s GenDrive power units into each facilities material handling operations will continue. Working with hydrogen providers Air Products and Linde, each of the five sites will incorporate hydrogen fueling into their daily activities. Table 2 provides detailed information on when the remaining sites will be fully operational.

FY 2010 Publications/Presentations

Introduction

The relevance of this project to the goals of the American Recovery and Reinvestment Act (ARRA) of 2009 is threefold. First, Sprint seeks to support the creation of new jobs, as well as maintain existing jobs, to successfully complete this deployment effort. Second, Sprint intends to spur economic activity through the positive impact to various industries and service providers at all levels of the supply chain. And finally, Sprint is confident that this investment in proton exchange membrane (PEM) hydrogen fuel cells (HFCs), to provide emergency power to our critical wireless network facilities, will truly benefit our nation’s long-term economic growth.

Objectives

- Eliminate Barriers to Siting and Permitting
- 72-Hours of Hydrogen Fuel Storage
- Eliminate Barriers to Re-Fueling Sites at the Required Level of Performance
- Collect and Analyze Data Sample to Evaluate Economic and Operational Metrics

Technical Barriers

The overarching goal of this project, as stated in our application originally, is to support the DOE Fuel Cell Technologies ARRA project goal of accelerating the commercialization and deployment of fuel cells. In order to accomplish this goal, specific barriers that were encountered during our initial HFC deployment need to be overcome.

One major barrier involves the difficulty associated with the siting and permitting required for the installation of an HFC. With the vast number of local municipalities that need to be engaged, and the fact that they may recognize various code authorities, as well as different issues of the same code, a fact-based presentation, citing specific code interpretations, must be crafted to educate the authorities having jurisdiction (AHJ).

Another barrier we must overcome deals with the difficulties associated with refueling the HFC. In our earlier deployment, low-pressure hydrogen storage tanks were utilized. Based upon the site loads, we were able to provide backup power for a period of 14–20 hours before refueling was required. This refueling methodology requires the replacement (bottle swap) of the low-pressure bottles - a slow, cumbersome process that is impractical, as well as unmanageable during a widespread power outage event (i.e. hurricane). In addition, the runtime provided by this low-pressure solution comes nowhere close to the 72-hour runtime available from the incumbent technology, the diesel generator.

Finally, the success of this effort cannot be determined until the HFC, with the medium-pressure hydrogen storage solution, is installed and placed in service. The unit’s performance in real world situations, based on financial and operational performance data collected, analyzed and reported, shall be the confirmation or denial of its ability to provide a cost-
effective, operationally accepted option for providing backup power at critical sites.

Technical Targets

This project is demonstrating the economic and operational viability of using PEM fuel cells to provide emergency power at critical code division multiple access sites on the Sprint Nextel Network. We plan to more than double the number of PEMs deployed in our network. In addition, we plan to retrofit approximately 25% of our current installed base with a new hydrogen storage solution to extend PEM runtime by a factor of three. The data collected from these newly deployed and/or modified units will, it is hopes, provide supporting documentation to create a “market pull” within the telecom space, as well as across various industries, for additional PEM fuel cell deployments. Project targets as follows (Figure 1):

- PEM sites currently in-service: 237
- Additional PEMs to be deployed: 260
- Low-pressure hydrogen storage runtime: 14–20 hours
- Medium-pressure hydrogen storage runtime: ~72 hours
- Deployment will expose three additional states, and impacted local municipalities, to the use of hydrogen fuel for backup power purposes:
  - Connecticut
  - New Jersey
  - New York
- Existing PEMs to convert to refillable on-site medium-pressure hydrogen storage: 70

These targets dovetail very well with the objectives stated under the ARRA. By doubling our installed base of HFCs, numerous jobs shall be created and maintained. From jobs within the equipment manufacturing facilities, to personnel engineering, constructing, maintaining, and refueling these devices, the ripple effect is enormous. Our expansion into three additional states, and our increased footprint in another, shall permit Sprint to interface with the AHJ personnel which will help acquaint them with the use of hydrogen as a fuel, and the associated codes to which we must adhere.

Approach

After reviewing the code division multiple access Network Site Inventory, a master candidate site list was created based upon the restoration priority of the facility, and whether or not the site was equipped with a fixed generator. Sprint focused on specific markets to exploit the site’s proximity to the hydrogen distribution facility (within 200 miles), as well as to concentrate on market clusters to minimize site acquisition, siting/permitting, installation, commissioning, and training expenditures. In addition, this cluster approach helps to minimize costs associated with the maintenance of a PEM spare parts inventory. Finally, this concentration permits a consistent presentation to the local building officials,
which in turn helps to clarify applicable code (Uniform Building Code, National Fire Protection Association, etc.) interpretations. In theory, all of these efforts should help to facilitate a rapid, safe, and successful deployment in the market.

**Accomplishments**

Following the execution of the contract with the Department of Energy on March 18, 2010 purchase orders (260 orders with a total value of $335,510) were generated to our architectural and engineering (A&E) project partners for Phase 1 (lease review and site assessment) work. Phase 1 progress, by state, is as follows:

- **New York** – 65 sites targeted; 155 in pool; 66 site surveys completed; as of this report, Phase 2 (site acquisition, permitting, pre-notice to proceed) orders are being prepared for 20 sites.
- **Connecticut** – 30 sites targeted for deployment; candidate pool consists of 131 sites; sites surveyed - 65 sites. Site surveys are being reviewed for determination of next steps.
- **California** - 100 targeted; pool of 331; sites surveyed - 81 sites. Uploaded site surveys are being reviewed.
- **New Jersey** – 65 targeted; 137 in pool. Site surveys began on Monday, July 12, 2010.

Design of the medium-pressure hydrogen storage solution is well underway with final drawings scheduled for completion by July 30, 2010.

Sprint is working internally to create purchase orders for equipment (fuel cells, as well as hydrogen storage modules). Our intent is to have orders in the pipeline so that material delivery can coincide with the start of Phase 3 (installation/commissioning).

Working with our project partners, on July 13, 2010, the Sprint Hydrogen Safety Plan was provided to our DOE Project Officer.

We are continuing to assemble the required information/documentation to request a National Environmental Policy Act Categorical Exclusion for this project – targeting a mid-August, 2010 submission.

Per our calculations, 6.5 jobs have been created/maintained during this portion of the Phase 1 activities completed to date.

**Future Directions**

Complete Phase 1 (Site Survey) work to identify the final site list for deployments. Once a site is selected for the final list, a purchase order is generated to our A&E project partner for Phase 2 work. In Phase 2, the A&E will perform all required site acquisition work, as well as secure all permits required by the AHJ. Also during Phase 2, purchase orders are generated to procure all required material (PEM, hydrogen storage, etc.). Phase 2 is considered complete when Sprint issues a notice to proceed to the A&E.

When the notice to proceed is issued, Phase 3 (installation and commissioning) purchase orders are generated to the A&E. The release of Phase 3 purchase orders shall coincide with the delivery date of all required material to the site.

After the PEM is commissioned on-site, two things happen. First, project closure activity is initiated to permit the shutdown of the project within the various impacted Sprint systems. Second, the newly commissioned PEM is added to our remote data collection/performance monitoring system to ensure contractually mandated operational reporting requirements are captured and delivered to the National Renewable Energy Laboratory.

**FY 2010 Publications/Presentations**

1. Presentation deck from the Department of Energy Project Kickoff Meeting conducted at the Sprint Executive Briefing Center in Reston, VA, on May 20, 2010.
XII. SMALL BUSINESS INNOVATION RESEARCH (SBIR) HYDROGEN PROGRAM NEW PROJECTS AWARDED IN FY 2010
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 research and development (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 50%) cooperative research collaboration between the small business and a non-profit research institution.

Table 1 lists the SBIR projects awarded in FY 2010 related to the Hydrogen Program. On the following pages are brief descriptions of each.

### TABLE 1. FY 2010 SBIR Projects Related to the Hydrogen Program

<table>
<thead>
<tr>
<th>Title</th>
<th>Company</th>
<th>City, State</th>
</tr>
</thead>
<tbody>
<tr>
<td>XII.1 Low-Cost, Durable Water Vapor Transport Exchanger (Phase I Project)</td>
<td>Creare Incorporated</td>
<td>Hanover, NH</td>
</tr>
<tr>
<td>XII.2 Hydrogen Fueling Station Cost Reduction; Study of a Cryogenic Liquid Phase Pump as an Alternative to Gas Compression (Phase I Project)</td>
<td>Engineering, Procurement &amp; Construction, LLC</td>
<td>Lakewood, CO</td>
</tr>
<tr>
<td>XII.3 Low Cost Metal Hydride Hydrogen Storage System for Forklift Applications (Phase I Project)</td>
<td>Hawaii Hydrogen Carriers, LLC</td>
<td>Honolulu, HI</td>
</tr>
<tr>
<td>XII.4 Low Cost Large Scale PEM Electrolysis for Renewable Energy Storage (Phase I Project)</td>
<td>Proton Energy Systems</td>
<td>Wallingford, CT</td>
</tr>
<tr>
<td>XII.5 Thermochemically Integrated Solid State Hydrogen Separator and Compressor (Phase I Project)</td>
<td>FuelCell Energy, Inc.</td>
<td>Danbury, CT</td>
</tr>
<tr>
<td>XII.6 A Novel Process for Improved Hydrogen Separation and Recovery (Phase I Project)</td>
<td>Reaction Systems, LLC</td>
<td>Parker, CO</td>
</tr>
<tr>
<td>XII.7 Poison-Tolerant WGS Catalyst for Biomass-Coal Co-Gasification Systems (Phase I STTR Project)</td>
<td>TDA Research, Inc.</td>
<td>Wheat Ridge, CO</td>
</tr>
<tr>
<td>XII.8 Novel Ceramic Membranes for Efficient Hydrogen Recover (Phase I Project)</td>
<td>Technology Assessment and Transfer, Inc.</td>
<td>Annapolis, MD</td>
</tr>
<tr>
<td>XII.9 Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5000 psi (Phase II Project)</td>
<td>Giner Electrochemical Systems, LLC</td>
<td>Newton, MA</td>
</tr>
<tr>
<td>XII.10 Process Intensification of Hydrogen Unit Operations Using an Electrochemical Device (Phase II Project)</td>
<td>H2 Pump, LLC</td>
<td>North Albany, NY</td>
</tr>
<tr>
<td>XII.11 Hydrogen by Wire Home Fueling System (Phase II Project)</td>
<td>Proton Energy Systems</td>
<td>Wallingford, CT</td>
</tr>
</tbody>
</table>
PHASE I PROJECTS

XII.1 Low-Cost, Durable Water Vapor Transport Exchanger

Creare Incorporated
16 Great Hollow Road
P.O. Box 71
Hanover, NH 03755-3116

This project will develop critical technology that will enable vehicle propulsion and stationary power generation using low-cost, durable fuel cell power systems. This water management technology will enable reliable fuel cell operation by preventing dryout of the fuel cell and providing water needed for fuel processing.

XII.2 Hydrogen Fueling Station Cost Reduction; Study of a Cryogenic Liquid Phase Pump as an Alternative to Gas Compression

Engineering, Procurement & Construction, LLC
12211 W Alameda Parkway
Suite #105
Lakewood, CO 80228-2825

This project will develop a database of hydrogen refueling costs, and create a methodology to evaluate technology lifecycle cost reduction. Hydrogen compression costs which currently account for a substantial portion for the total costs of hydrogen fueling infrastructure must be reduced for low cost dispensing to become commercially viable.

XII.3 Low Cost Metal Hydride Hydrogen Storage System for Forklift Applications

Hawaii Hydrogen Carriers, LLC
531 Cooke Street
Honolulu, HI 96813-5235

This project will develop a low cost metal hydride hydrogen storage solution for fork lift trucks thus to enable widespread consumer uptake of hydrogen fuel cell-powered fork lift trucks due to the increased overall value proposition and inherent safety of these low pressure systems.
XII.4 Low Cost Large Scale PEM Electrolysis for Renewable Energy Storage

Proton Energy Systems  
10 Technology Drive  
Wallingford, CT 06492-1955

This company manufactures hydrogen generation systems which can be integrated with renewable energy sources to generate hydrogen fuel while producing minimal carbon footprint. This project aims to reduce the cost of this technology through development of improved membrane technology designed to reduce raw material cost and improve electrical efficiency. (See II.E.4 for complete report.)

XII.5 Thermochemically Integrated Solid State Hydrogen Separator and Compressor

FuelCell Energy, Inc.  
3 Great Pasture Rd.  
Danbury, CT 06813-1305

This project focuses on the development of a thermally integrated solid-state hydrogen separator and compressor to produce high pressure, high purity hydrogen to meet future hydrogen refueling infrastructure needs. (See III.16 for complete report.)

XII.6 A Novel Process for Improved Hydrogen Separation and Recovery

Reaction Systems, LLC  
19039 E. Plaza Dr., Suite 290  
Parker, CO 80134-8704

This project will develop a technology that will allow hydrogen to be produced more economically facilitating the increased use of fuel cells, which will reduce our energy consumption.

XII.7 Poison-Tolerant WGS Catalyst for Biomass-Coal Co-Gasification Systems

TDA Research, Inc.  
12345 W. 52nd Ave.  
Wheat Ridge, CO 80033-1916

This project will develop an enabling technology for Coal-Biomass-to-Liquids (CBTL) processes. The CBTL system uses domestic feedstock and will have a greenhouse gas footprint better than conventional coal or petroleum fuels allowing a highly efficient and environmentally responsible utilization of coal.
XII. Small Business Innovation Research

STTR PROJECT

XII.8 Novel Ceramic Membranes for Efficient Hydrogen Recovery

Technology Assessment and Transfer, Inc.
133 Defense Hwy., Suite 212
Annapolis, MD 21401-8907

This project will develop an all-ceramic separation membrane module to cleanly recover hydrogen gas from coal. This module will increase the efficiency of the process and eliminate U.S. dependence on precious metals used for hydrogen separation.

PHASE II PROJECTS

XII.9 Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5000 psi

Giner Electrochemical Systems, LLC
89 Rumford Avenue
Newton, MA 02466-1311

This project will develop a “unitized” electrolyzer design that can be used as a home refueling appliance and will result in a safe, high efficiency, low capital cost system that will provide competitively-priced hydrogen for fuel-cell vehicles. (See II.1.5 for complete report.)

XII.10 Process Intensification of Hydrogen Unit Operations Using an Electrochemical Device

H2 Pump, LLC
11 Northway Lane
North Albany, NY 12110

This project will develop a technology that is a simplified, multi-functional device which pumps, purifies, and pressurized hydrogen in a single, low cost, efficient, non-mechanical process.

XII.11 Hydrogen by Wire Home Fueling System

Proton Energy Systems
10 Technology Drive
Wallingford, CT 06492-1955

This project will develop a high pressure hydrogen system that eliminates major noise pollution and frequent maintenance requirements. It is also an attractive option for backup power when integrated with a proton exchange membrane fuel cell and has advantages over batteries in factors such as available life and safety. (See II.1.7 for complete report.)
### XIII. Acronyms, Abbreviations and Definitions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>°F</td>
<td>Degrees Fahrenheit</td>
</tr>
<tr>
<td>(\alpha-\text{AlH}_3)</td>
<td>Alpha polymorph of aluminum hydride</td>
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<td>(\Delta)</td>
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<td>(\Delta G)</td>
<td>Gibbs free energy of reaction</td>
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<td>(\Delta H)</td>
<td>Enthalpy of reaction, enthalpy of hydrogenation</td>
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<td>(\Delta H^\circ)</td>
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<td>(\Delta K)</td>
<td>Stress intensity factor</td>
</tr>
<tr>
<td>(\Delta P)</td>
<td>Pressure drop, pressure change</td>
</tr>
<tr>
<td>(~)</td>
<td>Approximately</td>
</tr>
<tr>
<td>(\approx)</td>
<td>Equals approximately</td>
</tr>
<tr>
<td>(&gt;)</td>
<td>Greater than</td>
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<tr>
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<td>Greater than or equal to</td>
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<tr>
<td>(&lt;)</td>
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<td>(\leq)</td>
<td>Less than or equal to</td>
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<td>Percent</td>
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<tr>
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<tr>
<td>µA</td>
<td>Micro ampere(s)</td>
</tr>
<tr>
<td>µA/cm²</td>
<td>Micro ampere(s) per square centimeter</td>
</tr>
<tr>
<td>µc-Si</td>
<td>Microcrystalline silicon</td>
</tr>
<tr>
<td>µg</td>
<td>Microgram(s)</td>
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<tr>
<td>µm</td>
<td>Micrometer(s); micron(s)</td>
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<tr>
<td>µM</td>
<td>Micromolar</td>
</tr>
<tr>
<td>µmol</td>
<td>Micromole(s)</td>
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<tr>
<td>µΩ-cm²</td>
<td>Micro-ohm(s)-square centimeter</td>
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<tr>
<td>µV</td>
<td>Micro volt(s)</td>
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<td>η</td>
<td>Viscosity</td>
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<td>Ω-cm²</td>
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<td>United States dollars</td>
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<tr>
<td>(^{11}\text{B-NMR})</td>
<td>Boron 11 Nuclear Magnetic Resonance</td>
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<tr>
<td>(^{19}\text{FNMR})</td>
<td>Fluorine nuclear magnetic resonance</td>
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<td>1-D, 1D</td>
<td>One-dimensional</td>
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<td>1Q</td>
<td>First quarter of the fiscal year</td>
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<td>4Q</td>
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<td>8YSZ</td>
<td>8 mol% yttria-stabilized zirconia</td>
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<td>A</td>
<td>Ampere, amps</td>
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<td>Å</td>
<td>Angstrom</td>
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<td>AAO</td>
<td>Anodic aluminum oxide</td>
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<td>AB</td>
<td>Ammonia-borane, (\text{NH}_3\text{BH}_3)</td>
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<tr>
<td>ABH₂</td>
<td>Ammonium borohydride, (\text{NH}_4\text{BH}_4)</td>
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<td>Automated ball indentation</td>
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<td>Agent-based modeling and simulation</td>
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<td>A/cm²</td>
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<td>AER</td>
<td>Absorption-enhanced reforming, all-electric range</td>
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<td>Advanced Fuel Cells Implementing Agreement</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy; antiferromagnetic</td>
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<td>Automated fiber placement</td>
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<td>Silver</td>
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<td>Silver chloride</td>
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<td>Authorities having jurisdiction</td>
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<td>AIChE</td>
<td>American Institute of Chemical Engineers</td>
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<td>(\text{Ag(In}<em>{0.2}\text{Ga}</em>{0.8})\text{Se}_2)</td>
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<td>Japanese National Institute of Advanced Industrial Science and Technology</td>
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<td>Al₂O₃</td>
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<td>AlCl₃</td>
<td>Aluminum chloride</td>
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<td>ALD</td>
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<td>AlH₃</td>
<td>Aluminum hydride; alane</td>
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<td>ALT</td>
<td>Accelerated life test</td>
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<td>Air Mass 1.5 solar illumination</td>
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<td>AMPS</td>
<td>2-acrylamido-2-methyl-1-propanesulfonic acid</td>
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<td>Active magnetic regenerative liquefier</td>
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<td>AN</td>
<td>Acrylonitrile</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<td>American National Standards Institute</td>
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<td>$A_o$</td>
<td>Arrhenius constant, ml/[cm$^2$-min-atm$^{1/2}$]</td>
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<td>Poly(2,6-dimethyl-1,4-phenylene oxide) based carbon</td>
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<td>Aqueous-phase reforming</td>
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<td>APRxn</td>
<td>Aqueous phase reaction</td>
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<td>Advanced Photon Source</td>
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<td>Auxiliary power unit</td>
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<td>Argon</td>
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<td>Alternative and renewable energy technologies</td>
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<td>American Recovery and Reinvestment Act</td>
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<td>Arsenic</td>
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<td>Amorphous silicon</td>
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<td>a-SiC</td>
<td>Amorphous silicon carbide</td>
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<td>a-SiGe</td>
<td>Amorphous silicon germanium</td>
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<td>a-SiN</td>
<td>Amorphous silicon nitride</td>
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<tr>
<td>ASME</td>
<td>American Society of Mechanical Engineers</td>
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<tr>
<td>ASPEN</td>
<td>Modeling software, computer code for process analysis</td>
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<td>ASR</td>
<td>Area-specific resistance</td>
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<td>AST</td>
<td>Accelerated stress test</td>
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<td>ASTM International, originally known as the American Society for Testing and Materials</td>
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<td>at%</td>
<td>Atomic percent</td>
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<td>A-T-P</td>
<td>Aerosol through plasma</td>
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<td>ATP</td>
<td>Adenosine triphosphate</td>
</tr>
<tr>
<td>ATPase</td>
<td>Adenosine triphosphatase</td>
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<tr>
<td>ATR</td>
<td>Autothermal reformer; autothermal reforming, attenuated total reflection</td>
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<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflectance Fourier transform infrared</td>
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<td>ATV</td>
<td>All-terrain vehicle</td>
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<td>Au</td>
<td>Gold</td>
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<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
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<td>Average</td>
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<td>Boron</td>
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<td>Ba</td>
<td>Barium</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-centered cubic</td>
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<td>BCM</td>
<td>Battery-charging mode</td>
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<tr>
<td>BCN</td>
<td>Boron carbon nitride</td>
</tr>
<tr>
<td>BCP</td>
<td>Block copolymers</td>
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<td>Be</td>
<td>Beryllium</td>
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<td>BE-O</td>
<td>Binding energy of oxygen</td>
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<td>BET</td>
<td>Brunauer-Emmett-Teller surface area analysis method</td>
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<td>BFR</td>
<td>Base-facilitated reforming</td>
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<td>BFZ0</td>
<td>$\text{BaFe}<em>{0.975}\text{Zr}</em>{0.025}\text{O}_3$</td>
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<td>$\text{BaFe}<em>{0.90}\text{Zr}</em>{0.10}\text{O}_3$</td>
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<td>B-H, BH, BH$_4$</td>
<td>Borohydride</td>
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<td>Bi</td>
<td>Bismuth</td>
</tr>
<tr>
<td>BKDF</td>
<td>Bioenergy Knowledge Discovery Framework</td>
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<tr>
<td>bmimCl</td>
<td>1-butyl-3-methyl-imidazolium chloride</td>
</tr>
<tr>
<td>BN</td>
<td>Boron-nitrogen</td>
</tr>
<tr>
<td>BNH</td>
<td>Boron-nitrogen-hydrogen</td>
</tr>
<tr>
<td>BNHx</td>
<td>Dehydrogenated ammonia-borane</td>
</tr>
<tr>
<td>BNL</td>
<td>Brookhaven National Laboratory</td>
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<tr>
<td>BOL</td>
<td>Beginning of life</td>
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<td>BOP, BoP</td>
<td>Balance of plant</td>
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<tr>
<td>$^{11}$B-NMR</td>
<td>Boron 11 Nuclear Magnetic Resonance</td>
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<tr>
<td>BP</td>
<td>Bisphenol</td>
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<td>BPS</td>
<td>Ballard Power Systems, biphenyl sulfone</td>
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<tr>
<td>BPS100</td>
<td>fully disulfonated poly(arylene ether sulfone)</td>
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<td>BPSH</td>
<td>Block polysulfone ether polymers, biphenyl sulfone: H form</td>
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<td>BPSH-30</td>
<td>Biphenyl sulfone H form, 30% molar fraction of disulfonic acid unit (30% level of sulfonation)</td>
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<tr>
<td>BPSH-x</td>
<td>BiPhenyl-based disulfonated polySulfone (H$^+$ form) (x denotes degree of sulfonation)</td>
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<td>Br$_2$</td>
<td>Diatomic bromine</td>
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<td>BSC</td>
<td>Bi-electrode supported cell</td>
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<td>BSE</td>
<td>Bachelor of Science in Engineering</td>
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<tr>
<td>BSET</td>
<td>Bachelor of Science in Engineering Technology</td>
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<tr>
<td>BTB</td>
<td>1,3,5-benzenetribenzoate</td>
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<tr>
<td>BTC</td>
<td>1,3,5-benzenetricarboxylate</td>
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<tr>
<td>BTT</td>
<td>Benzene tris-tetrazole</td>
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<tr>
<td>BTU, Btu</td>
<td>British thermal unit(s)</td>
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<td>BZYC</td>
<td>$\text{BaZr}<em>{0.1}\text{Ce}</em>{0.7}\text{Y}<em>{0.1}\text{Yb}</em>{0.1}\text{O}_{3+\delta}$</td>
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<td>C</td>
<td>Carbon</td>
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<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CA</td>
<td>Carbon aerogel</td>
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<tr>
<td>CaCO$_3$</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer-aided design</td>
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<tr>
<td>CAE</td>
<td>Computer-assisted engineering</td>
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<td>CAES</td>
<td>Compressed air energy storage</td>
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### XIII. Acronyms, Abbreviations and Definitions

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<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>CaFCP</td>
<td>California Fuel Cell Partnership</td>
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<td>CAFE</td>
<td>Corporate Average Fuel Economy</td>
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<td>CALPHAD</td>
<td>Calculation of phase diagrams</td>
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<td>Caltech</td>
<td>California Institute of Technology</td>
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<td>CaO</td>
<td>Calcium oxide</td>
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<td>CARB</td>
<td>California Air Resources Board</td>
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<td>CaS</td>
<td>Calcium sulfide</td>
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<td>CB</td>
<td>Conduction band</td>
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<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
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<tr>
<td>CBN</td>
<td>Carbon-boron-nitrogen</td>
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<tr>
<td>CBS</td>
<td>Casa Bonita strain, complete basis set</td>
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<tr>
<td>cc</td>
<td>Cubic centimeter(s)</td>
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<td>CC&amp;S</td>
<td>Carbon capture and sequestration</td>
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<td>CCD</td>
<td>Charge-coupled device</td>
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<td>CCh2</td>
<td>Cryo-compressed hydrogen</td>
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<td>CCM</td>
<td>Catalyst-coated membrane, coordinate measuring machine</td>
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<tr>
<td>Cc/min, ccm</td>
<td>Cubic centimeters per minute</td>
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<tr>
<td>ccp</td>
<td>Cubic close-packed</td>
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<td>CCP</td>
<td>Combined cooling and power</td>
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<td>CCS</td>
<td>Carbon capture and storage</td>
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<td>Cd</td>
<td>Cadmium</td>
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<td>CD</td>
<td>Compact disk, charge depleting, cathode dewpoint</td>
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<td>cDNA</td>
<td>Complementary DNA</td>
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<td>CDO</td>
<td>Code development organization</td>
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<td>CDP</td>
<td>Composite data product</td>
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<td>CDR</td>
<td>Component design requirement</td>
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<td>CdS</td>
<td>Cadmium sulfide</td>
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<td>C-DSM™</td>
<td>Chemically etched dimensionally stable membrane</td>
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<td>Ce</td>
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<td>California Energy Commission</td>
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<td>CEM</td>
<td>Compressor/expander motor</td>
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<td>CEMM</td>
<td>Compressor-expander motor module</td>
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<td>CeO₂</td>
<td>Ceric oxide</td>
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<td>CERL</td>
<td>Construction Engineering Research Laboratory</td>
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<td>CESAl</td>
<td>Clean Energy States Alliance</td>
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<tr>
<td>CF</td>
<td>Carbon fiber, carbon foam</td>
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<td>CFCC</td>
<td>Colorado Fuel Cell Center</td>
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<td>CFD</td>
<td>Computational fluid dynamics</td>
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<td>cfm</td>
<td>Cubic feet per minute</td>
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<td>CGA</td>
<td>Compressed Gas Association</td>
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<td>CGH2</td>
<td>Compressed gaseous hydrogen</td>
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<td>CGS</td>
<td>Copper gallium diselenide, CuGaSe₂</td>
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<td>CGSe</td>
<td>Copper gallium diselenide</td>
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<td>Propane</td>
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<td>Cost-effective High-efficiency Advanced Reforming Module</td>
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<td>Continuous catalytic heat exchanger</td>
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<td>CHHP</td>
<td>Combined heat, hydrogen, and power</td>
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<td>Chl</td>
<td>Chlorophyll</td>
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<td>CHP</td>
<td>Combined heat and power</td>
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<td>Chemical Hydrogen Storage Center of Excellence</td>
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<td>CI</td>
<td>Compression ignition</td>
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<td>CIGS</td>
<td>Copper indium gallium diselenide</td>
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<td>CIGSe</td>
<td>Copper indium gallium diselenide</td>
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<td>CIRRUS</td>
<td>Cell Ice Regulation &amp; Removal Upon Start-up</td>
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<td>CuInSe (alloy of copper, indium, and selenium)</td>
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<td>CL</td>
<td>Catalyst layer, ε-caprolactone</td>
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<td>cm</td>
<td>Centimeter</td>
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<td>Composite membrane reactor</td>
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<td>Carnegie Mellon University</td>
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<td>CMWNT</td>
<td>Carbon multi-walled nanotube</td>
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<td>Compressed natural gas</td>
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<td>Carbon nanotube</td>
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<td>Center of Excellence</td>
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<td>Cost of electricity</td>
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<td>Carbonyl fluoride</td>
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<td>COMSOL</td>
<td>Multiphysics modeling and engineering simulation software</td>
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<td>COPV</td>
<td>Composite overwrapped pressure vessel</td>
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<td>COS</td>
<td>Carbon oxysulfide; carbonyl sulfide</td>
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<td>CPO, CPOX</td>
<td>Catalytic partial oxidation</td>
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<td>Cr</td>
<td>Chromium</td>
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<tr>
<td>CRADA</td>
<td>Cooperative Research and Development Agreement</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
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</tr>
<tr>
<td>Cs</td>
<td>Cesium</td>
</tr>
<tr>
<td>CS</td>
<td>Ceramic support</td>
</tr>
<tr>
<td>CSA</td>
<td>Canadian Standards Association</td>
</tr>
<tr>
<td>CSD</td>
<td>Compression-storage-delivery</td>
</tr>
<tr>
<td>CSM</td>
<td>Colorado School of Mines, combined structure and material</td>
</tr>
<tr>
<td>CSR</td>
<td>Catalytic steam reforming, compressive stress relaxation</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>CTIV</td>
<td>Chevron Technology Ventures LLC</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>Cu2O</td>
<td>Cuprous oxide</td>
</tr>
<tr>
<td>cu. in.</td>
<td>Cubic inch</td>
</tr>
<tr>
<td>CuO</td>
<td>Cupric oxide, copper(II) oxide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry, cyclic voltammogram</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<td>CWRU</td>
<td>Case Western Reserve University</td>
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<td>CY</td>
<td>Calendar year</td>
</tr>
<tr>
<td>CZO</td>
<td>Ceria-zirconia</td>
</tr>
<tr>
<td>D</td>
<td>Day(s)</td>
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<td>D2</td>
<td>Deuterium</td>
</tr>
<tr>
<td>DAC</td>
<td>Direct air cooling</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DDP</td>
<td>Detailed data products</td>
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<tr>
<td>dpr</td>
<td>Dubini-Radushkevich average micropore diameter</td>
</tr>
<tr>
<td>Deg</td>
<td>Degree</td>
</tr>
<tr>
<td>ΔK</td>
<td>Stress intensity factor</td>
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<tr>
<td>DFMA</td>
<td>Design for Manufacturing and Assembly</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>D</td>
<td>Deionized, de-ionized water</td>
</tr>
<tr>
<td>DLC</td>
<td>Diamondlike carbon</td>
</tr>
<tr>
<td>dL/g</td>
<td>Deciliters per gram</td>
</tr>
<tr>
<td>DM</td>
<td>Diffusion media</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
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<tr>
<td>DMC</td>
<td>Diffusion Monte Carlo, direct manufactured cost</td>
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<tr>
<td>DMDF</td>
<td>2,5-dimethoxy 2,5-dihydrofuran</td>
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<tr>
<td>DME</td>
<td>Dimethyl ether, dimethoxyethane</td>
</tr>
<tr>
<td>DMEA</td>
<td>Dimethylethylamine</td>
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<tr>
<td>DMEAA</td>
<td>Dimethylethylamine alane</td>
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<td>Direct methanol fuel cell</td>
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<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
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<td>DOD</td>
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<td>DOE</td>
<td>U.S. Department of Energy</td>
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<td>DOS</td>
<td>Density of states</td>
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<td>DOT</td>
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<td>DP</td>
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<td>DRIFTs</td>
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<td>DSC</td>
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<td>DSM™</td>
<td>Dimentionally stable membrane</td>
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<td>Directed Technologies, Inc.</td>
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<td>E</td>
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<tr>
<td>EASA</td>
<td>Electrochemically active surface area</td>
</tr>
<tr>
<td>EC</td>
<td>European Commission, electro-chemical</td>
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<tr>
<td>ECA</td>
<td>Electro-catalytic additive, electrochemical area</td>
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<td>ECSA</td>
<td>Electrochemically active surface area, electrochemical area</td>
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<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy, energy dispersive spectrum</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediamine tetraacetic acid</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
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<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
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<tr>
<td>EERE</td>
<td>U.S. DOE Office of Energy Efficiency and Renewable Energy</td>
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<tr>
<td>EFP</td>
<td>External fuel processor</td>
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<tr>
<td>EFTE</td>
<td>Ethylene-tetrafluoroethylene</td>
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<tr>
<td>EHC</td>
<td>Electrochemical hydrogen compressor</td>
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<tr>
<td>EH&amp;S</td>
<td>Environmental Health and Safety</td>
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<tr>
<td>EIA</td>
<td>Energy Information Administration of the U.S. Department of Energy</td>
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<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<tr>
<td>ELAT®</td>
<td>Registered Trademark of De Nora North America, Inc., covers GDLs and GDEs</td>
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<tr>
<td>EMP</td>
<td>Electron microprobe</td>
</tr>
<tr>
<td>EMTEC</td>
<td>Edison Materials Technology Center</td>
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<td>cNMR</td>
<td>Electrochemical nuclear magnetic resonance</td>
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<tr>
<td>EOL</td>
<td>End of life</td>
</tr>
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<td>EPA</td>
<td>U.S. Environmental Protection Agency</td>
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<tr>
<td>EPDM</td>
<td>Ethylene propylene diene monomer</td>
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<td>ePTFE</td>
<td>Expanded polytetrafluoroethylene</td>
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<td>ESA</td>
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<td>ESCO</td>
<td>Energy service company</td>
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<td>ESEM</td>
<td>Environmental scanning electron microscopy</td>
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<td>Ethanol steam reforming, electron spin resonance</td>
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<td>Energy storage system</td>
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<td>Division of De Nora North America, Inc.</td>
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<tr>
<td>ETFE</td>
<td>Ethylene-tetrafluoroethylene</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>ETR</td>
<td>Electron transfer rate</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>EVOH</td>
<td>Ethylene vinyl alcohol</td>
</tr>
<tr>
<td>EW</td>
<td>Equivalent weight</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure analysis</td>
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<tr>
<td>F</td>
<td>Fluorine constant, the amount of electric charge in one mole of electrons (96,485.3383 coulomb/mole)</td>
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<tr>
<td>F</td>
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</tr>
<tr>
<td>FAT</td>
<td>Fleet Analysis Toolkit</td>
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<td>Florida Atlantic University</td>
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<tr>
<td>FC</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>FCB</td>
<td>Fuel cell bus</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FCE</td>
<td>FuelCell Energy</td>
</tr>
<tr>
<td>F-Cell</td>
<td>Daimler Fuel Cell vehicle</td>
</tr>
<tr>
<td>FCEV</td>
<td>Fuel cell electric vehicle</td>
</tr>
<tr>
<td>FCS</td>
<td>Fuel cell system</td>
</tr>
<tr>
<td>FCT</td>
<td>Fuel Cell Technologies (Program)</td>
</tr>
<tr>
<td>FCTESQA</td>
<td>Fuel Cell Testing, Safety and Quality Assurance (an international effort to harmonize fuel cell testing procedures)</td>
</tr>
<tr>
<td>FCTESTNET</td>
<td>Fuel Cell Testing and Standardization Network</td>
</tr>
<tr>
<td>FCTS</td>
<td>Fuel cell test station</td>
</tr>
<tr>
<td>FCCTT</td>
<td>Fuel Cell Technical Team</td>
</tr>
<tr>
<td>FCV</td>
<td>Fuel cell vehicle</td>
</tr>
<tr>
<td>Fd</td>
<td>Ferredoxin</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
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<tr>
<td>FE</td>
<td>U.S. DOE Office of Fossil Energy</td>
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<tr>
<td>Fe₂O₃</td>
<td>Ferric oxide</td>
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<tr>
<td>FEA</td>
<td>Finite element analysis</td>
</tr>
<tr>
<td>FEP</td>
<td>Fluorinated ethylene propylene, Teflon®</td>
</tr>
<tr>
<td>FERC</td>
<td>Federal Energy Regulatory Commission</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast fourier transform</td>
</tr>
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<td>FHI</td>
<td>Florida Hydrogen Initiative</td>
</tr>
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<td>FHWA</td>
<td>Federal Highway Administration</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FLUENT</td>
<td>Computer code for computational fluid dynamics</td>
</tr>
<tr>
<td>FMEA</td>
<td>Failure modes and effects analysis</td>
</tr>
<tr>
<td>¹⁹FNMR</td>
<td>¹⁹Fluorine nuclear magnetic resonance</td>
</tr>
<tr>
<td>FNR</td>
<td>Ferredoxin NADP⁺ oxidoreductase</td>
</tr>
<tr>
<td>FOM</td>
<td>Federated object model, figure of merit</td>
</tr>
<tr>
<td>fpi</td>
<td>Fins per inch</td>
</tr>
<tr>
<td>fpm</td>
<td>Feet per minute</td>
</tr>
<tr>
<td>FPS</td>
<td>Bis(4-fluorophenyl)sulfone, fuel processing system</td>
</tr>
<tr>
<td>FRC</td>
<td>Fiber-reinforced composite</td>
</tr>
<tr>
<td>FRP</td>
<td>Fiber-reinforced polymer</td>
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<td>FRR</td>
<td>Fluoride release rate</td>
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<td>FSEC</td>
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<td>ft</td>
<td>Feet</td>
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<td>FT</td>
<td>Fault tree</td>
</tr>
<tr>
<td>ft²</td>
<td>Square feet</td>
</tr>
<tr>
<td>ft³</td>
<td>Cubic feet</td>
</tr>
<tr>
<td>FTA</td>
<td>Federal Transit Administration</td>
</tr>
<tr>
<td>FT-IR, FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FTIR-ATR</td>
<td>Fourier transform infrared attenuated total reflection</td>
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<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>FTP</td>
<td>Federal Test Procedure</td>
</tr>
<tr>
<td>FW</td>
<td>Filament winding</td>
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<tr>
<td>FY</td>
<td>Fiscal year</td>
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<tr>
<td>ΔG</td>
<td>Gibbs free energy of reaction</td>
</tr>
<tr>
<td>g</td>
<td>Gram; acceleration of gravity</td>
</tr>
<tr>
<td>G</td>
<td>Graphite</td>
</tr>
<tr>
<td>Ga</td>
<td>Gallium</td>
</tr>
<tr>
<td>GA</td>
<td>General Atomics</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium arsenic</td>
</tr>
<tr>
<td>GADDIS</td>
<td>General area diffraction system</td>
</tr>
<tr>
<td>gal</td>
<td>Gallon</td>
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<tr>
<td>GAMS</td>
<td>Generalized Algebraic Modeling System, a commercially available software designed for linear and non-linear optimization</td>
</tr>
<tr>
<td>GaP</td>
<td>Gallium phosphide</td>
</tr>
<tr>
<td>GB</td>
<td>Gigabyte</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy, or vitreous carbon; a pure carbon that is amorphous (non-crystalline)</td>
</tr>
<tr>
<td>g/cc</td>
<td>Grams per cubic centimeter</td>
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<tr>
<td>GCLP</td>
<td>Grand-canonical linear programming</td>
</tr>
<tr>
<td>GCNC</td>
<td>Grand Canonical Monte Carlo</td>
</tr>
<tr>
<td>GCMS</td>
<td>Gas chromatograph mass spectroscopy</td>
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<tr>
<td>Gd</td>
<td>Gadolinium</td>
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<tr>
<td>GDC</td>
<td>Gadolinium-doped ceria</td>
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<tr>
<td>GDE</td>
<td>Gas diffusion electrode</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>GDM</td>
<td>Gas diffusion media</td>
</tr>
<tr>
<td>GDS</td>
<td>Galvanodynamic scan</td>
</tr>
<tr>
<td>Acronym/Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>----------------------</td>
<td>------------</td>
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<tr>
<td>Ge</td>
<td>Germanium</td>
</tr>
<tr>
<td>Gen I</td>
<td>First generation</td>
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<tr>
<td>GES</td>
<td>Giner Electrochemical Systems, LLC</td>
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<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
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<tr>
<td>GGA+U-SP</td>
<td>Generalized gradient approximation with Hubbard-type interaction parameter and spin polarized approach</td>
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<tr>
<td>GGE, gge</td>
<td>Gasoline gallon equivalent</td>
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<td>GH₂</td>
<td>Gaseous hydrogen</td>
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<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hourly space velocity</td>
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<td>GIS</td>
<td>Geographic information system</td>
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<tr>
<td>GJ</td>
<td>Gigajoule(s)</td>
</tr>
<tr>
<td>g/kW</td>
<td>Gram(s) per kilowatt</td>
</tr>
<tr>
<td>GLAD</td>
<td>Glancing angle deposition</td>
</tr>
<tr>
<td>gm</td>
<td>Gram(s)</td>
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<td>GM</td>
<td>General Motors, Gifford McMahon</td>
</tr>
<tr>
<td>gm/day</td>
<td>Gram(s) per day</td>
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<tr>
<td>g/min</td>
<td>Gram(s) per minute</td>
</tr>
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<td>GNF</td>
<td>Graphite nanofiber</td>
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<td>GO</td>
<td>Gate opening, graphene oxide</td>
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<td>GPA</td>
<td>Gigapascal(s)</td>
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<td>GPC</td>
<td>Gel permeation chromatography</td>
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<td>GPS</td>
<td>Global positioning system</td>
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<td>GRC</td>
<td>Glass-reinforced concrete</td>
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<td>GREET</td>
<td>Greenhouse gases, Regulated Emissions and Energy use in Transportation model</td>
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<td>GRPE</td>
<td>Working Party on Pollution and Energy</td>
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<tr>
<td>g/s</td>
<td>Grams per second</td>
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<td>GTI</td>
<td>Gas Technology Institute</td>
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<td>GTR</td>
<td>Global Technical Regulations</td>
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<td>GUI</td>
<td>Graphical user interface</td>
</tr>
<tr>
<td>GV</td>
<td>Gasoline vehicle</td>
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<td>GWe</td>
<td>Gigawatt(s) electric</td>
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<tr>
<td>h</td>
<td>Hour(s)</td>
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<tr>
<td>ΔH</td>
<td>Enthalpy of reaction, enthalpy of hydrogenation</td>
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<tr>
<td>ΔH⁰ᵣ</td>
<td>Standard heat of formation</td>
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<tr>
<td>H</td>
<td>Hydrogen</td>
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<tr>
<td>H+</td>
<td>Proton</td>
</tr>
<tr>
<td>H⁻</td>
<td>Hydride</td>
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<td>H₂</td>
<td>Diatomic hydrogen</td>
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<td>H₂A</td>
<td>Hydrogen Analysis project sponsored by DOE</td>
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<tr>
<td>H₂-FCS</td>
<td>Stationary fuel cell system designs that co-produce hydrogen</td>
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<tr>
<td>H₂-ICE, H₂ICE</td>
<td>Hydrogen internal combustion engine</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
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<td>Hydrogen peroxide</td>
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<td>H₂S</td>
<td>Hydrogen sulfide</td>
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<td>H₂SO₄</td>
<td>Sulfuric acid</td>
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<td>H₃PO₄</td>
<td>Phosphoric acid</td>
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<tr>
<td>HAADF</td>
<td>High-angle annular dark-field</td>
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<tr>
<td>HAADF-STEM</td>
<td>High angle annular dark field scanning transmission electron microscopy</td>
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<td>HAMMER</td>
<td>Hazardous Materials Management and Emergency Response</td>
</tr>
<tr>
<td>HARC</td>
<td>Houston Advanced Research Center</td>
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<td>HATCI</td>
<td>Hyundai-KIA America Technical Center Inc.</td>
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<tr>
<td>HAVO</td>
<td>Hawaii Volcanoes National Park</td>
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<td>HAZ</td>
<td>Heat affected zone</td>
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<td>HAZID</td>
<td>Hazard identification analysis</td>
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<td>HAZOP</td>
<td>Hazards and operational safety analysis, hazards and operability analysis</td>
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<tr>
<td>HBr</td>
<td>Hydrogen bromide</td>
</tr>
<tr>
<td>HCG</td>
<td>Hydrogen Coordinating Group</td>
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<tr>
<td>HCGB</td>
<td>Hydrocarbon-based guanidine base</td>
</tr>
<tr>
<td>HCl, HCL</td>
<td>Hydrochloric acid, hydrogen chloride</td>
</tr>
<tr>
<td>HClO₄</td>
<td>Perchloric acid</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Bicarbonate</td>
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<td>hcp</td>
<td>Hexagonal close-packing</td>
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<td>HC&amp;S</td>
<td>Hawaiian Commercial and Sugar Company</td>
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<tr>
<td>HD</td>
<td>Deuterium hydride</td>
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<td>HDF</td>
<td>Hydrogen dispensing facility</td>
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<td>HDPE</td>
<td>High-density polyethylene</td>
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<td>Hydrogen desulfurization</td>
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<td>Hydrogen Delivery Scenario Analysis Model</td>
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<td>Helium</td>
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<td>Hydrogen embrittlement</td>
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<tr>
<td>HEI</td>
<td>HyPerComp Engineering, Inc.</td>
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<tr>
<td>HEMA</td>
<td>2-hydroxyethyl methacrylate</td>
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<tr>
<td>HEPA</td>
<td>High efficiency particulate air filter</td>
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<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
</tr>
<tr>
<td>HEX</td>
<td>Heat exchanger</td>
</tr>
<tr>
<td>Hf</td>
<td>Hafnium</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluorhydric acid, hydrogen fluoride, Hartree Fock</td>
</tr>
<tr>
<td>HFB</td>
<td>Hexafluorobenzene</td>
</tr>
<tr>
<td>HFC</td>
<td>Hydrogen fuel cell</td>
</tr>
<tr>
<td>HFCIT</td>
<td>Hydrogen, Fuel Cells and Infrastructure Technologies Program</td>
</tr>
<tr>
<td>HFCT</td>
<td>Hydrogen and fuel cell technology</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
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<tr>
<td>HFCTF</td>
<td>Hawaii Fuel Cell Test Facility</td>
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<td>HFCV</td>
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<td>HFR</td>
<td>High-frequency resistance</td>
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<td>HFV</td>
<td>Hydrogen-fueled vehicle</td>
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<td>HHR</td>
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<td>HHV</td>
<td>Higher heating value</td>
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<td>HI</td>
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<td>HIA</td>
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<tr>
<td>HIC</td>
<td>Hydrogen-induced cracking</td>
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<td>HMC</td>
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<td>HNEI</td>
<td>Hawaii Natural Energy Institute</td>
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<tr>
<td>HNO₃</td>
<td>Nitric acid</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly-ordered pyrolytic graphite</td>
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<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
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<tr>
<td>hp</td>
<td>Horsepower</td>
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<td>HP</td>
<td>High-pressure</td>
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<td>Heteropoly acid</td>
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<td>H-PEMFC</td>
<td>Hydrogen polymer electrolyte membrane fuel cell</td>
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<td>HPIT</td>
<td>Hydrogen powered industrial trucks</td>
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<td>HPLC</td>
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<td>HPPS</td>
<td>N,N-diisopropylethylammonium 2,2-bis(p-hydroxyphenyl) pentafluoropropanesulfonate</td>
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<td>HPRD</td>
<td>Hydrogen pressure relief device</td>
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<tr>
<td>hr</td>
<td>Hour(s)</td>
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<td>HRA</td>
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<td>HREELS</td>
<td>High resolution electron energy loss spectroscopy</td>
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<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
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<tr>
<td>HRXRT</td>
<td>High-resolution X-ray tomography</td>
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<tr>
<td>HS</td>
<td>Hydrogen sorption</td>
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<tr>
<td>HSC</td>
<td>Database name derived from the letters for enthalpy, entropy and heat capacity</td>
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<tr>
<td>HSCoE</td>
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<td>HSDC</td>
<td>Hydrogen Secure Data Center</td>
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<tr>
<td>HSECoE</td>
<td>Hydrogen Storage Engineering Center of Excellence</td>
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<tr>
<td>HSM</td>
<td>Hydrogen storage material, hydrogen storage module</td>
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<td>HSMCoE</td>
<td>Hydrogen Storage Material Center of Excellence</td>
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<td>HSO₄</td>
<td>Bisulfate anion</td>
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<td>Hydrogen Storage SIMulator</td>
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<td>HTAC</td>
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<tr>
<td>HTM</td>
<td>Hydrogen transport membrane</td>
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<td>HTMG</td>
<td>High Temperature Membrane Working Group</td>
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<td>HTS</td>
<td>High-temperature shift, high-throughput screening</td>
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<td>HTWGS</td>
<td>High-temperature water-gas shift</td>
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<td>HU</td>
<td>Heat utilization</td>
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<td>HyDRA</td>
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<td>HyQRA</td>
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<td>Hertz</td>
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<tr>
<td>i</td>
<td>Current density (mA/cm²)</td>
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<td>I</td>
<td>Current</td>
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<td>I₂</td>
<td>Diatomic iodine</td>
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<td>Internal combustion</td>
</tr>
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<td>ICC</td>
<td>International Code Council</td>
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<tr>
<td>ICE</td>
<td>Internal combustion engine</td>
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<tr>
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<td>Internal combustion engine vehicle</td>
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<tr>
<td>ICP</td>
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<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
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<td>ICR</td>
<td>Interfacial contact resistance</td>
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<td>ID</td>
<td>Inside diameter</td>
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<td>IEA</td>
<td>International Energy Agency</td>
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<td>IEA-HIA</td>
<td>International Energy Agency Hydrogen Implementing Agreement</td>
</tr>
<tr>
<td>IEC</td>
<td>Ion exchange capacity</td>
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<td>IEEE</td>
<td>Institute of Electrical and Electronics Engineers, Inc.</td>
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<tr>
<td>IFC</td>
<td>International Fire Code</td>
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<tr>
<td>IFF</td>
<td>Integrated flow field</td>
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<td>IGCC</td>
<td>Integrated gasification combined cycle</td>
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<td>IHPV</td>
<td>Internally heated high-pressure vessel</td>
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<tr>
<td>IL</td>
<td>Ionic liquid</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
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</tr>
<tr>
<td>In</td>
<td>Indium</td>
</tr>
<tr>
<td>In., in</td>
<td>Inch</td>
</tr>
<tr>
<td>in²</td>
<td>Square inch</td>
</tr>
<tr>
<td>InP</td>
<td>Indium phosphorus</td>
</tr>
<tr>
<td>INS</td>
<td>Inelastic neutron scattering</td>
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<tr>
<td>IOS</td>
<td>Intelligent Optical Systems, Inc.</td>
</tr>
<tr>
<td>IP</td>
<td>Intellectual property</td>
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<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
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<tr>
<td>IPCE</td>
<td>Incident photon conversion to electrons, incident photon conversion efficiency</td>
</tr>
<tr>
<td>IPHE</td>
<td>International Partnership for the Hydrogen Economy</td>
</tr>
<tr>
<td>IPTG</td>
<td>Isopropyl β-D-1-thiogalactopyranoside</td>
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<tr>
<td>iR</td>
<td>Internal resistance, voltage loss due to resistance</td>
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<tr>
<td>Ir</td>
<td>Iridium</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>IRMOF</td>
<td>Isoreticular metal organic framework</td>
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<tr>
<td>IrOₓ</td>
<td>Iridium oxide</td>
</tr>
<tr>
<td>IRR</td>
<td>Internal rate of return</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
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<tr>
<td>ITM</td>
<td>Ion transport membrane</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>ITP</td>
<td>Indium tin phosphate</td>
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<tr>
<td>IV</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>IUG</td>
<td>Interagency Working Group</td>
</tr>
<tr>
<td>J</td>
<td>Current, Joule(s)</td>
</tr>
<tr>
<td>JFK</td>
<td>John F. Kennedy (airport)</td>
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<tr>
<td>JMFC</td>
<td>Johnson-Matthey Fuel Cells, Inc.</td>
</tr>
<tr>
<td>JNAIST</td>
<td>Japanese National Institute of Advanced Industrial Science and Technology</td>
</tr>
<tr>
<td>JPL</td>
<td>Jet Propulsion Laboratory</td>
</tr>
<tr>
<td>JRC</td>
<td>Joint Research Centre</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density-voltage</td>
</tr>
<tr>
<td>K</td>
<td>Sievert's constant, ml/[cm²-min-atm½]</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin, absolute temperature</td>
</tr>
<tr>
<td>K</td>
<td>Potassium</td>
</tr>
<tr>
<td>Kثل</td>
<td>Fracture toughness measured in hydrogen gas</td>
</tr>
<tr>
<td>Kثل</td>
<td>Hydrogen-assisted crack growth threshold</td>
</tr>
<tr>
<td>kÅ</td>
<td>1,000 angstroms</td>
</tr>
<tr>
<td>KAERI</td>
<td>Korea Atomic Energy Research Institute</td>
</tr>
<tr>
<td>KAIST</td>
<td>Korea Advanced Institute of Science and Technology</td>
</tr>
<tr>
<td>kA/m²</td>
<td>Kilo-ampere(s) per square meter</td>
</tr>
<tr>
<td>kb</td>
<td>Kilo-base pair, a unit of measurement used in genetics equal to 1,000 nucleotides</td>
</tr>
<tr>
<td>KBr</td>
<td>Potassium bromide</td>
</tr>
<tr>
<td>kcal</td>
<td>Kilocalorie(s)</td>
</tr>
<tr>
<td>kcal/mol</td>
<td>Kilocalorie(s) per mole</td>
</tr>
<tr>
<td>KeV</td>
<td>Kilo electron volt(s)</td>
</tr>
<tr>
<td>kg</td>
<td>Kilogram(s)</td>
</tr>
<tr>
<td>kg/d</td>
<td>Kilogram(s) per day</td>
</tr>
<tr>
<td>kg/hr</td>
<td>Kilogram(s) per hour</td>
</tr>
<tr>
<td>kg/m³</td>
<td>Kilogram(s) per cubic meter</td>
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<tr>
<td>KH</td>
<td>Potassium hydride</td>
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<td>kHz</td>
<td>Kilohertz</td>
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<tr>
<td>KIA</td>
<td>Kia Motor Company</td>
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<tr>
<td>kJ</td>
<td>Kilojoule(s)</td>
</tr>
<tr>
<td>kJ/mol</td>
<td>Kilojoule(s) per mole</td>
</tr>
<tr>
<td>km</td>
<td>Kilometer(s)</td>
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<tr>
<td>KMC</td>
<td>Kinetic Monte Carlo, Kilauea Military Camp, Kia Motors Corporation</td>
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<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilopascal(s)</td>
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<tr>
<td>kph</td>
<td>Kilometer(s) per hour</td>
</tr>
<tr>
<td>ksi</td>
<td>1,000 pound-force per square inch</td>
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<tr>
<td>Kth</td>
<td>Fracture toughness threshold</td>
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<tr>
<td>kT/y</td>
<td>Kiloton(s) per year</td>
</tr>
<tr>
<td>kW</td>
<td>Kilowatt(s)</td>
</tr>
<tr>
<td>kWₑ</td>
<td>Kilowatt(s) electric</td>
</tr>
<tr>
<td>kWh</td>
<td>Kilowatt-hour(s)</td>
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<tr>
<td>kWh/kg</td>
<td>Kilowatt-hour(s) per kilogram</td>
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<tr>
<td>kWh/L</td>
<td>Kilowatt-hour(s) per liter</td>
</tr>
<tr>
<td>kW/kg</td>
<td>Kilowatt(s) per kilogram</td>
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<tr>
<td>kWt</td>
<td>Kilowatt(s) thermal</td>
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<tr>
<td>L, l</td>
<td>Liter(s)</td>
</tr>
<tr>
<td>La</td>
<td>Lanthanum</td>
</tr>
<tr>
<td>LA</td>
<td>Los Angeles</td>
</tr>
<tr>
<td>LA-92</td>
<td>Los Angeles dynamometer driving cycle</td>
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<tr>
<td>LACVP</td>
<td>Chemistry basis set</td>
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<tr>
<td>λ</td>
<td>Lambda, hydration number</td>
</tr>
<tr>
<td>LANL</td>
<td>Los Alamos National Laboratory</td>
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<tr>
<td>LAO</td>
<td>Lanthanum-modified alumina</td>
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<tr>
<td>LAX</td>
<td>Los Angeles International Airport</td>
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<tr>
<td>lb</td>
<td>Pound(s)</td>
</tr>
<tr>
<td>LBM</td>
<td>Lattice Boltzmann method</td>
</tr>
<tr>
<td>lbmol</td>
<td>Pound-mole(s)</td>
</tr>
<tr>
<td>LBNL</td>
<td>Lawrence Berkeley National Laboratory</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid carrier</td>
</tr>
<tr>
<td>LCA</td>
<td>Life cycle assessment</td>
</tr>
<tr>
<td>LCH₂</td>
<td>Hydrogenated liquid carrier, liquid to compressed hydrogen</td>
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<tr>
<td>LCOE</td>
<td>Levelized cost of energy</td>
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<tr>
<td>L/D</td>
<td>Length to diameter ratio</td>
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<tr>
<td>L-DSM™</td>
<td>Laser-drilled dimensionally stable membrane</td>
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<tr>
<td>LDV</td>
<td>Light-duty vehicle</td>
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<td>LED</td>
<td>Light emitting diode</td>
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<td>LFG</td>
<td>Landfill gas</td>
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<td>LFL</td>
<td>Lower flammability limit</td>
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<td>LFM</td>
<td>Load-following mode</td>
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<td>L/h, l/h</td>
<td>Liter(s) per hour</td>
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<td>LH₂, LH₂</td>
<td>Liquid hydrogen</td>
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<td>LHC</td>
<td>Light-harvesting chlorophyll</td>
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<td>LHS</td>
<td>Lawrence Hall of Science</td>
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<td>LHSV</td>
<td>Liquid hourly space velocity, h⁻¹</td>
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<tr>
<td>LHV</td>
<td>Lower heating value</td>
</tr>
<tr>
<td>Li</td>
<td>Lithium</td>
</tr>
<tr>
<td>Li-AB</td>
<td>Lithium amidoborane, Li-NH₂-BH₃</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>Lithium borohydride</td>
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<td>LIBS</td>
<td>Laser-induced breakdown spectroscopy</td>
</tr>
<tr>
<td>LiH</td>
<td>Lithium hydride</td>
</tr>
<tr>
<td>LIM</td>
<td>Liquid injection molding, liquid injection moldable</td>
</tr>
<tr>
<td>LLC</td>
<td>Limited Liability Company, lessons learned corner</td>
</tr>
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<td>LLNL</td>
<td>Lawrence Livermore National Laboratory</td>
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<tr>
<td>L/min, l/min</td>
<td>Liter(s) per minute</td>
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<td>Liquid nitrogen</td>
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<td>Liquefied natural gas</td>
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<td>LOD</td>
<td>Limit of detection</td>
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<tr>
<td>LOI</td>
<td>Letter of interest</td>
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<td>LPG</td>
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<td>LPM</td>
<td>Liters per minute</td>
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<td>LPR</td>
<td>Liquid-phase reforming</td>
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<td>LRS</td>
<td>Laser raman spectroscopy</td>
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<td>LSC</td>
<td>Lanthanum strontium cobalt oxide, (La, Sr)CoO₃, strontium-doped lanthanum cobaltite, La₉Sr₂CoO₅₆</td>
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<tr>
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<td>Lanthanum strontium cobalt iron oxide, (La, Sr)(Co, Fe)O₅</td>
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<td>Lanthanum strontium manganese</td>
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<tr>
<td>LSX</td>
<td>Low-silica type-X</td>
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<td>LTDMS</td>
<td>Laser induced thermal desorption mass spectrometry</td>
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<td>LTM</td>
<td>Late-transition-metal</td>
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<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<tr>
<td>m</td>
<td>Meter(s)</td>
</tr>
<tr>
<td>M</td>
<td>Mole, molar</td>
</tr>
<tr>
<td>M</td>
<td>Million</td>
</tr>
<tr>
<td>m²</td>
<td>Square meter(s)</td>
</tr>
<tr>
<td>m²/g</td>
<td>Square meter(s) per gram</td>
</tr>
<tr>
<td>m²/s</td>
<td>Square meter(s) per second</td>
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<td>m³</td>
<td>Cubic meter(s)</td>
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<td>mA</td>
<td>MilliAmps(s)</td>
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<tr>
<td>MA</td>
<td>Mass activity, methyl acrylate</td>
</tr>
<tr>
<td>µA</td>
<td>Micro ampere(s)</td>
</tr>
<tr>
<td>mA/cm²</td>
<td>Milliamp(s) per square centimeter</td>
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<td>µA/cm²</td>
<td>Micro ampere(s) per square centimeter</td>
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<td>Metal ammonia-borane</td>
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<td>Metal amidoboranes</td>
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<td>MAS</td>
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<td>Magic angle spinning boron-11 nuclear magnetic resonance spectroscopy</td>
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<td>MB</td>
<td>Megabyte</td>
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<td>mC²</td>
<td>Multi-component composite (membrane)</td>
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<td>mC·cm⁻²</td>
<td>MilliCoulomb(s) per square centimeter</td>
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<td>MCFC</td>
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<td>MEOP</td>
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<td>MeV</td>
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<td>Acronym/Abbreviation</td>
<td>Definition</td>
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<tr>
<td>μg</td>
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<tr>
<td>MgCl₂</td>
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<td>mg/cm²</td>
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<td>Magnesium hydride</td>
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<tr>
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<td>Magnesium oxide</td>
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<td>MHz</td>
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<td>ms</td>
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<td>MS</td>
<td>Mass spectroscopy, mass spectrometry</td>
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<td>mS/cm</td>
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<td>Membrane steam reformer</td>
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<td>Materials and Systems Research, Inc.</td>
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<td>Montana State University</td>
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<td>MSW</td>
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<td>MT</td>
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<td>MTI</td>
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<td>mtorr</td>
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<td>μV</td>
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<td>MV</td>
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<td>mW</td>
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<td>MW</td>
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<tr>
<td>MWh</td>
<td>Megawatt-hour(s)</td>
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<td>MWNT</td>
<td>Multi-wall carbon nanotube</td>
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<td>MYRDD, MYRD&amp;DP</td>
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<td>Nafion® 1,100 equivalent weight, 2 millimeter thick membrane</td>
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<tr>
<td>N₂</td>
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<td>N₂O</td>
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<tr>
<td>Na</td>
<td>Sodium</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>Na₂S</td>
<td>Sodium sulfide</td>
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<tr>
<td>NaAlH₄</td>
<td>Sodium aluminum hydride, sodium tetrahydroaluminate, sodium alanate</td>
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<td>NaBH₄</td>
<td>Sodium borohydride</td>
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<td>NaBO₂</td>
<td>Sodium metaborate</td>
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<td>NADPH</td>
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<td>Nafion®</td>
<td>Registered Trademark of E.I. DuPont de Nemours; sulfonated tetrafluoroethylene based fluoropolymer-copolymer</td>
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<td>Niobium</td>
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<tr>
<td>N/cm²</td>
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<tr>
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<td>NIST Center for Neutron Research</td>
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<td>NCSL</td>
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<td>National Fuel Cell Research Center</td>
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<td>NL</td>
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<td>Open circuit potential</td>
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<td>Acronym</td>
<td>Definition</td>
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<td>Opening Reading Frame indicating the occurrence of a protein coding region in the DNA sequence</td>
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<td>OSC</td>
<td>Orlando Science Center, oxygen storage capability</td>
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<td>U.S. Occupational Safety and Health Administration</td>
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<td>Ohio State University</td>
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<td>OTM</td>
<td>Oxygen transport membrane</td>
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<td>ΔP</td>
<td>Pressure drop, pressure change</td>
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<td>P</td>
<td>Phosphorus, pressure</td>
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<td>Pa</td>
<td>Pascal(s)</td>
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<td>Polymer assisted deposition</td>
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<td>PAES</td>
<td>Poly(arylene-ether-sulfone)</td>
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<td>Photoelectrochemical, photoelectrocatalyst</td>
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<td>Plasma-enhanced chemical vapor deposition</td>
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<td>PEFC</td>
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<td>Polyethylene glycol</td>
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<td>PEGMEMA</td>
<td>Monomethoxy(poly(ethyleneglycol)methacrylate</td>
</tr>
<tr>
<td>PEGS</td>
<td>Prototype electrostatic ground state</td>
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<tr>
<td>PEI</td>
<td>Polyetherimide, polyethylene imine</td>
</tr>
<tr>
<td>PEKK</td>
<td>Poly (ether ketone ketone)</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton exchange membrane, polymer electrolyte membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer electrolyte membrane fuel cell, proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PES</td>
<td>Polyether sulfone</td>
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<tr>
<td>PFA</td>
<td>Perfluoroalkoxy (a type of fluoropolymer), polyfurfuryl alcohol</td>
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<td>PFC</td>
<td>Polymer electrolyte membrane fuel cell</td>
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<tr>
<td>PFD</td>
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<tr>
<td>PFGB</td>
<td>Perfluorinated guanidine base</td>
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<tr>
<td>PFPO-PSS</td>
<td>Poly(perfluoropropylene oxide)-b-poly(styrene sulfonate)</td>
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<tr>
<td>PFSA</td>
<td>Perfluorinated sulfonic acid, perfluorosulfonic acid, poly(fluorosulfonic acid)</td>
</tr>
<tr>
<td>PGM</td>
<td>Precious group metal, platinum group metal</td>
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<tr>
<td>P-H₂</td>
<td>Para-hydrogen</td>
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<tr>
<td>pH</td>
<td>Power of the hydronium ion</td>
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<td>PI</td>
<td>Principal investigator, polyimide</td>
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<tr>
<td>PIL, pIL</td>
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<td>Protonic ionic membrane</td>
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<td>PLLA</td>
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<td>PM</td>
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<td>pO₂</td>
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<td>POM</td>
<td>Polyoxometallate</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
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<tr>
<td>POP</td>
<td>Porous organic polymers</td>
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<td>POSS</td>
<td>Polyhedral oligomeric silsesquioxane, Petroleum Offshore Survey Support</td>
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<td>Partial oxidation</td>
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<td>PPA</td>
<td>Polyphosphoric acid</td>
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<tr>
<td>ppb</td>
<td>Part(s) per billion</td>
</tr>
<tr>
<td>ppbv</td>
<td>Part(s) per billion by volume</td>
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<td>Pore(s) per inch</td>
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<tr>
<td>ppm</td>
<td>Part(s) per million</td>
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<tr>
<td>ppmv</td>
<td>Part(s) per million by volume</td>
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<tr>
<td>ppmw</td>
<td>Part(s) per million by weight</td>
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<td>PPO</td>
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<td>PPS</td>
<td>Polyphenylene sulfide</td>
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<td>PPISA</td>
<td>Partial pressure swing adsorption</td>
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<td>PPSU</td>
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<td>PPy</td>
<td>Poly(2-pyrrolyl)phenylmethane</td>
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<td>PSA</td>
<td>Pressure swing adsorption, adsorber</td>
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<td>PSD</td>
<td>Particle size distribution, pore size distribution</td>
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<td>Perfluoro (4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride</td>
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<td>psi, PSI</td>
<td>Pound(s) per square inch</td>
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<td>psia</td>
<td>Pound(s) per square inch absolute</td>
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<td>Pound(s) per square inch differential</td>
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<td>psig, PSIG</td>
<td>Pound(s) per square inch gauge</td>
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<td>QMC</td>
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<td>Research, development &amp; demonstration</td>
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<td>Rhenium</td>
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<td>Radio frequency</td>
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<td>Rhodium</td>
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<td>Reference hydrogen electrode; reversible hydrogen electrode</td>
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<td>Ribo nucleic acid</td>
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<td>ROMP</td>
<td>Ring Opening Metathesis Polymerization</td>
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<td>Small angle neutron scattering</td>
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<tr>
<td>SAXS</td>
<td>Small angle X-ray scattering</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
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<tr>
<td>SBAB</td>
<td>Sec-butylamineborane</td>
</tr>
<tr>
<td>S&lt;sub&gt;BET&lt;/sub&gt;</td>
<td>BET specific surface area</td>
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<td>Sodium borohydride</td>
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<tr>
<td>SBIR</td>
<td>Small Business Innovation Research</td>
</tr>
<tr>
<td>SBR</td>
<td>Sterylene-butadiene rubber</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary building unit</td>
</tr>
<tr>
<td>Sc</td>
<td>Scandium</td>
</tr>
<tr>
<td>S/C</td>
<td>Steam to carbon ratio</td>
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<tr>
<td>sccm, SCCM</td>
<td>Standard cubic centimeter(s) per minute</td>
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<td>SCE</td>
<td>Saturated calomel electrode</td>
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<tr>
<td>SCF, scf</td>
<td>Standard cubic feet, supercritical fluid</td>
</tr>
<tr>
<td>scfd</td>
<td>Standard cubic feet per day</td>
</tr>
<tr>
<td>SCFH, scfh</td>
<td>Standard cubic feet per hour</td>
</tr>
<tr>
<td>SCFM</td>
<td>Standard cubic feet per minute</td>
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<tr>
<td>S/cm</td>
<td>Siemen(s) per centimeter</td>
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<tr>
<td>SCOIF</td>
<td>Single cell with open flowfield</td>
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<td>SCPO</td>
<td>Staged catalytic partial oxidation</td>
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<td>SCR</td>
<td>Selective catalytic reduction, semi-conductor rectifier</td>
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<td>SD</td>
<td>Standard deviation</td>
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<td>SDO</td>
<td>Standards development organization</td>
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<td>Selenium</td>
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<tr>
<td>sec</td>
<td>Second(s)</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy, scanning electron microscope</td>
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<tr>
<td>SENT</td>
<td>Single edge notch tension</td>
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<tr>
<td>SEPUP</td>
<td>Science Education for Public Understanding Program</td>
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<tr>
<td>SERA</td>
<td>Scenario Evaluation, Regionalization and Analysis</td>
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<tr>
<td>SERC</td>
<td>Schatz Energy Research Center</td>
</tr>
<tr>
<td>SFA</td>
<td>Sulfonic acid</td>
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<tr>
<td>SFC</td>
<td>Stationary fuel cell</td>
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<tr>
<td>SFM</td>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;Fe&lt;sub&gt;1.5&lt;/sub&gt;Mo&lt;sub&gt;0.5&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;δ</td>
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<td>SFTI</td>
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<tr>
<td>SGD</td>
<td>Spontaneous galvanic displacement, system gravimetric density</td>
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<td>SGIP</td>
<td>Self Generation Incentive Program</td>
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<td>SHE</td>
<td>Standard hydrogen electrode</td>
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<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>Si&lt;sub&gt;N&lt;/sub&gt;</td>
<td>Silicon nitride</td>
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<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>SiCN</td>
<td>Silicon carbonitrde</td>
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<td>SIMS</td>
<td>Secondary ion emission spectroscopy</td>
</tr>
<tr>
<td>Si-NS</td>
<td>Silica nanosprings</td>
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<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Silicon dioxide</td>
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<td>sL</td>
<td>Standard liter (0°C, 1 atm)</td>
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<td>SLAC</td>
<td>Stanford Linear Accelerator Center</td>
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<td>SLD</td>
<td>Simplified local density</td>
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<td>SLPH</td>
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<td>SLPm, slpm, slm, sL/min</td>
<td>Standard liter(s) per minute</td>
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<td>SLT</td>
<td>Strontium-doped lanthanum titanate</td>
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<tr>
<td>SMMM</td>
<td>Supported molten metal membrane</td>
</tr>
<tr>
<td>SMORS</td>
<td>Sub-scale molded o-ring seal</td>
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<td>SMR</td>
<td>Steam methane reformer, steam methane reforming</td>
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<td>SMR-ECM</td>
<td>Steam methane reformer with electrochemical purifier</td>
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<td>SMR-PSA</td>
<td>Steam methane reformer with pressure swing adsorption</td>
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<td>Tin</td>
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<td>Tin oxide</td>
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<td>Sulfur trioxide</td>
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<td>Solid oxide electrolysis cell, solid oxide electrolyzer cell</td>
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<td>Solid oxide fuel cell</td>
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<td>Oxides of sulfur</td>
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<td>Sulfonated poly(arylene ether sulfone)</td>
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<td>Sulfonated poly(ether ether ketone)</td>
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<td>SPEK</td>
<td>Sulfonated poly-etherketone-ketone</td>
</tr>
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<td>SPEKK</td>
<td>Sulfonated polyether(ether ketone ketone)</td>
</tr>
<tr>
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<td>Type of milling machine</td>
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<td>SPM</td>
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<td>sPOSS</td>
<td>sulfonated octaphenyl polyhedral oligomeric silsesquioxanes</td>
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<td>sq. in.</td>
<td>Square inch(es)</td>
</tr>
<tr>
<td>Sr</td>
<td>Strontium</td>
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<td>SR</td>
<td>Steam reformer, steam reforming</td>
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<td>SR-M</td>
<td>Steam reformer membrane</td>
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<td>SrO</td>
<td>Strontium oxide</td>
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<td>SrTiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Strontium titanate, the proton conducting material</td>
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<td>SS</td>
<td>Stainless steel</td>
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<td>SSA</td>
<td>Specific surface area</td>
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<td>SSAWG</td>
<td>Storage System Analysis Working Group</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
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</tr>
<tr>
<td>SSNMR</td>
<td>Solid-state nuclear magnetic resonance</td>
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<td>SSRL</td>
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<td>SSRS</td>
<td>Solid-state reactive sintering</td>
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<td>SSWAG</td>
<td>Storage System Working Analysis Group</td>
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<td>STCH</td>
<td>Solar Thermochemical Hydrogen</td>
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<td>STM</td>
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<td>T, t</td>
<td>Ton, tonne</td>
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<td>To be determined</td>
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