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Exploratory Technology Research Program for Electrochemical Energy Storage

K. Kinoshita, Editor
Energy and Environment Division

June 1996

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EXPLORATORY TECHNOLOGY RESEARCH PROGRAM FOR ELECTROCHEMICAL ENERGY STORAGE

ANNUAL REPORT FOR 1995

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June 1996

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EXECUTIVE SUMMARY

The U.S. Department of Energy's Office of Transportation Technologies provides support for an Electrochemical Energy Storage Program, that includes research and development (R&D) on advanced rechargeable batteries and fuel cells. A major goal of this program is to develop electrochemical power sources suitable for application in electric vehicles (EVs) and hybrid systems. The program centers on advanced electrochemical systems that offer the potential for high performance and low life-cycle costs, both of which are necessary to permit significant penetration into commercial markets.

The DOE Electric Vehicle Technology Program is divided into two project areas: the United States Advanced Battery Consortium (USABC) and Advanced Battery R&D which includes the Exploratory Technology Research (ETR) Program managed by the Lawrence Berkeley National Laboratory* (LBNL). The USABC, a tripartite undertaking between DOE, the U.S. automobile manufacturers and the Electric Power Research Institute (EPRI), was formed in 1991 to accelerate the development of advanced batteries for EVs. The role of the ETR Program is to perform supporting research on the advanced battery systems under development by the USABC and the Sandia National Laboratories (SNL) Electric Vehicle Advanced Battery Systems (EVABS) Program, and to evaluate new systems with potentially superior performance, durability and/or cost characteristics. The specific goal of the ETR Program is to identify the most promising electrochemical technologies and transfer them to the USABC, the battery industry and/or other Government agencies for further development and scale-up. This report summarizes the research, financial and management activities relevant to the ETR Program in CY 1995. This is a continuing program, and reports for prior years have been published; they are listed at the end of this Executive Summary.

The general R&D areas addressed by the program include identification of new electrochemical couples for advanced batteries, determination of technical feasibility of the new couples, improvements in battery components and materials, establishment of engineering principles applicable to electrochemical energy storage and conversion, and the development of fuel cell technology for transportation applications. Major emphasis is given to applied research which will lead to superior performance and lower life-cycle costs.

The ETR Program is divided into three major program elements: Exploratory Research, Applied Science Research, and Air Systems Research. Highlights of each program element are summarized according to the appropriate battery system or electrochemical research area.

* Participants in the ETR Program include the following LBNL scientists: E. Cairns, J. Evans, K. Kinoshita, F. McLarnon and J. Newman of the Energy and Environment Division; and L. De Jonghe, P. Ross and C. Tobias (Professor Emeritus)** of the Materials Sciences Division.

** Professor Tobias died March 6, 1996.

EXPLORATORY RESEARCH

The objectives of this program element are to identify, evaluate and initiate development of new electrochemical couples with the potential to meet or exceed the electrochemical performance goals for advanced batteries and capacitors. Research was conducted on novel Na cells that contain polymer or molten-salt electrolytes, an all-solid state Li/Mn oxide cell and carbons for electrochemical double-layer capacitors.

- LBNL redirected a project in mid-year from an emphasis on development of sodium/polymer cells to polymer electrolytes and composite electrolyte membranes for lithium cells. Thin solid films of Li_3N were prepared by hydraulically pressing powders under an inert atmosphere.
- Oak Ridge National Laboratory (ORNL) observed that the least-resistive cells with LiMn_2O_4 electrodes were obtained by low-pressure deposition with a positive substrate bias. However, Li transport in the cathode or through the cathode-electrolyte interface limits the current density of the cell discharge.
- Georgia Institute of Technology observed that ambient-temperature, protonated molten salt electrolytes comprised of mixtures of NaAlCl_4 and various alkylimidazolium chlorides allow repetitive Na plating and stripping with high efficiencies only if there is a short delay between plating and stripping. However, the Na slowly reacts with the molten salt, giving rise to a self-discharge rate of 5% per day.
- PolyPlus Battery Co. completed a project to evaluate the performance of Na/organosulfur (Na/SRPE) cells. Cell cycling showed persistent capacity decline, and the cells were prone to shorting during charging.
- A subcontract was awarded on the basis of a Request-for-Proposals to SAFT Research & Development Center to evaluate activated carbons in electrochemical double-layer capacitors. A systematic study of various electrode binders was initiated.

APPLIED SCIENCE RESEARCH

The objectives of this program element are to provide and establish scientific and engineering principles applicable to batteries and electrochemical systems; and to identify, characterize and improve materials and components for use in batteries and electrochemical systems. Projects in this element provide research that supports a range of battery systems that contain solid electrolyte and nonaqueous electrolytes, both liquid and polymer. Other cross-cutting research efforts are directed at improving the understanding of electrochemical engineering principles, minimizing corrosion of battery components, analyzing the surfaces of electrodes, and electrocatalysis.

Electrode Characterization studies are an important research element for the successful development of rechargeable electrodes for advanced secondary batteries. Efforts are underway to evaluate the

performance of cells utilizing Li intercalation electrodes, and use advanced spectroscopic techniques to investigate the chemical state of electrode materials during charge/discharge cycling.

- TEM and XRD analysis of Li intercalated graphite by LBNL showed the presence of both LiC_6 and LiC_{12} phases, which can co-exist together.
- Lawrence Livermore National Laboratory (LLNL) observed that electrodes fabricated from various graphites (Superior Graphite Co.) yielded Li intercalation capacities that range from 320 to 360 mAh/g (equivalent to x in Li_xC_6 from 0.85 to 0.95), approaching the theoretical value of 372 mAh/g corresponding to LiC_6 . The capacity of Superior graphitized cokes are comparable to that obtained with petroleum cokes from other sources ($x=0.62$) but the irreversible capacity loss is only 68 mAh/g.
- Brookhaven National Laboratory (BNL) used extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge spectroscopy (XANES) to study zincate solutions. EXAFS showed that the structure of supersaturated zincate is identical to regular zincate solutions. XANES indicated ion pairing of zincate with the lighter alkali ions (Li^+ and Na^+).

Electrodes for Electrochemical Cells are being developed to identify low-cost metal hydrides for metal-hydride cells and improved metal oxides for electrochemical capacitors.

- X-ray absorption spectroscopy (XAS) studies of AB_2 alloy hydrides by BNL indicated the presence of strong interactions between the interstitial H atom and Ti, V and Zr. Very little interaction between H and Ni was observed, suggesting that the role of Ni in the AB_2 alloys is primarily catalytic in nature.
- A subcontract was awarded on the basis of a Request-for-Proposals to the University of South Carolina to improve the performance of metal hydride electrodes. Experimental hydrogen storage capacities of bare and Cu-coated $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ alloys were found to be 270 and 275 mAh/g, respectively, about 76 and 78% of the theoretical capacity.
- A subcontract was awarded on the basis of a Request-for-Proposals to the University of Michigan to model the performance of MH/ NiOOH batteries. Materials were characterized microscopically, and simulations were initiated to characterize transport in model microstructures.
- A subcontract was awarded on the basis of a Request-for-Proposals to the University of Wisconsin to investigate metal oxides for double-layer capacitors. It was observed that the specific capacitance of NiO/Ni electrodes in 1 M LiOH was as high as 120 F/g of active material per cell, double the value obtained in 1 M KOH .
- The University of California at Davis has developed a spreadsheet model to analyze the performance of ultracapacitors in hybrid/electric vehicles. The results confirmed that ultracapacitors, which meet the DOE goal of 5-15 Wh/kg, would be beneficial for load leveling in hybrid/electric vehicles.

Components for Ambient-Temperature Nonaqueous Cells, particularly metal/electrolyte combinations that improve the rechargeability of these cells, are under investigation.

- Preliminary modeling studies by LBNL indicated that smaller sulfur particles are needed to improve the sulfur utilization in the electrode of Li/S cells
- Case Western Reserve University (CWRU) demonstrated that a LiClO_4 /polyethylene oxide (PEO) solid polymer electrolyte (SPE) exhibits sufficiently low volatility and stable physicochemical properties to enable conventional electrochemical experiments to be performed in ultrahigh vacuum (UHV).
- Northwestern University (NWU) synthesized polymer electrolytes based on aluminosilicate-polyether hybrid electrolytes, $(\text{amorphous PEO})_{25}\text{LiTf}$ and $(\text{amorphous PEO})_{38}\text{Li}[\text{Al}(\text{OSiEt}_3)_4]$. The ionic conductivity of the electrolyte is too low at room temperature, but was acceptable for cell tests at 70°C ($1 \times 10^{-4} \text{ S/cm}$).
- NWU demonstrated conclusively, using hopping models within a relaxing environment, that polymer electrolytes will generally exhibit higher mobilities than polyelectrolytes, although the transference properties are less attractive.
- CWRU completed a study of the synthesis of phosphonated poly(2,6-dimethyl phenylene oxide).
- The University of Dayton successfully prepared three liquid-crystalline monomers terminated by benzo-12-crown-4, benzo-15-crown-5 and benzo-18-crown-6 by a multistep synthetic route and determined the pertinent liquid crystalline properties. A procedure for preparation of films polymerized between indium/tin oxide (ITO) glass slides was developed and equipment for aligning the liquid crystal monomers with both an electric field and a magnetic field was assembled.
- The State University of New York (Binghamton) found that the mild hydrothermal aqueous decomposition reaction of potassium permanganate at 170°C produces a layered manganese oxide structure. Electrochemical intercalation and deintercalation of Li into the dehydrated potassium manganese oxide lattice shows a continuous curve indicative of single-phase behavior, $\text{Li}_x\text{K}_{0.25}\text{MnO}_2$ where $0 \leq x \leq 0.6$.
- SRI International completed a project to identify a polyorganopolydisulfide (polyHTB) positive electrode for Na/polymer cells. Performance was hampered by problems with the electrode structure.
- Southern University built an electrochemical system for *in situ* EXAFS studies of Li/ FeS_2 cells. Spectroscopic analysis indicated the presence of Li_2S . This project has been completed.
- Covalent Associates Inc. synthesized Cr-doped LiMn_2O_4 , $\text{LiCr}_{0.14}\text{Mn}_{1.86}\text{O}_4$ (7 mol% Cr), which showed stable charge/discharge cycling, but the performance was lower than that obtained with the spinel LiMn_2O_4 .

Cross-Cutting Research is carried out to develop mathematical models of electrochemical systems and to address fundamental problems in electrocatalysis and current-density distribution; solutions will lead to improved electrode structures and performance in batteries and fuel cells.

- LBNL has developed mathematical models to explore the design and optimization of Li and Li-ion batteries, the discharge behavior of nickel oxide/KOH/LaNi₅ battery systems and electrochemical capacitors, based on pseudohomogeneous porous-electrode theory.
- Analysis of a mathematical model by LBNL indicate that during normal operation, the temperature of a Li-ion battery is unlikely to reach the onset temperature for thermal runaway, however if a battery is continuously cycled under high-rate charge and discharge, significant heat accumulation may occur.
- LBNL observed that the co-precipitation of Co²⁺ ions into the Ni/Ni(OH)₂ electrode reduced the drop in charge efficiency to ~25% after long-term cycling, compared to ~50% drop in electrodes without Co.

AIR SYSTEMS RESEARCH

The objectives of this program element are to identify, characterize and improve materials for air electrodes; and to identify, evaluate and initiate development of fuel-cell technology for transportation applications.

Fuel Cell Research at Los Alamos National Laboratory (LANL) includes research in several areas of electrochemistry, theoretical studies, fuel-cell testing, fuel processing, and membrane characterization. Major achievements of the fuel-cell program during 1995 are listed below:

- LBNL has found that both the structure sensitivity and the high catalytic activity of the Pt₃Sn surface to CO oxidation is attributed to an adsorbed state of CO unique to this alloy and occurs at relatively high coverage on the (111) surface.
- *In situ* probe beam deflection (PBD) studies of anion adsorption at polycrystalline Pt electrode surfaces by LBNL showed that the onset of anion adsorption began at ~200 mV in 0.1 M solutions of H₃PO₄, H₂SO₄ and HClO₄.
- LANL obtained improved performance with a direct methanol fuel cell (DMFC) that contained Pt-RuO_x ("unsupported") anode catalysts and unsupported Pt cathode catalysts.
- An analysis of the characteristics of a DMFC and PEM fuel cell with a methanol steam reformer (RAFC) by LANL indicated that the key issue to improving the performance of DMFCs is to reduce the methanol cross-over.
- LANL demonstrated encouraging results with a new type of ultra-thin composite inorganic membrane developed by W.L. Gore, power densities of 0.9 W/cm² were achieved in hydrogen/air cells with 3000 h of cell life.

MANAGEMENT ACTIVITIES

During 1995, LBNL managed 20 subcontracts and conducted a vigorous research program in electrochemical energy storage. LBNL staff members attended project review meetings, made site visits to subcontractors, and participated in technical management of various ETR projects. LBNL staff members also participated in the following reviews, meetings, and workshops:

BES and OTT Contractors' Meeting, Arlington VA, March 5-8, 1995.

Spring Meeting of the Materials Research Society, San Francisco, CA, April 16-21, 1995

Workshop on Carbons for Li-Ion Batteries and Supercapacitors, Reno, NV, May 19-20, 1995

187th Meeting of the Electrochemical Society, Reno, NV, May 21-26, 1995

PNGV Meeting on High Power Batteries and Supercapacitors, Dearborn MI, June 12, 1995.

30th IECEC, Orlando, FL, July 30-August 3, 1995

International Symposium on Electrochemical Science and Technology (ISEST), Hong Kong, August 24-27, 1995

46th ISE, Xiamen, China, August 28-September 1, 1995

10th National Convention of the Royal Australian Chemical Institute, Adelaide, Australia, September 1995

188th Meeting of the Electrochemical Society, Chicago, IL, October 8-13, 1995:

10th International Conference on Solid State Ionics, Singapore, December 3-8, 1995

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16. Applied Battery and Electrochemical Research Program Report for Fiscal Year 1980, LBL-12514 (April 1981).

LIST OF ACRONYMS

AES	Auger electron spectroscopy
ATR-FTIR	attenuated total reflection-Fourier transform infrared spectroscopy
BNL	Brookhaven National Laboratory
CAMD	Center for Advanced Microstructures and Devices
CV	cyclic voltammetry
CWRU	Case Western Reserve University
DMC	dimethyl carbonate
DMFC	direct methanol fuel cell
DOE	Department of Energy
DSC	differential scanning calorimetry
DST	Dynamic Stress Test
EIS	electrochemical impedance spectroscopy
EMF	electromotive force
EPRI	Electric Power Research Institute
ETR	Exploratory Technology Research
EV	electric vehicle
EVABS	Electric Vehicle Advanced Battery Systems
EXAFS	extended X-ray absorption fine structure
FTIR	Fourier transform infrared spectroscopy
HOPG	highly ordered pyrolytic graphite
HREM	high-resolution electron microscopy
HTB	hexathiobenzene
IECEC	Intersociety Energy Conversion Engineering Conference
ISE	International Society of Electrochemistry
ITO	indium/tin oxide
LANL	Los Alamos National Laboratory
LBNL	Lawrence Berkeley National Laboratory
LEED	low-energy electron diffraction
LEIS	low-energy ion scattering
LIPON	lithium phosphorous oxygen nitrogen
LLNL	Lawrence Livermore National Laboratory
NEXAFS	near-edge X-ray absorption fine structure
NMR	nuclear magnetic resonance
NWU	Northwestern University
OCV	open circuit voltage
ORNL	Oak Ridge National Laboratory
PBD	probe beam deflection
PBI	polybenzimidazole
PDS	photothermal deflection spectroscopy
PE	polyethylene

PEFC	polymer electrolyte fuel cells
PEM	proton-exchange membrane
PEO	poly(ethylene oxide)
PFSA	perfluorinated sulfuric acid
PHTB	polyhexathiobenzene
PNGV	Partnership for a New Generation Vehicle
PPO	polydimethylphenylene oxide
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene difluoride
RAFC	reformat/air fuel cell
RDE	rotating disk electrode
RF	radio frequency
SEM	scanning electron microscopy
SERS	surface-enhanced Raman spectroscopy
SFUDS	Simplified Federal Urban Driving Schedule
SNL	Sandia National Laboratories
SOC	state-of-charge
SOFC	solid oxide fuel cell
SPE	solid polymer electrolyte
SRPE	solid redox polymerization electrode
SSH	stainless steel holder
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TMA	tetramethyl ammonium
UHV	ultrahigh vacuum
UPD	underpotential deposition
USABC	United States Advanced Battery Consortium
VTF	Vogel-Tamman-Fulgher
WLF	Williams-Landel-Ferry
XANES	X-ray absorption near-edge spectroscopy
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction

SUBCONTRACTOR FINANCIAL DATA - CY 1995

Subcontractor	Principal Investigator	Project	Contract Value (K\$)	Term (months)	Expiration Date	Status in CY 1995*
<u>EXPLORATORY RESEARCH</u>						
Solid-State Cells						
Oak Ridge National Laboratory	J. Bates	Rechargeable Li Batteries	65	12	9-96	C
PolyPlus Battery Company	M.-Y. Chu	Na/SRPE EV Batteries	185	12	12-95	T
SAFT America, Inc.	G. Chagnon	Novel Cell Components	115	12	12-96	C
<u>APPLIED SCIENCE RESEARCH</u>						
Lawrence Berkeley National Laboratory	E. Cairns, L. DeJonghe, J. Evans, K. Kinoshita, F. McLarnon, J. Newman, P. Ross and C. Tobias	Electrochemical Energy Storage	2200	12	9-95	C
Electrode Characterization						
Brookhaven National Laboratory	J. McBreen	Battery Materials	140	12	9-95	C
Lawrence Livermore National Lab.	R. Pekala	Li-Ion Battery Testing	200	12	9-95	T
Electrodes for Electrochemical Cells						
Brookhaven National Laboratory	J. Reilly	Metal Hydride Electrodes	185	12	9-96	C
University of South Carolina	R. White	Metal Hydride Properties	90	12	8-96	C
University of Michigan	A.M. Sastry	Novel Cell Components	150	24	8-97	C
University of Wisconsin	M. Anderson	Sol-Gel Derived Metal Oxides	119	12	8-96	C
Components for Ambient-Temperature Nonaqueous Cells						
Case Western Reserve University	D. Scherson	<i>In Situ</i> Studies	145	12	11-95	T
Northwestern University	M. Ratner	Polymer Electrolytes	145	12	3-96	C
Northwestern University	D. Shriver	Polymer Electrolytes	113	12	3-96	C
Case Western Reserve University	M. Litt	Polymer Electrolytes	166	12	1-96	T
University of Dayton	G. Glasgow	Polymer Electrolytes	99	12	2-96	C
SUNY at Binghamton	S. Whittingham	Cathode Materials	143	12	5-97	C
SRI International	S. Smedley	Na/Polymer Cells	153	12	5-96	T
Southern University	B. Rambabu	LiFeS ₂ Battery System	98	12	9-95	T
Covalent	W.F. Howard	Li Polymr Batteries	250	18	8-96	
<u>AIR SYSTEMS RESEARCH</u>						
Metal/Air Cell Research						
Eltech Research Corporation	E. Rudd	Oxygen Electrodes	104	18	3-95	T
Fuel Cell R&D						
Los Alamos National Laboratory	S. Gottesfeld	Fuel Cell R&D	1200	12	9-96	C

* C = continuing, T = terminating

I. INTRODUCTION

This report summarizes the progress made by the Exploratory Technology Research (ETR) Program for Electrochemical Energy Storage during calendar year 1995. The primary objective of the ETR Program, which is sponsored by the U.S. Department of Energy (DOE) and managed by Lawrence Berkeley National Laboratory (LBNL), is to identify electrochemical technologies that can satisfy stringent performance, durability and economic requirements for electric vehicles (EVs). The ultimate goal is to transfer the most-promising electrochemical technologies to the private sector or to another DOE program for further development and scale-up. Besides LBNL, which has overall responsibility for the ETR Program, LANL, LLNL, ORNL and BNL have participated in the ETR Program by providing key research support in several of the program elements. The ETR Program consists of three major elements:

Exploratory Research

Applied Science Research

Air Systems Research

The objectives and the specific battery and electrochemical systems addressed by each program element are discussed in the following sections, which also include technical summaries that relate to the individual programs. Financial information that relates to the various programs and a description of the management activities for the ETR Program are described in the Executive Summary.

II. EXPLORATORY RESEARCH

The major thrust of this program element is to evaluate promising electrochemical couples for advanced batteries for EVs. Exploratory research was conducted on novel Na cells that contain polymer or molten-salt electrolytes, an all-solid state Li/Mn oxide cell and carbons for electrochemical double-layer capacitors.

A. SOLID-STATE CELLS

Efforts are underway to develop all-solid-state cells. The studies focus on demonstrating the viability of a sodium/sodium-alloy negative or a lithium negative and a metal oxide positive or an organosulfur positive in a rechargeable cell. In addition, the feasibility of an ambient-temperature molten-salt electrolyte cell was investigated.

Solid Electrolytes

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Objectives

- Fabricate and study novel composite electrolytes which combine the advantages of a protective thin-film single-ion conductor with a conventional elastomeric polymer electrolyte for electric vehicle (EV) applications.
- Develop a suitable composite electrolyte material for use in alkali metal/polymer cells.

Approach

- Synthesize and characterize a Li single-ion conductor combined in a single composite membrane acting as a separator in rechargeable Li batteries.
- Employ AC and DC techniques (*e.g.*, galvanostatic charging and discharging, four-probe techniques, impedance spectroscopy and pulse testing) and thermal measurements to characterize solid-state batteries, as well as the properties of the individual components and interfaces.

Accomplishments

- Thin solid films of Li_3N were prepared by hydraulically pressing powders under an inert atmosphere.
- A study of the transport properties of PEO-NaTFSI ($\text{TFSI}=\text{N}(\text{CF}_3\text{SO}_2)_2$) electrolytes is nearly complete.

Future Directions

- Transport property measurements will be directed towards electrolytes for Li systems.
- Research on thin-film single-ion conductors and composite membranes will be expanded. A particular challenge in the Li_3N system will be to decrease the thickness of the hydraulically pressed films.

This project was re-directed mid-year from an emphasis on development of sodium/polymer batteries to polymer electrolytes and composite electrolyte membranes for lithium cells.

Fabrication of thin-film, single-ion-conducting films is now underway, but the bulk of the work during 1995 was geared towards Na battery research, particularly that involving transport

properties of polymer electrolytes. However, the techniques remain the same. Valuable information concerning the effect of cation size and size/charge ratio upon transport processes can also be obtained by a comparison of Na and Li electrolyte systems, and is therefore relevant to Li systems.

Thin solid films of Li_3N are now being prepared by hydraulically pressing powders under an inert atmosphere. Films several hundred microns thick are reproducibly and reliably fabricated using this simple method, and are currently being characterized using AC impedance methods and DC cycling in symmetrical ($\text{Li}/\text{Li}_3\text{N}/\text{Li}$) cells. Li_3N is a super-ionic conductor of Li ions stable in a reducing environment (e.g., when placed next to Li metal). Although it is a well-studied material, it has proven difficult to prepare monolithic pinhole and crack-free layers by other preparation methods (for example, by exposing fresh Li to nitrogen gas).

Synthesis of montmorillonite-poly(ethylene) oxide (PEO) nano-composites is also underway. Montmorillonite is a naturally occurring smectic clay, consisting of charged aluminosilicate layers between which Na ions and water are inserted. It is naturally a single-ion conductor, although conductivities are typically too low for practical applications. Recent research by Lerner et al. at Oregon State University show, however, that conductivities are enhanced 2-3 orders of magnitude by incorporation of PEO between the layers due to the increase in gallery spacings. Prior to use in electrochemical systems, the montmorillonite must be purified, ion-exchanged (Li for Na) and dried to remove water. It is then suspended in acetonitrile and PEO is added. At a weight ratio of approximately 0.3 g PEO per g of montmorillonite, nanocomposites self-assemble. The product is then filtered and dried. X-ray diffraction is used to determine the inter-layer spacings; a significant increase in 001 d-spacings is a positive confirmation that PEO has been inserted between the aluminosilicate layers. Thermogravimetric analysis (TGA) was used to determine the polymer content of the nanocomposite; it typically burns out at elevated temperatures, leading to a characteristic weight loss. AC impedance measurements were made on samples to determine conductivities. Clay nanocomposites can be puddle-cast into thin films (about 10 μm) readily, a distinct advantage over single-ion conductors based on traditional ceramic materials.

A study of the transport properties of PEO-NaTFSI (TFSI = $\text{N}(\text{CF}_3\text{SO}_2)_2$) electrolytes is nearly complete. Differential scanning calorimetry (DSC) and AC conductivity measurements indicate a

eutectic temperature of about 46°C for compositions near $\text{P}(\text{EO})_{12}\text{NaTFSI}$. This is lower than the eutectic of the PEO-LiTFSI system, which occurs at 53°C. Compositions ranging from $\text{P}(\text{EO})_6$ - $\text{P}(\text{EO})_{120}$ NaTFSI were completely molten above 60°C, and no high-melting complexes were detected. Conductivities were as high as $1 \times 10^{-3} \text{ S/cm}$ at 60°C for some samples; this is more than an order of magnitude higher than the PEO- NaCF_3SO_3 system, and is also somewhat higher than that of the PEO-LiTFSI system. This indicates that it should be possible to operate Na cells with PEO-NaTFSI electrolytes at 60°C at high rates, and at moderate rates as low as 45°C. Figure 1a and b show conductivity data as a function of temperature for two compositions, $\text{P}(\text{EO})_{12}\text{NaTFSI}$ and $\text{P}(\text{EO})_{30}\text{NaTFSI}$. The transition from Arrhenius to VTF behavior at the melting point for these two samples is clearly seen. A DSC trace for the $\text{P}(\text{EO})_{30}\text{NaTFSI}$ sample is also shown, and shows good agreement with the conductivity data.

Figure 1. Conductivity data as a function of temperature for two compositions of $\text{P}(\text{EO})_n\text{NaTFSI}$ electrolytes. A) $n = 12$, B) $n = 30$. The changeover from Arrhenius to VTF behavior is clearly seen at the melting transition of the electrolyte. The DSC scan for $\text{P}(\text{EO})_{30}\text{NaTFSI}$ is also shown in Figure 1b. Also note the high conductivities at moderately low temperatures.

Salt diffusion coefficients for compositions ranging from $\text{P(EO)}_6\text{-P(EO)}_{120}\text{NaTFSI}$ have also been measured. Figure 2 shows a $\ln(\Delta\Phi)$ vs. time plot for the relaxation of a $\text{Na/P(EO)}_8\text{NaTFSI/Na}$ cell after undergoing a 6 min discharge at 0.1 mA/cm^2 at 85°C . The least squares fit is also shown. A diffusion coefficient of $5.9 \times 10^{-8} \text{ cm}^2/\text{sec}$ is calculated for this particular sample. Again, salt diffusion coefficients for the $\text{P(EO)}_n\text{NaTFSI}$ system are greater than for either the $\text{P(EO)}_n\text{NaCF}_3\text{SO}_3$ or P(EO)LiTFSI systems at the same temperature.

Figure 2. $\ln(\Delta\Phi)$ vs. relaxation time for a $\text{Na/P(EO)}_8\text{NaTFSI/Na}$ cell polarized at 0.1 mA/cm^2 for six minutes at 85°C . The plot is linear for long times and the slope is proportional to the diffusion coefficient.

Concentration cell data for the $\text{P(EO)}_n\text{NaTFSI}$ system at 85°C have also been obtained (Fig. 3). The final set of experiments needed to calculate the cation transference numbers are currently in progress. Once these data are complete, a rigorous assessment of the effect of anion type on transport properties in PEO electrolytes can be made for the first time. While researchers have long noted marked improvement in cell performance when LiTFSI is used as the electrolyte salt instead of LiCF_3SO_3 , and have attributed this to the higher conductivity of the former, no quantitative analysis of transport properties has been carried out until now.

Figure 3. Concentration cell data for the $\text{P(EO)}_n\text{NaTFSI}$ system at 85°C . The local slope of this plot is used to calculate transference numbers.

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Development of a Thin-Film Rechargeable Lithium Battery for Electric Vehicles

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Objectives

- Identify methods for depositing at temperatures below 180°C acceptable thin-film $\text{Li}_x\text{Mn}_2\text{O}_4$ positive electrodes for rechargeable thin-film Li batteries.
- Develop solid-state Li/ $\text{Li}_x\text{Mn}_2\text{O}_4$ rechargeable batteries for EV applications that meet or exceed the long-term goals of the USABC.

Approach

- Fabricate $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes at temperatures below 180°C by radio frequency (rf) magnetron sputtering using different process variables and substrate bias.
- Fabricate and test 4 V thin-film solid-state Li cells with $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x < 1$) positive electrodes.
- Fabricate and test hybrid cells consisting of bulk processed LiMn_2O_4 electrode plates, a thin LiPON electrolyte film and a thick Li film.

Accomplishment

- The least-resistive cells with LiMn_2O_4 electrodes were obtained by low-pressure deposition with a positive substrate bias.

Future Direction

- Fabricate cells from dense tape-cast ribbons of LiMn_2O_4 with thicknesses of 10-100 μm .
-

Cells with thin-film LiMn_2O_4 electrodes, 0.3-2.5 μm thick, were fabricated on alumina substrates by successive film depositions of: (1) Ni or Pt current collectors, (2) the LiMn_2O_4 electrode by magnetron sputtering, (3) the LiPON electrolyte by rf magnetron sputtering of Li_3PO_4 in N_2 , (4) an evaporated Li metal electrode, and (5) a protective multilayer coating if the cell was to be exposed to air. All films were deposited at near ambient temperatures. The complete cells were subjected to constant-current cycling at different current densities. The cycling behavior was observed under a variety of extreme conditions: temperatures to 100°C, very deep discharge to 1.5 V (giving $\text{Li}_2\text{Mn}_2\text{O}_4$), and overcharge to 5.3 V. Impedance measurements were made at various stages of cycling to determine the sources of cell polarization. In all cases Li transport in the positive electrode or through the electrode-electrolyte interface limits the current density of the cell discharge. Some cells have been under test for over a year at this time.

Results for cells with LiMn_2O_4 electrodes fabricated with a wide variation of the sputter processing conditions were collected and compared. The least-resistive cathodes were obtained by low-pressure deposition with a positive substrate bias. The open-circuit cell voltage (OCV) of the as-prepared cells varied widely, ~3-4.7 V, and clearly correlated with the Li concentration in the as-deposited cathode film. Figure 4 shows the initial cell voltage as a function of the Li extracted from the positive electrode upon the first charge (•). The results agree well with a complete open circuit discharge-charge cycle for a typical cell (dashed curve). Interestingly, the subsequent low current discharge capacity of the cells was found to be independent of the initial electrode film composition (x). This suggests that the local atomic structure and oxygen stoichiometry of the electrode films are insensitive to the concentration of Li incorporated into the film during film growth. We plan to test films which initially contain no Li. The films will be deposited by sputtering a metallic Mn target in Ar + O_2 .

Figure 4. Initial open circuit voltage of 12 different cells plotted as a function of the specific charge extracted upon their initial charge to 4.5 V (•). For comparison, an open-circuit discharge-charge cycle (dashed line) and the specific charge upon subsequent low-current discharge of the cells (x) have been included.

The shape of the constant-current discharge curves indicate that the films deposited on substrates at $\leq 100^\circ\text{C}$ were not fully stable. As the cells were cycled at room temperature, the discharge curves gradually change shape because of a decrease in the electrode polarization at the lowest Li concentrations; this results in the gradual formation of a knee at ~ 4 V in the constant-current discharge curves. In contrast, cells fabricated with films deposited at substrate temperatures, $\sim 200^\circ\text{C}$, showed a clear knee even in the initial discharge curves. In Fig. 5, cycles 25 and 110 illustrate the gradual change in the discharge curve upon 25°C cycling of a low-temperature positive electrode. Cycling cells at elevated temperature accelerates this change. Cycle 170 of Fig. 5 was recorded after ~ 50 cycles at 60 – 100°C . The knee is clearly due to polarization effects as it is not present in the equilibrated open-circuit discharge curves. The only cell cycled to date which has not displayed this knee in the discharge curve upon prolonged cycling had a positive electrode formed with a small amount of dispersed carbon nanoparticles. This suggests that the change in the discharge behavior may correlate with an evolution of the microstructure of the electrode film. In future experiments, we will look for evidence of high diffusivity paths formed by a coarsening of the grain structure.

Cycling results have also shown evidence of a true hysteresis in the Li insertion reaction. As shown in Fig. 6, the hysteresis occurs for the single-

Figure 5. Constant-current discharge curves showing the change in shape as the cell was cycled first at 25°C and then at 100°C . Labels indicate the cycle number. Cycles 120–165 and 260–280 were done at 100°C .

Figure 6. Discharge-charge curve obtained for open-circuit conditions at 100°C . For each point, the cycle was interrupted and the cell allowed to equilibrate until the rate of change was less than $5\text{ mV} / 90\text{ m}$.

time to equilibrate at each step in the cycle. Continuous cycling at both 25 and 100°C between different voltage limits is also consistent with a hysteresis effect. We have observed similar behavior with another amorphous electrode, $\alpha\text{-V}_2\text{O}_5$, and hysteresis was evident in the cycling data of a titanium oxysulphide thin-film electrode reported in the literature.¹ Further experiments will be required to identify the structural changes giving rise to the hysteresis, but in general the

material can be visualized as composed of domains which transform to a metastable state at varying critical Li concentrations.

Work has begun on a new type of electrode fabrication. This was initiated to achieve a much higher capacity per cell area than can be obtained with any of the thin-film cells investigated to date. We will attempt to make dense tape-cast ribbons of LiMn_2O_4 with thicknesses of 10-100 μm . Ribbons with thicknesses below $\sim 30 \mu\text{m}$ are expected to be very flexible and also to have a high enough Li diffusivity to be used as a single-phase material, rather than the composite electrode mixtures required for most rechargeable Li cells. The complete cell will be fabricated by thin-film depositions of the current collector, Lipon

electrolyte, and Li directly on the self-supporting positive electrode ribbon.

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Room Temperature Sodium/Iron Chloride Battery Development *

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Objectives

- To synthesize and characterize new room-temperature electrolytes that contain organic salts to provide improved Na-ion transport.
- To develop advanced Na/metal chloride batteries that operate at ambient temperatures.

Approach

- Evaluate room-temperature molten salt electrolytes containing Na ions along with a solid Na anode and metal/metal chloride cathode.

Accomplishment

- Ambient-temperature, protonated molten salt electrolytes comprised of mixtures of NaAlCl_4 and various alkylimidazolium chlorides allow repetitive Na plating and stripping with high efficiencies if there is only a short delay between plating and stripping. However, the Na slowly reacts with the molten salt, giving rise to a self-discharge rate of 5% per day.

Future Direction

- Project has been completed.

This project focused on the preparation and examination of ambient-temperature molten salt electrolytes comprised of mixtures of NaAlCl_4 and various alkylimidazolium chlorides. The vital role of protonating the melts by adding proton donors, such as HCl, was addressed in some detail. Sodium plating and stripping in three molten salt electrolytes were studied extensively, with a focus on coulombic efficiency and self-discharge. Both sweep voltammetry and chronopotentiometry at

constant current were applied. The chlorides of Fe, Ni and Cu were investigated regarding their charge/discharge behavior in the ambient-temperature molten salts. Finally, preliminary full cell studies were conducted in three different cell geometries.

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Extensive negative-electrode half-cell experiments were performed using 1-methyl-3-ethylimidazolium chloride (MEIC), 1,2-dimethyl-3-propylimidazolium chloride (DMPIC), and 1-methyl-3-propylimidazolium chloride (MPIC) electrolytes. In neutral buffered MEIC melts at room temperature, Na was plated and stripped from W substrates with efficiencies up to 94% if stripping immediately followed plating and HCl was added at a minimum partial pressure of 6 torr. Plating thicknesses were typically 0.05 to 0.1 mm for potential sweeps at 0.1 V/s, corresponding to plating/stripping times of 2 to 4 s and charge densities of 20 to 40 mAs/cm². Constant-current plating/stripping was performed in a range of current densities from 0.25 to 20 mA/cm² and times from 2 to 60 s, resulting in charge densities from 15 to 150 mAs/cm² and corresponding to Na layers from 0.04 to 0.4 μ m thick. Typical coulombic efficiencies were 80-90% in the MEIC; somewhat lower in DMPIC.

MPIC melts were developed to address the need for higher coulombic efficiency. It was found that the reduction of the imidazolium cation was dependent upon the electron-donating nature of the ring substituents and not by the steric hindrance of the substituents. Although equally high coulombic efficiencies (compared with MEIC) were obtained (ca. 94%), the reduction of other melt components remained a problem.

The coulombic efficiencies decreased with increasing open-circuit time between Na plating and stripping. For example, a Na layer plated in MPIC with 7 torr HCl having a thickness of 1.5 μ m, equivalent to plating with 2 mA/cm² for 300 sec (charge density = 600 mAs/cm² or 0.17 mAh/cm²) could be stripped with 77% efficiency when no open-circuit period was inserted before discharge. However, the efficiency decreased to 39% after the Na layer was kept on open circuit for 3 h. During the extended period tests, the open-circuit voltage remained constant at -2.1 V vs. Al.

A self-discharge current density of 22 mA/cm² was determined for this case. Based on a charge density of interest to battery applications, for example 10 mAh/cm², corresponding to plating with 2 mA/cm² for 5 h and stripping with 5 mA/cm² for 2 h, the rate of self-discharge was calculated as 5% per day. Higher self-discharge rates were observed in DMPIC.

Research into positive electrodes focused on the evaluation of three metal/metal chloride systems in the NaCl-buffered, neutral MEIC:AlCl₃ melt. The metals examined were Fe, Cu, and Ni. The iron

electrode contained a redox couple at more negative potentials than desired (which would result in low battery voltage); therefore, the research shifted to the examination of Cu.

Copper has a redox couple at more positive potentials, ~700 mV more positive than Fe; however, the oxidized Cu species was soluble in the melt. The desired metal/metal chloride electrode must be a solid-solid redox couple so that a battery separator is not needed. With this requirement, the copper/copper chloride was viewed as unsatisfactory.

The nickel/nickel (II) chloride system showed passivation of the Ni electrode by the formation of NiCl₂ at potentials >2.5 V positive of Na/Na⁺. The nickel/nickel (II) chloride electrode used in experiments thus far supported a charge density of 3.5 mC/cm², suggesting that a high-surface-area electrode will be needed for a viable cell.

Full-cell studies were performed on initially discharged cells, using stainless steel substrates and initially charged cells, using a Na-coated stainless steel rod negative electrode and a negative electrode comprised of a Fe foil with a bonded or cemented FeCl₂ layer. Charging the discharged cell at 1 mA/cm² occurred at a cell voltage of 4 V. The positive electrode was at a potential of 1.7 V vs. an Al reference electrode in a 0.6 melt, suggesting a highly resistive FeCl₂ layer. Cell voltages during discharge at 1 to 2 mA/cm² were typically below 1 V, far below expected values of just below 2.5 V. This behavior was caused by the Fe electrode which polarized rapidly. Even the initially charged cell was unable to sustain a discharge current of 2 mA/cm². Cyclic voltammetry of the Fe/FeCl₂ electrode confirmed that the slow electrode kinetics was responsible for the unfavorable cell discharge behavior. However, coulombic efficiency was nearly 100%.

In conclusion, ambient-temperature, protonated molten salt electrolytes comprised of mixtures of NaAlCl₄ and various alkylimidazolium chlorides allow repetitive Na plating and stripping with high efficiencies only if there is a short delay between plating and stripping. However, the Na slowly reacts with the molten salt, giving rise to a self-discharge rate of 5% per day if based on a reasonable charge density of 10 mAh/cm². Among the three positive electrode materials evaluated, namely, the chlorides of Fe, Ni and Cu, none of them result in viable electrodes. This is caused either by slow kinetics (FeCl₂ and NiCl₂) or excessive solubility (CuCl₂).

Na/SRPE Electric Vehicle Batteries

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Objectives

- Evaluate the performance of Na/PEO cells using organosulfur-based electrodes (SRPE).
- Develop a low-cost high-performance Na/PEO/SRPE cell for EVs.

Approach

- Fabricate Na/PEO/SRPE cells with various electrode and separator compositions, and test cells for maximum discharge, power capabilities, and cycling behavior.
- Test stability of electrode interfaces with AC impedance.

Accomplishments

- Na/PEO/SRPE cells were constructed and evaluated.
- Maximum single discharge of 450 Wh/kg of positive electrode *vs.* Na and peak power of 800 W/kg of positive electrode *vs.* Na were demonstrated.
- Limited cycling of 5 cycles above 250 Wh/kg for the positive electrode *vs.* Na and 20 cycles above 100 Wh/kg for the positive electrode *vs.* Na were achieved.
- Initial evaluation by AC impedance demonstrated the stability of the Na/PEO interface after temperature excursions above the melting point of Na.

Future Direction

- Project has been completed.
-

The objective of this work is to evaluate Na and organosulfur (SRPE) electrodes in secondary cells which may provide a low-cost high-performance alternative battery for EV applications. This evaluation included the determination of maximum accessible capacity in a single discharge, peak power capability, and cycling behavior. Cell engineering and optimization has not yet been considered.

Standardized methods of cell assembly were used to produce cells with electrode and electrolyte films made by casting using acetonitrile as a solvent. A number of cells was made with either the X1(dimercaptothiadiazole) or X8(ethane dithiol) polymer with different salts including NaTf(sodium triflate), NaClO₄, NaBF₄, NaPF₆, LiClO₄, and LiDTf(lithium ditriflate). Positive electrode compositions were formulated that were suitable for use at 80-90°C. Operation of the cells at lower temperatures was also explored, together with the effects of heating/cooling cycles.

Heating/cooling cycles did not alter the performance of the cells, a result that can be extended to other alkali/polymer cells. The reported specific energy and specific power are determined for the weights of the practical positive electrode composites only, which included carbon, PEO, and additional salts. For laboratory cells, in which neither the negative electrode, current collectors or packaging are optimized, positive electrode reported specific energy and specific power are the more appropriate basis for comparison with other systems. High positive electrode specific energies in excess of 450 Wh/kg have been obtained. Corresponding specific energies for complete, fully engineered cells would be projected to be approximate 150 Wh/kg. Positive electrode specific powers as high as 800 W/kg have also been demonstrated in our laboratories. However, cell cycling did show persistent capacity decline, and the cells were prone to shorting during charging. The problem of

limited cell cycling and shorting is similar to that observed in the early stages of most Li cell developments, and definitive remedies were not identified in the contract period. In spite of extensive efforts, while in the first few cycles specific energies over 250 Wh/kg were obtained, only about 20 cycles above 100 Wh/kg could be demonstrated, with continued capacity decline

thereafter. While these first results are encouraging, it can be concluded that substantive modifications to Na/SRPE systems will be needed, particularly with respect to stabilization of the Na/electrolyte interface, as revealed by AC impedance studies. This project has been completed.

B. ELECTROCHEMICAL DOUBLE-LAYER CAPACITORS

Research was initiated to evaluate carbons for electrochemical double-layer capacitors which can be used in EVs. Carbons are attractive electrode materials for capacitors because of their low cost relative to that of metal oxides which are commonly used.

Novel Cell Components for Capacitors

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Objectives

- Evaluate the double-layer capacitance of high-surface-area carbons.
- Develop low-cost carbon electrodes for electrochemical double-layer capacitors that meet the DOE goal of 1600 W/kg, 10 Wh/kg and \$1/kW.

Approach

- Identify commercially available carbons for double-layer capacitors.
- Evaluate carbon electrode performance in "4/5A" test cells.

Accomplishments

- Various binders for fabricating the carbon electrodes were evaluated.
- Determined that both particle size classification and low levels of admatal stabilizer can benefit performance.

Future Directions

- Continue studies to identify a viable binder.
 - Fabricate and evaluate carbon electrodes in test cells.
-

The purpose of this program is to develop electrochemical capacitors meeting DOE requirements. Consequently, this effort focuses on the material evaluation and the cell fabrication processes. After defining the cell design, a systematic evaluation of binders was started to identify a binder having excellent mechanical properties (binding, flexibility) and low

resistivity. This is a two-step evaluation. Small batches of selected binders are mixed with activated carbon and coated on aluminum foil. After a qualitative adhesion evaluation and electrolyte compatibility check, the optimum mix (minimum binder percentage providing good adherence) was processed and a few 4/5A cells were

fabricated and tested. To date the following binders have been tested:

- Polyvinyl Alcohol (PVA) - MW: 160,000
- Polyvinyl Formal (PVF) - MW: 100 to 150,000
- Polyvinyl Butyral (PVB) - MW: 170 to 250,000
- Polyacrylic Acid (PAA) - MW: 240,000
- Polyacrylonitrile (PAN) - MW: 150,000
- Polyvinyl Acetate - MW: 500,000

An activated carbon is mixed with a small amount of binder and acetylene black (15 wt%) to enhance the conductivity. This mixture is coated on

aluminum foil and tested in small 4/5A cells which contain a 2-mil Celgard separator. The tests were initiated with the activated carbon (Norit SX Ultra) which has a specific surface area of 1150 m²/g and an average particle size of 60 μ m. The results of the study are summarized in Table 1. The highest specific power was obtained with PVB, and the highest specific energy was obtained with PVA. It is too early to propose any conclusions at this stage because the program was initiated in September 1995.

Table 1. Evaluation of binders for double-layer capacitors.

Binder Type	Percentage Binder %	Power Density W/l	Specific Power W/kg	Energy Density Wh/l	Specific Energy Wh/kg
PVA	7.5	1363	798	2.24	1.31
PVF	7.5	827	487	1.29	0.76
PVB	5	1917	1126	1.85	1.08
PAA	10	1065	628	1.89	1.11
PAN	Good C to C bond, but poor C to Al bond. No electrodes were made.				
Polyvinyl Acetate	Not compatible with the electrolyte. No electrodes were made.				
Note: Data based at the cell level (4/5A). The hardware is made of stainless steel. All the electrodes had the same length. No design optimization was intended during this phase.					

III. APPLIED SCIENCE RESEARCH

The objectives of this program element are to provide and establish scientific and engineering principles applicable to batteries and electrochemical systems; and to identify, characterize and improve materials and components for use in batteries and electrochemical systems. Projects in this element provide research that supports a wide range of battery systems based on solid electrolytes and nonaqueous electrolytes, both liquid and polymer. Other projects are directed at research on improving the understanding of electrochemical engineering principles, corrosion of battery components, surface analysis of electrodes, and electrocatalysis.

A. ELECTRODE CHARACTERIZATION

Characterization of electrode morphology and chemical composition are important for the successful development of rechargeable electrodes for advanced secondary batteries. Efforts are underway to utilize advanced microfabrication techniques and spectroscopy to characterize electrode properties.

Carbon Electrochemistry/Surface Morphology of Metals in Electrodeposition

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Objectives

- Identify the critical parameters that control the reversible intercalation of Li in carbonaceous materials and to determine their maximum capacity for Li intercalation.
- Develop a pragmatic understanding of the component processes and their interactions in the macrocrystallization of metals, necessary for the design and optimization of rechargeable galvanic cells.
- Investigate the role of electric field and solution-side mass transport in the electrocrystallization of metals and the physical processes involved in the evolution of gases at electrodes, with emphasis on their effect on ohmic resistance and mass transfer.

Approach

- Couple electrochemical studies with physical measurements to correlate the relationship between the physicochemical properties of carbonaceous materials and their ability to intercalate Li.
- Apply mathematical modeling and experimental studies to understand mass transport phenomena involving small protrusions in a hydrodynamic flow field and the dynamics of gas bubble coalescence.

Accomplishments

- Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis of Li intercalated graphite showed the presence of both LiC_6 and LiC_{12} phases, which can co-exist together.
- The local mass transport distribution around microscale protrusions was studied by measuring the local currents for a redox couple ($\text{Fe}^{3+}/\text{Fe}^{2+}$). Measurements show that with laminar flow, mass transport is impeded in the vicinity of the protrusion, and it is most impeded in the immediate wake.
- Observation of coalescing gas bubbles showed that the position of the interface in the coalescence plane (*i.e.*, saddle point between two bubbles) rapidly accelerates to 200 to 400 cm/s, and the initial motion is followed by large-amplitude oblate-prolate oscillations at frequencies of 0.4 to 17 kHz which dampen in 0.3 to 10 ms.

Future Directions

- Complete study of mass transport distribution around microscale protrusions.
 - Complete the evaluation of the dynamics of bubble phenomena in electrolytic gas evolution.
 - Continue *in situ* TEM studies of lithiated carbons, and characterize the properties of heat-treated petroleum cokes for lithium intercalation.
-

The objective of this project is to develop a pragmatic understanding of the component processes and their interactions in the macrocrystallization of metals necessary for the design and optimization of rechargeable galvanic cells and to identify the critical parameters that control the reversible intercalation of Li in carbonaceous materials. This project involves investigations of *i*) the role of electric field and solution-side mass transport in the electrocrystallization of metals: mechanisms of initiation, growth and propagation of imperfections and development of surface textures; *ii*) the characterization of the physical processes involved in the evolution of gases at electrodes, with emphasis on their effect on ohmic resistance and mass transfer; and *iii*) the role of physicochemical properties of carbonaceous materials on their ability to reversibly intercalate Li. This latter effort is coordinated with the research conducted at Lawrence Livermore National Laboratory (LLNL) to evaluate the intercalation of Li in carbonaceous materials for rechargeable Li batteries (see discussion in "Fabrication and Testing of Carbon Electrodes as Lithium Intercalation Anodes").

Surface Morphology of Metals in Electrodeposition. The local mass transport distribution around microscale protrusions in an electrolyte flow channel was studied by measuring the local currents for a redox couple ($\text{Fe}^{3+}/\text{Fe}^{2+}$) at a segmented electrode. The segmented electrode was designed and fabricated in the Microfabrication Laboratory of EECS on the Berkeley campus and consisted of an array of 22 Pt microelectrodes (50- μm square) positioned around the protrusion (~ 50 μm height and ~ 85 μm diameter). With this array of microelectrodes, the following results were obtained. When the bulk fluid flow is laminar, mass transport is impeded in the vicinity of the protrusion, and it is most impeded in the immediate wake. For example, at $\text{Re}_p = 0.56$ the current density is reduced (relative to the current density which would be measured in the absence of a protrusion) by 25% at a location of 100 μm downstream of the protrusion but by only 15% at 100 μm in front of the protrusion. This effect

changes with increasing Reynolds number. At $\text{Re}_p = 3.4$, the current is reduced by 30% downstream and by only 7% upstream at the same microelectrode locations. The influence of protrusions on mass transport is qualitatively similar in turbulent flow for Re_p of up to about 50. At higher Reynolds numbers, mass transport is enhanced by a factor of about 1.5 at 100 μm in front of the protrusion and about 1.5 at 250 μm downstream.

Bubble Coalescence. A high-speed laser-illuminated photodetector array and associated data acquisition system were employed for the study of coalescence between electrolytically generated gas bubbles. The fast phenomena associated with the coalescence and separation from the surface of two electrolytically generated hydrogen bubbles, 50 to 600 μm in diameter, is recorded with a resolution of 10^{-5} . In agreement with theoretical predictions, the coalescence event is completed in less than 10^{-3} . The experimental results show that the position of the interface in the coalescence plane (*i.e.*, the saddle point between two bubbles) rapidly accelerates to 200 to 400 cm/s. The initial motion is followed by large amplitude oblate-prolate oscillations at frequencies of 0.4 to 17 kHz which dampen in 0.3 to 10 ms during bubble coalescence. The oscillation frequency is proportional to the square root of the surface tension, inversely proportional to the bubble radius raised to the $3/2$ power, and independent of the electrolyte viscosity. The oscillations decay at a rate that is proportional to the viscosity and inversely proportional to the square of the radius.

Carbon Electrochemistry. This effort is coordinated with the research conducted at LLNL to evaluate the intercalation of Li in carbonaceous materials for rechargeable Li batteries. Studies of samples obtained from commercial vendors, as well as several that were synthesized in-house, are continuing. In particular, the systematic study of the physical properties of carbonaceous materials by utilizing electron microscopy (facilities at the National Center for Electron Microscopy) and XRD analysis is underway. The results to date show that graphite powders, both natural and synthetic,

which have $d(002)$ spacing of 0.3354 nm, yield the theoretical capacity for Li intercalation, LiC_6 .

A new effort was initiated to understand the mechanism of Li storage by exploring the use of *in situ* TEM to investigate the microscopic changes that occur during Li intercalation/de-intercalation of carbonaceous materials. The preliminary design and component fabrication of a hermetically sealed cell for *in situ* TEM studies have been completed. The cell is fabricated by growing thin Si_3N_4 membranes on top of a Si wafer. The backside of the wafer is then etched to form small windows of the electron-transparent membrane which should be about 100-nm thick. Electrode materials are subsequently patterned on the membranes such that the desired electrode/electrolyte interfaces are visible through the window. The cell is completed by "sandwiching" the electrolyte between two membranes and sealing the edges of the cell with a suitable material. Several cells have been fabricated and the structure of the thin Si_3N_4 membranes are being examined by TEM. As a prelude to the *in situ* studies, lithiated carbon samples were prepared *ex situ*, and examined by TEM. Samples of Li intercalated graphite, which were synthesized by chemical lithiation, were examined by TEM and XRD analysis. The samples, which are dark yellow in color and indicative of a stage-one compound, showed the presence of both LiC_6 and LiC_{12} phases. In the future, lithiated graphite that is formed on a Si_3N_4 membrane will be examined by TEM.

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Battery Materials: Structure and Characterization

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Objective

- Elucidate the molecular aspects of battery materials and processes by *in situ* synchrotron X-ray techniques.

Approach

- Apply *in situ* extended X-ray absorption fine structure (EXAFS) studies to obtain chemical information on components for advanced rechargeable batteries.
- Apply EXAFS to the study of Li_xCoO_2 , Li_xNiO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes.

Accomplishments

- A new apparatus was set up for *in situ* high-resolution XRD studies of battery electrodes.
- EXAFS shows that the structure of supersaturated zincate is identical to regular zincate solutions. X-ray absorption near-edge spectroscopy (XANES) indicates ion pairing of zincate with the lighter alkali ions (Li^+ and Na^+).
- EXAFS shows that complete removal of Li from Li_xNiO_2 eliminates the long-range order in the crystal.

Future Direction

- Continue *in situ* high-resolution XRD and EXAFS studies of Li battery electrodes.
-

The objective of this research is to elucidate the molecular aspects of materials and electrode processes in batteries and to use this information to develop electrode and electrolyte structures with good performance and long life. Work during the year included EXAFS studies of regular and supersaturated zincate electrodes and positive electrodes for Li batteries.

EXAFS Studies of Zincate Electrolytes. X-ray absorption studies were performed on zincate solutions with equilibrium solubility and *in situ* studies on supersaturated zincate generated in a discharging Zn/AgO cell. The supersaturated solutions had up to three times the equilibrium solubility. Because of the short Zn-O bond distances it was necessary to consider multiple scattering effects in the data analysis. The results indicated that the zincate species in both types of solution were identical and consisted of tetrahedral $\text{Zn}(\text{OH})_4$ species. The near-edge part of the spectra (XANES) indicated that there was some ion pairing between the zincate ions and the lighter alkali ions such as Li^+ and Na^+ . The ion pairing causes a split in the white line of the XANES. This appears as a peak at ~ 5 eV above the edge in the

derivative spectrum, shown in Fig. 7. In CsOH the peak becomes a diffuse shoulder indicating much less ion pairing. The degree of ion pairing is inversely proportional to the ion radius.

Figure 7. Derivative of the Zn K edge XANES for 0.74 M ZnO in 8.4 M NaOH (—), KOH (---) and CsOH (···).

In Situ EXAFS Studies of LiCoO₂ and LiNiO₂. Hermetically sealed cells were designed and built for *in situ* X-ray absorption studies in the transmission mode of these electrode materials for Li batteries. The cells are suitable for X-ray Absorption Spectroscopy (XAS) studies of Li, Li-ion and Li/polymer electrolyte cells at various temperatures up to 120°C. The electrolyte was 1 M CF₃SO₃ in a 1:1 EC/DMC mixed solvent. Cathodes were prepared from mixtures of the active material, acetylene black, graphite, carbon fibers and a polyvinylidene difluoride (PVDF) binder. The separator was polypropylene. XAS spectra were taken at the respective Co and Ni K edges when the electrodes were charged and discharged. Figure 8 shows the typical XANES spectra for LiNiO₂. The Fourier transform of the corresponding EXAFS are shown in Fig. 9. The edge shift on removal of the Li can be seen in Fig. 7. The Fourier transform of the EXAFS for LiNiO₂ has peaks out to almost 8 Å. With removal of the Li on charge the peaks beyond 3 Å disappear indicating elimination of long-range order.

Figure 8. *In situ* Ni XANES for LiNiO₂ (—) and Li_{0.2}NiO₂ (---).

EXAFS Studies of the Effect of Temperature and Stoichiometry on Li_xMn₂O₄. These studies were done because of reports of a first-order Jahn-Teller structural phase transition in LiMn₂O₄ in the vicinity of 0°C, and on the effects of the initial Li_xMn₂O₄ stoichiometry on electrode stability on cycling. Mn XANES data at ambient and at liquid nitrogen temperatures indicate structural changes. No changes were observed in the EXAFS for several compositions of Li_{1+x}Mn_{2-x}O₄ (x = 0 - 0.092).

High-Resolution XRD of Battery Materials. A new apparatus was set up at Beam Line X27A at NSLS for *in situ* high-resolution XRD of battery electrodes. The X-ray probe was tuned to 24.5 keV ($\lambda = 0.5$ Å) using a bent Si (111) crystal operating in the Laue (transmission) mode. The cells were mounted in a transmission geometry on a two-circle goniometer, and a LiF (200) crystal was used as an analyzer. The high energy of the probe permits examination of thick electrodes and prevents surface layers from dominating the signal. This is important in the studies of intercalation reactions in Li and metal hydride batteries. The technique is being used to study structural changes in LiMn₂O₄ and an AB₂ metal hydride electrode during cycling.

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Figure 9. Fourier transform of *in situ* Ni EXAFS for LiNiO₂ (—) and Li_{0.2}NiO₂ (---).

Fabrication and Testing of Carbon Electrodes as Lithium Intercalation Anodes

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Objectives

- Evaluate the performance of carbonaceous materials as hosts for Li intercalation negative electrodes.
- Develop reversible Li intercalation negative electrodes for advanced rechargeable Li cells.

Approach

- Fabricate electrodes from various commercial carbons and graphites and evaluate in small Li-ion cells.
- Correlate electrode performance (*i.e.*, capacity, irreversible capacity) with carbon structure and properties in collaboration with LBNL.

Accomplishments

- Electrodes fabricated from natural vein graphites (Superior Graphite Co.) yielded Li intercalation capacities that range from 320 to 360 mAh/g (equivalent to x in Li_xC_6 from 0.85 to 0.95), approaching the theoretical value of 372 mAh/g corresponding to LiC_6 . Natural-flake and purified-flake graphites tend to have a lower capacity than the LiC_6 composition
- Graphitized cokes from Superior Graphite exhibited reversible capacities of about 230 mAh/g (x near 0.62), comparable to that obtained with petroleum cokes from other sources.

Future Direction

- Continue evaluation of commercial and chemically modified carbon materials for Li intercalation.
-

Various commercial carbons and graphites are being studied as Li intercalation compounds for negative electrodes in Li-ion rechargeable cells. Electrode performance (*i.e.*, capacity, irreversible capacity) is obtained and related to carbon structure and properties. The non-graphitic carbons are tested in propylene carbonate-based electrolytes with a 9:1 mixture of 0.5 M lithium trifluoromethane-sulfonimide (HQ115 tradename, 3M Corp.) and 0.5 M lithium hexafluoroarsenate (FMC Corp.). Graphitic materials are studied in 0.5 M HQ115/ethylene carbonate/dimethyl carbonate (50/50) electrolytes. Graphite materials are used as-received from the manufacturer without further treatment. Cokes are ground and sieved to between 30 and 60 μm and then pyrolyzed at various temperatures. Several polymer-based carbons were also synthesized. The electrodes were prepared using a commercial carbon fiber (Lydall Corp., 5 mil thick) as the support matrix, and polytetrafluoroethylene, PTFE (8%), PVDF (6%) or a

polymer-derived carbon binder. A thick slurry containing the carbon particles, binder and acetone was spread onto the fiber support and allowed to dry. The composite was then hot-pressed at 10,000 psi. The electrode was dried in a vacuum oven at 110°C for 1 h, followed by heat treatment at 170°C (PVDF-electrodes, 1 h) or at 350°C (PTFE-electrodes, in air for 30 min). Electrodes with the polymer-derived carbon-based binder were heated without compression to form a carbon-foam electrode. The electrochemical experiments were carried out in a 15-ml, three-electrode cylindrical cell in which the electrodes and separator are placed horizontally and stacked vertically. The geometric surface area of the working electrode was 1.12 cm^2 . The major effort in 1995 was to evaluate carbonaceous materials provided by the Superior Graphite Co.

Graphite and graphitized cokes. The Superior natural graphites are highly crystalline materials with varying microstructure and morphology

depending on their sources. They are classified based on three characteristic microstructures: flake, vein or amorphous. The flake graphites are highly anisotropic in nature. The TEM and scanning electron microscopy (SEM) observations show that these graphite particles resemble flat platelets (flat lamellae) with well-defined basal planes. They look similar to synthetic graphite particles from Lonza G+T (Switzerland). Superior flake graphites (e.g., SG2933), however, have large L_c (> several 1000 Å), which is larger than the L_c reported for Lonza (synthetic) graphites ($L_c \sim 1000$ Å). The vein graphite particles are granular in shape. The reversible capacities observed with natural graphites range from 320 to 360 mAh/g (correspond to x between 0.85 to 0.95 in Li_xC_6 composition). Natural-flake and purified-flake graphites from Superior Graphite (SG2933 and BG39, respectively) tend to have a considerably lower capacity than the LiC_6 composition. Both flake- and vein-type natural graphites exhibit the graphite-like potential curves (i.e., deintercalation/intercalation takes places below 0.3 V). However, there are distinct differences between the profiles of flake and vein materials. Flake graphites showed plateaus below 0.3 V that could be identified with the formation of staged phases. For vein-type graphites, the curve appears smooth in this region with no apparent plateaus. Additional experiments and characterization are being conducted to elucidate this difference. The granular morphology associated with the vein structure would perhaps expose higher fraction of edge-oriented surfaces. Because of the high performance and desirable microstructure obtained with vein graphites, further experiments were conducted to evaluate their rate capabilities. Preliminary data on the effect of rate on the performance of SG4941A (~ 7 μm diameter) indicated that these particles are capable of supporting high discharge (deintercalation) rate (i.e., C rate) without a significant decrease in reversible capacity. The high-rate performance is comparable to those investigated earlier for Lonza SFG6 graphites.

Two types of graphitized cokes (SG9400 and Desulco materials, SG9035 and SG9039) were tested. Desulco materials are petroleum cokes that are purified and partially graphitized at up to 2700°C to eliminate sulfur and other volatile components. SG9400 powders are (spherical) petroleum cokes that were heat treated to temperatures near 2000°C. The reversible capacities observed with these materials are about 230 mAh/g (x near 0.62). The capacity is

comparable to that obtained with petroleum cokes from other sources. The potential profiles of these materials, however, exhibit graphite-like (flat plateau) profiles. Deintercalation occurs at a potential <0.3 V (vs. Li^+/Li). The irreversible capacity loss associated with the formation of the solid-electrolyte interface is 68 mAh/g, which is among the lowest capacity loss observed in the literature. Desulco carbons (SG9035 and SG9039) have capacities near 230 mAh/g ($x = 0.60$). They also exhibit graphite-like potential profiles but at lower capacities than those of graphites (LiC_6).

Cokes. Two grades of petroleum cokes (Superior Graphite) that have varying amount of sulfur were investigated for Li intercalation. Coke #1 has less than 1% of sulfur. Coke #3 has considerably more sulfur ($\sim 3\%$). The potential-capacity curves for these non-graphitic materials have a sloping shape with varying Li capacity, typical for amorphous carbons. The low-sulfur petroleum coke (coke #1) has x near 0.70 with an irreversible capacity around 83 mAh/g. The performance data are comparable to or better than other types of cokes that were investigated in our laboratory (e.g., Lonza FC250, Conoco XP30). High-sulfur cokes tend to have a lower capacity ($x \sim 0.51$) and larger irreversible capacities (110 mAh/g). The capacity of Coke #1 was stable for more than 20 cycles whereas the capacity of coke #3 decreases significantly after 4 cycles.

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B. ELECTRODES FOR ELECTROCHEMICAL CELLS

Electrodes are being developed to identify low-cost metal hydrides for MH/NiOOH cells and improved metal oxides for electrochemical capacitors

Preparation of Improved, Low Cost Metal Hydride Electrodes for Automotive Applications

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Objectives

- Increase the energy density of metal hydride electrodes by preparing improved AB_5 and AB_2 electrodes.
- Develop an improved mathematical model for the electrochemical behavior of the MH_x electrode.

Approach

- Determine thermodynamic properties of alloy hydrides used in electrodes.
- Fabricate and test hydride electrodes.
- Apply XAS methods to determine the electronic structure, the local atomic environment and corrosion of alloy hydride electrode materials.

Accomplishments

- The thermodynamic properties of two hydride alloys were determined and related to their performance as electrodes.
- XAS studies of AB_2 alloy hydrides indicated the presence of strong interactions between the interstitial H atom and Ti, V and Zr. Very little interaction between H and Ni was observed, suggesting that the role of Ni in the AB_2 alloys is primarily catalytic in nature.

Future Direction

- Determine the role of individual metal components in complex alloy hydride electrodes.
-

Even though MH_x /NiOOH batteries are currently competitive in certain high-end applications, their potential as inexpensive, reliable energy storage devices for automotive applications is far from realized: a severe penalty has been incurred in storage capacity and materials costs in order to inhibit corrosion and attain

acceptable electrode cycle life. This is a serious problem which this program addresses. The major goals of this effort are to improve the specific energy of the metal hydride electrode, decrease corrosion, increase electrode cycle life, and decrease materials costs. In pursuit of these goals a variety of alloy hydrides (particularly AB_5 and AB_2

materials) is being studied with respect to their thermodynamic, electrochemical and surface properties, as well as their bulk crystal structure. Other goals are to *i*) expand the operating temperature of $MH_x/NiOOH$ batteries, *ii*) develop a mathematical model for the MH_x electrode, *iii*) improve the low-temperature discharge kinetics, and *iv*) improve or replace the $NiOOH$ electrode. This effort involves the use of various tools and techniques including the development of *in situ* and *ex situ* XAS methods at the National Synchrotron Light Source.

Thermodynamics and Operating Temperature Range of Metal Hydride Electrodes. The thermodynamic properties of two candidate AB_5 metal hydride electrodes were determined and related to their electrochemical behavior in the temperature range -30 to 65°C. The alloys were prepared using two different types of mischmetal (Mm), normal and Ce-free (Mm*). The alloy compositions were $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ and $Mm^*Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$. Note that both alloys had the same B_5 composition and will henceforth be referred to as MmB_5 or Mm^*B_5 . XRD patterns of both alloys were taken; both were single phase having the $CaCu_5$ structure.

Pressure-composition isotherms for both alloy-H systems were determined and the data were used to construct van't Hoff plots which are shown in Fig. 10. The relationship is linear and may be expressed in the form of the van't Hoff equation,

$$\ln P_{eq} = (\Delta H/RT) - \Delta S/R.$$

The pertinent thermodynamic quantities for both systems are given in Fig. 10.

Figure 10. van't Hoff plots for Mm^*B_5 and MmB_5 .

It is apparent that MmB_5 is quite unstable at 65°C with an absorption plateau pressure, P_{eq} , of 4.3 atm as calculated *via* the van't Hoff equation. Thus, in a cell open to the atmosphere the hydride

phase does not form during the charging cycle, consequently its storage capacity will be low at elevated temperatures. This is demonstrated in Fig. 11 which illustrates a plot of electrochemical storage capacity *vs.* charge-discharge cycles at two temperatures for an MmB_5H_x electrode. However, the low-temperature performance is quite good as low as -20°C. The behavior of Mm^*B_5 is very different due to the increased stability of the hydride phase. At 65°C, P_{eq} is 0.5 atm and its initial storage capacity is only moderately decreased as shown in Fig. 12. However, continuous operation at 65°C will reduce electrode lifetime as indicated by the increased slope of the plot relative to that at room temperature. At low temperatures this electrode behaves similarly to that of the normal Mm electrode.

Figure 11. Performance of MmB_5 at 45 and 65°C.

Figure 12. Performance of Mm^*B_5 electrode.

Cycle life of AB₅ electrodes of varying Co Content. Two AB₅ electrodes were prepared of the following compositions; MmNi_{4.3}Mn_{0.4}Al_{0.3} and MmNi_{4.3}Mn_{0.4}Al_{0.3}. These alloys are similar to those used in commercial batteries except neither contains Co. Electrodes were fabricated from each alloy and were subjected to repeated electrochemical cycling using an Arbin battery cycler. The cycle life of both electrodes was rather poor.

In view of the these results, a series of homologous alloys was prepared, LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3} where x = 0, 0.2, 0.4, 0.75. Mm was replaced by La to assure reproducibility since the composition of mischmetal varies from vendor to vendor. Inspection of the plots indicated that electrode corrosion is a function of Co content. We have determined that the molar volume of hydrogen, V_H, in the hydride phase is lowered by the presence of Co, i.e., for x = 0.0 and x = 0.75, V_H is 3.26 and 2.99 Å³ respectively. The lattice expansion of the unit cell can be calculated *via* the equation,

$$\Delta\varepsilon = V_H \times n$$

where Δε is the actual volume change of the unit cell in Å³ in each charge or discharge cycle and n is the number of H atoms inserted into the unit cell and subsequently discharged. For the alloys cited,

the presence of Co reduces lattice expansion from 16.5 Å³ (x = 0) to 15.5 Å³ (x = 0.75) upon formation of the hydride phase. Thus, Co may inhibit corrosion merely by reducing alloy expansion and contraction in the hydriding-dehydriding process. However, preliminary XAS results indicate that Co tends to accumulate on the electrode surface as Co(OH)₂ in concert with Ni(OH)₂, which may also affect the corrosion process.

XAS Studies Of AB₂ Electrodes. The alloys studied were two pure C14 Laves phases, Ti_{0.5}Zr_{0.5}M₂ and Ti_{0.75}Zr_{0.25}M₂ (M = V_{0.5}Ni_{1.1}Fe_{0.2}Mn_{0.2}), and a similar mixed-phase alloy, Ti_{0.51}Zr_{0.49}V_{0.67}Ni_{1.18}Cr_{0.21}, having mostly the C14 Laves phase structure with a small cubic impurity phase. *In situ* XAS studies were carried out at the Ti, Zr, V, Mn, Fe and Ni K-edges. The XANES spectra at the Ni K edge indicate that, unlike the AB₅ alloys, there is very little interaction between the hydrogen and Ni but rather strong interactions with Ti, V and Zr. The hydrogen is presumably located in tetrahedra that contain large fractions of these three elements. The Ni-rich sites are probably empty and the function of Ni may be primarily to serve as a catalyst for the electrochemical reaction.

Optimization of Metal Hydride Properties in MH/NiOOH Cells for Electric Vehicle Applications

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Objectives

- Optimize the alloy composition of metal hydride electrodes by microencapsulation of hydrogen-storage alloys.
- Determine the exchange current density, diffusion coefficient, symmetry factor and equilibrium potential of bare and Cu-coated LaNi_{4.27}Sn_{0.24} electrodes as a function of the state of charge.
- Develop improved metal hydride electrodes for MH/NiOOH batteries..

Approach

- Prepare bare and Cu-coated LaNi_{4.27}Sn_{0.24} electrodes for determination of transport and electrochemical kinetic parameters.
- Apply porous electrode theory to data obtained from the LaNi_{4.27}Sn_{0.24} electrodes in alkaline solutions to determine kinetic parameters.
- Determine the diffusion coefficient of hydrogen in the hydride.

Accomplishments

- The polarization resistance of a copper-coated $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ alloy was found to be lower when compared with the corresponding resistance estimated for the bare alloy for the same state of charge.
- The constant-current discharge technique was used to determine the hydrogen diffusion coefficient in $\text{LaNi}_{4.27}\text{Sn}_{0.24}$.

Future Directions

- Determine the kinetic parameters of Ni-coated alloys.
- Determine the cycle life of bare and coated alloys as a function of temperature.

The focus of this research is to determine the exchange current density, diffusion coefficient, symmetry factor and equilibrium potential of bare and Cu-coated $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ electrodes as a function of the state of charge. Copper plating of the hydride particles was carried out in steps. The hydride surface was activated by immersing the powder in an aqueous HCl solution containing SnCl_2 , and then in an aqueous HCl solution containing PdCl_2 . Electroless Cu deposition was then carried out in alkaline electrolyte containing HCHO . The Cu-to-metal-hydride-alloy ratio was 1/4 by weight, which yielded a metallic Cu layer with a thickness of the less than 1 μm . The process of electroless Cu plating was terminated when the deep blue color arising from the Cu complex vanished. Experiments (linear polarization) were carried out and porous-electrode theory was used to determine exchange current densities as a function of the state-of-charge (SOC). The calculated exchange current densities are plotted against SOC in Fig. 13. The Cu coating increases the exchange current density, which is favorable for battery operation, and this is particularly true for high SOC. For a fully charged electrode the exchange current increases from 4.75 mA/g for the bare electrode to 17.5 mA/g for the Cu-coated electrode. Similarly, the calculated polarization resistances as a function of SOC indicated that the polarization resistance of the Cu-plated alloy is lower than the corresponding resistance estimated for the bare alloy at the same SOC. The Cu coating acts as a microcurrent collector and facilitates the charge transfer reaction on the alloy surface. A conventional Tafel polarization method cannot be applied for the porous metal hydride system because of the internal mass-transfer effects and the internal ohmic drop of the electrode. Thus, the symmetry factor was determined from the slope of E vs. $\log[i/\exp(F\eta/RT)-1]$ (Fig. 14), according to the following equation.

$$E = E_e + \frac{2.3RT}{\beta F} \log i_0 - \frac{2.3RT}{\beta F} \log \left[\frac{i}{\exp(F(E - E_e)/RT) - 1} \right]$$

which is valid in the low overpotential region. The symmetry factor was evaluated to be 0.53 for the bare electrode and 0.52 for the Cu-coated electrode and does not depend upon the hydrogen content in the electrodes. Assuming that 5.51 hydrogen atoms are adsorbed by one formula of the alloy (atom ratio $\text{H}/\text{M}=1$), the theoretical capacity was calculated to be 353 mAh/g. The experimental capacities of bare and Cu-coated $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ alloy are 270 and 275 mAh/g, and are about 76 and 78% of the theoretical capacity, respectively. Galvanostatic discharge curves were used to estimate the hydrogen diffusion coefficient by determining the transition time, τ . The estimated τ obtained at constant current per mass of 27.0 mAh/g for the bare electrode and 27.5 mAh/g for the Cu-coated electrode were 9.40 and 9.38 h, respectively. The initial charge of the electrode, Q_0 , was 972 C/g (270 mAh/g) for the bare electrode and 990 C/g for the Cu-coated electrode. Thus, the calculated values of $\bar{D}/a^2$ by using the equation¹

$$Q_1 = Q_0 - \tau i = \frac{i a^2}{15 \bar{D}}$$

are 3.1×10^{-5} and $3.0 \times 10^{-5} \text{ s}^{-1}$. For an average particle radius $a = 15 \mu\text{m}$, the effective diffusion coefficient ($\bar{D}$) through $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ was calculated to be $6.75 \times 10^{-11} \text{ cm}^2/\text{s}$. The charge remaining in the electrode (Q_1) after discharge for τ seconds was estimated to be 58 C/g for the bare electrode and 61 C/g for the Cu-coated electrode.

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Figure 13. Exchange current density of bare and Cu-coated electrode as a function of state of charge.

Figure 14. Dependence of E upon $i/\exp(\eta F/RT)-1$ for bare electrode at different states of charge.

Microstructural Modeling of Highly Porous MH/NiOOH Battery Substrates

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Objectives

- Develop predictive capability for determining performance of MH/NiOOH secondary cells through microstructural modeling of the NiOOH electrode.
- Improve the specific energy of MH/NiOOH batteries by determining optimal microstructures for NiOOH substrates.

Approach

- Develop closed-form approaches for efficient calculation of transport coefficients in porous fibrous microstructures.
- Develop standards for cell cycling which allow verification of closed-form models for electrode failure.
- Use microstructural descriptions of actual materials to initiate coupled stochastic/mechanical simulations of failure progression.

Accomplishments

- Materials have been characterized microscopically, and simulations have been initiated to characterize transport in model microstructures.
- Bounds have been established on transport properties in porous fibrous networks.
- An efficient interaction technique has been developed to model effects of varying microstructure in substrates.

Future Directions

- Expand interaction approach to accommodate all microstructures present in substrates.
- Conduct large-scale simulation of transport behavior in random networks and full-scale cell testing to assess accuracy of models.
- Develop new standards for cell testing to better assess electrode performance.

The objective of this program is to develop predictive capability of the performance of MH/NiOOH secondary cells through microstructural modeling of electrode behavior. The study is focused on the effects of the microstructure of fibrous composite electrodes on thermal and electrical conductivity, strength, and lifetime. Several candidate materials have been acquired and studied. Electrode failures after multiple charge-discharge cycles are being modeled at the microstructural level, incorporating failure mechanisms of the constituent materials, e.g., Ni fatigue and subsequent loss of conductivity. The theoretical approaches incorporate closed-form solutions for transport in electrode substrates with statistical, microstructural simulations.

Sample substrate materials are being optically characterized; these materials vary in staple fiber length, connectivity of microstructure, and porosity. Materials under study are comprised of a variety of fibers, including carbon (7-12 μm diameter) and polypropylene (~10 μm diameter), both coated

with Ni and sinter-bonded, and pure sinter-bonded Ni fibers. Nickel foams and sinters have also been investigated. Porosities have ranged between 80-95%, with substantial variability within samples. Software has been acquired to perform detailed, digital micrographic analysis on these dry samples.

A new analytical approach has been developed to account for the high variability encountered in actual microstructures. An interaction analysis to provide computational efficiency in modeling transport has been devised and used on simple geometries. Bounds on transport behavior have been identified, and explain earlier results in the application of classic approaches. Simulations of random structures are being performed concurrently with the optical analysis, based on characteristic geometric variables for real materials.

A custom battery test system has been ordered to allow independent control of four cell channels, to provide accurate data for benchmarking the micromechanical models.

Sol-Gel Derived Metal Oxides for Electrochemical Capacitors

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Objectives

- Investigate the chemical and materials properties of the NiO/Ni system for electrochemical capacitors.
- Model and design metal oxide electrodes for improved electrochemical capacitors.

Approach

- Utilize sol-gel processing techniques to fabricate thin-film electrodes for electrochemical capacitors.

Accomplishments

- The specific capacitance of NiO/Ni electrodes in 1 M LiOH was as high as 120 F/g of active material per cell, double the value obtained in 1 M KOH.

Future Direction

- Optimize performance of NiO/Ni electrodes in LiOH electrolyte.
-

The objective of this research is to investigate the chemical and materials properties of the NiO/Ni system for electrochemical capacitors (ultracapacitors). This project continues exploratory research on using sol-gel processing methods to fabricate thin-film ultracapacitors.

Prior to the start of this project, several sol-gel-derived metal oxide systems were investigated as potential active elements in electrochemical capacitors. Nickel oxide was selected as a promising material for this application. Two sol-gel processes (one aqueous, the other non-aqueous) were developed for preparing stable suspensions of

nickel oxide. These suspensions were used to fabricate thin films of nickel oxide particles by dipping pieces of Ni foil into the suspensions, withdrawing the coated foils at a uniform rate, and then drying and firing the coated foils. Thin films of nickel oxide prepared from aqueous suspensions provide specific capacitances as high as 60 F/g. Based on these results, the following optimized processing scheme for preparing thin-film NiO ultracapacitors was developed for use in this project: i) hydrolyze heat-treated nickel acetate tetrahydrate at room temperature; ii) after coating the resulting suspension on a suitable substrate, fire the samples in air at 300°C for one hour.

To better understand the mechanisms controlling the behavior of these nickel oxide-based electrochemical capacitors, the thin films were studied using XPS/ESCA. The results support the following hypothesis concerning the charge-storage mechanism in NiO-based capacitors. It appears that the Ni atoms on the surface of nanometer-sized nickel oxide particles are either reduced from Ni³⁺ to Ni²⁺ or oxidized from Ni²⁺ to Ni³⁺. During the charge cycle, pre-existing Ni³⁺ ions (present because the films are non-stoichiometric) in the negative electrode are reduced to Ni²⁺, while Ni²⁺ ions in the positive electrode are oxidized to Ni³⁺ ions. In the discharge cycle, the reverse reactions occur. These reactions appear to be both reversible and fast. Such characteristics are not surprising given that the redox reactions occur at the surfaces of the nickel oxide particles on both the electrodes, that the non-stoichiometric nickel oxide film has a low resistivity, and that these materials are fabricated in a thin-film configuration. During the charge and discharge cycles, electrons flow between the two electrodes and the ratios of Ni²⁺ and Ni³⁺

on each electrode change until an equilibrium state is reached.

For this process, the electrolyte should offer enough active ions to support the redox reaction. Since KOH solution was used as the electrolyte in these tests, the redox reaction may be written as:

The double-layer capacitance contribution to this material system may not be prominent. When these electrodes were tested in 1 M KCl electrolyte solution, the specific capacitances were ca. 5 F/g. Thus, the double-layer capacitance contributes about 10% of the total capacitance, so pseudo-capacitance provides the major charge-storage capability in these systems.

Alternative electrolytes have been employed with these nickel oxide electrochemical capacitors, including 1 M LiOH, 1 M KCl, 1 M LiCl and 0.5 M KCl/0.5 M LiOH aqueous solutions. The specific capacitances observed for the 1 M LiOH system were as high as 120 F/g of active material per cell. This value is twice that obtained for 1 M KOH (60 F/g). The 0.5 M KCl/0.5 M LiOH electrolyte also provided capacitances of 80 F/g of active material per cell. However, the other electrolytes only supplied about 5 F/g of active material per cell. Thus, LiOH provides higher specific capacitances with this material system than KOH. Further optimization should be performed using the LiOH electrolyte.

PUBLICATION

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Ultracapacitor and Battery Systems Studies

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Objectives

- Assess the trade-offs between specific energy, peak specific power, cost, and cycle life for several types of batteries as a means of estimating the effects of load leveling with ultracapacitors on battery economics.
- Investigate the performance of ultracapacitors based on the material characteristics and run simulations of vehicles with powertrains using ultracapacitors on SIMPLEV.
- Determine the effect of load leveling on battery performance for the DST cycle.

Approach

- Develop a generic battery model and associated spreadsheet that describes the internal construction of the battery in sufficient detail that its performance and material and manufacturing costs can be calculated from nearly first principles for a wide range of battery designs.
- Model ultracapacitors based on the material characteristics of the electrodes and the electrolyte.
- Perform preliminary designs and simulations of electric and hybrid vehicles using ultracapacitors as the pulse power device in electric drivelines.
- Perform an experimental study of the load leveled discharge of sealed lead-acid batteries on the DST cycle using a second battery pack as the pulse power unit.

Accomplishments

- Developed analytical relationships between electrode material properties and ultracapacitor specific energy and maximum usable power.
- Developed a spreadsheet model to calculate the effects of battery load leveling on the initial and life cycle costs of the energy storage system in electric and hybrid vehicles as a function of vehicle acceleration and range.
- Demonstrated load-leveled battery discharge on the DST cycle using simple electronics and batteries as the pulse power unit controlled to act as ultracapacitors of limited energy storage capacity.

Future Directions

- Complete the generic battery model and apply it to MH/NiOOH and Li-ion batteries to determine battery design trade-offs and optimized designs for use with ultracapacitors.
- Complete the battery load-leveling tests and the characterization of battery-ultracapacitor systems by determining the losses associated with the ultracapacitor and the electronics.

The research on this contract supports the DOE Ultracapacitor Development Program and investigates the use of ultracapacitors in high efficiency, ultra-clean vehicles being developed in the Partnership for a New Generation Vehicle (PNGV) program. One of the tasks is to quantify the battery trade-offs that are possible if the battery is load-leveled and does not meet both the energy storage and power requirements in an electric or hybrid vehicle. This is done by developing a generic battery model that considers in detail the electrochemistry of the battery without solving in space and time the mass transfer and kinetics equations by treating each porous electrode as a lumped mass carrying the average charge and species fluxes, which depend primarily on the current density (A/cm^2) to the electrodes. The model is applied to lead-acid, Cd/NiOOH, MN/NiOOH and Li-ion battery types.

Laboratory studies of a load-leveled battery are being performed using simple electronics (a DC chopper) to control the discharge of a 36 V "energy"

battery in parallel with a 24 V "pulse power" battery being used to mimic ultracapacitors. This arrangement results in the near-ideal load-leveled discharge of the "energy" battery as long as the "pulse" battery stores sufficient energy (Wh) to meet the high power portions of the DST cycle. Complete load-leveled discharges of the "energy" battery on the DST cycle indicate that its energy capacity is about 20% higher, including the effects of losses, than would be the case if it had been discharged alone on the DST cycle.

Analytical relationships were derived between the specific energy, resistance and maximum usable power of ultracapacitors and electrode and electrolyte material properties and the cell geometry. These relationships were used to project material requirements and cell designs that can be expected to meet the near-term and long-term specific energy goals of the DOE Ultracapacitor Development program — 5 Wh/kg and 15 Wh/kg, respectively. The relationships derived are

consistent with the experience to date in the DOE program.

Vehicle systems studies were undertaken to evaluate the use of ultracapacitors in high-fuel-economy passenger cars like those being considered in the PNGV program and in hybrid/electric transit buses. In these studies, vehicles utilizing electric and hybrid drivelines with ultracapacitors as pulse-power units were evaluated using the SIMPLEV vehicle simulation program. The ultracapacitor units for the passenger cars were sized to store 350-750 Wh and those for the transit buses were sized to store about 3500 Wh. The ultracapacitors were modeled like a battery with an open-circuit voltage that varies linearly with state-of-charge and a constant resistance. In this way, both the charge storage in capacitors and energy losses from resistance were included in the vehicle calculations. The simulation results confirmed that ultracapacitors meeting the DOE program goals of 5-15 Wh/kg would make excellent energy storage components for load leveling an engine/generator or fuel cell in hybrid/electric passenger cars yielding fuel economy values near to and beyond the PNGV goals. This was found to be true for both series and parallel hybrid driveline designs. The simulation results also indicated the ultracapacitors were suitable for use in electric/hybrid transit bus drivelines resulting in lower fuel consumption and emissions than would be predicted using batteries, because of the higher efficiency and lighter weight of the ultracapacitors.

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C. COMPONENTS FOR AMBIENT-TEMPERATURE NONAQUEOUS CELLS

Metal/electrolyte combinations that improve the rechargeability of ambient-temperature, nonaqueous cells are under investigation.

Novel Lithium/Polymer-Electrolyte/Sulfur Cells

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Objectives

- Investigate the behavior of sulfur electrodes in Li/polymer electrolyte/S cells and improve their lifetime and performance.
- Improve the utilization of the S electrode.

Approach

- Fabricate and test Li/polymer electrolyte/sulfur cells.

Accomplishments

- Preliminary modeling and experimental studies indicated that smaller S particles are needed to improve the S utilization in the electrode.

Future Directions

- Improve the utilization of the S electrode by reducing the size of the S particles in the electrodes.
 - Use Scanning Electron Microscopy/Electron Spectroscopy for Chemical Analysis (SEM/ESCA) to characterize the electrodes and employ phase-contrast microscopy to examine the uniformity and material distribution in as-prepared electrodes.
-

Variants of Li/S cells have been under investigation since the 1950's, including systems as different as high-temperature (380-500°C) LiAl/FeS₂ cells and ambient-temperature Li/Li₂S_n (lithium polysulfide) cells. Interest in the Li/S couple stems from its high theoretical specific energy (~2600 Wh/kg) as well as its environmentally benign components. In principle, this system is well-suited to EV applications, however a practical Li/S battery showing promise for EVs has not been developed. Problems have ranged from positive-electrode swelling to dissolution of partially-reduced active material (polysulfides) into the electrolyte. These problems have resulted in low utilization of active material, short cell lifetimes, and low delivered specific energy and specific power. The major thrust of this work is to investigate the behavior of S electrodes in Li/polymer electrolyte/sulfur cells and improve their lifetime and performance.

Sulfur electrodes were prepared from suspensions of elemental sulfur powder, graphitic carbon, PEO, lithium trifluoromethanesulfonate (LiTf), and Brij 35 surfactant in acetonitrile. These suspensions were cast onto Teflon-coated plates to produce 100-200 µm thick films. Galvanostatic cycling of Li/S cells fabricated from these electrodes and PEO-LiTf electrolytes showed good charge-discharge behavior at low currents (~10 µA/cm²), but resulted in only 1-2% utilization of the active material. SEM and ESCA studies revealed the presence of 10-µm S islands in the as-prepared S electrodes. Our preliminary phenomenological model of the S electrode postulates the creation of a Li₂S reaction zone

characterized by slightly higher ionic conductivity but equally poor electronic conductivity, compared to elemental S. According to our model, volume changes that accompany the electrochemical reaction may cause a loss of available active material. Smaller S particles are needed to minimize this problem. Our most successful method to produce smaller particles involves the dissolution of S in carbon disulfide followed by the addition of this solution to a suspension of the other electrode components. Galvanostatic cycling of some of these electrodes resulted in a utilization of several percent of the active material. Some unusual results were obtained, however, when the cells were subjected to extended cycling, including much longer charges than discharges and some discharges bearing two distinct plateaus. In addition, many charging plateaus exhibited large, prolonged voltage fluctuations. These results suggest that parasitic reactions may be taking place in the cells or that Li dendrites may be present.

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***In Situ* and *Ex Situ* Spectroscopic Applications to the Study of Rechargeable Lithium Batteries**

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Objectives

- Gain better understanding of the nature of the passive films at the interface of Li and Li-C with nonaqueous-liquid and solid-polymer electrolytes (SPE).

Approach

- Develop *in situ* and *ex situ* spectroscopic techniques to examine the reactivity of metallic Li toward these electrolytes under conditions of optimum cleanliness.
- Adapt such methodologies to gain *in situ* spectroscopic information under conditions which resemble those found in practical devices in terms of uniform current distribution and other operating parameters.

Accomplishments

- Demonstrated that a $\text{LiClO}_4/\text{PEO}$ SPE exhibits a sufficiently low volatility and stable physicochemical properties to enable conventional electrochemical experiments to be performed in ultrahigh vacuum (UHV).
- Voltammetric curves for Li underpotential deposition (UPD) on polycrystalline Au were found to be similar to those reported in nonaqueous electrolytes, displaying deposition and stripping peaks with a charge equivalent to the adsorption and desorption of a single Li^+ per surface site.

Future Directions

- Continue electrochemistry in UHV to examine the nature of films at the Li^+ -based PEO electrolytes
 - Investigate kinetics of Li intercalation/deintercalation in carbon in UHV.
 - Develop new model systems for Li intercalation in carbon-based materials, including the UHV synthesis of graphite on Ni substrates using CO and/or ethylene as a precursor.
-

The objective of this project is to develop and implement *in situ* and *ex situ* techniques and procedures to study interfacial phenomena at the Li/electrolyte interface under charge/discharge cycling. A new experimental approach has been developed and implemented for the study of various aspects of Li electrochemistry under the conditions of high cleanliness. This novel strategy takes advantage of the low vapor pressure of ultrapure Li salt/PEO electrolytes for conducting conventional electrochemical experiments in UHV environments with a wide variety of electrodes prepared and characterized by surface analytical techniques. Two processes were investigated using a $\text{LiClO}_4/\text{PEO}$ electrolyte at temperatures in the range of 55–70°C: i) electrochemical insertion of Li into the basal plane of highly ordered pyrolytic

graphite (HOPG); ii) UPD of Li onto polycrystalline Au.

Cyclic voltammetry curves obtained in a glove box were recorded using a specially designed electrochemical cell configured in a sandwich-type arrangement. The working electrode was a Au film sputtered on a glass slide (ca. 100–200 nm thick). A polyethylene (PE) gasket, 50 μm thick, cut in the form of a frame (16 mm x 50 mm, outer, and 9 mm x 40 mm, inner dimensions) was then laid down on the Au-coated substrate followed by a (8 mm x 39 mm) $\text{PEO}(\text{LiClO}_4)$ electrolyte film positioned in the center of the PE gasket. The counter electrode was a piece of a Li ribbon (0.3 mm x 12 mm x 45 mm) placed over the SPE so that all its edges were within the boundaries of the PE gasket. To complete the arrangement, a Ni-coated glass slide or current collector was placed directly on the Li ribbon.

The Li counter-reference electrode (Li[C/R])/LiClO₄/PEO SPE arrangement used in the UHV electrochemical experiments was assembled in the glove box. The actual Li[C/R] was a small circular foil of freshly scraped metallic Li pressed against the flat end of a stainless steel holder (SSH), which was then covered by a tightly held circular piece of an ultrapure LiClO₄ (PEO) film with a small stainless steel (SS) clamp.

Intercalation of Lithium in HOPG. The Auger electron spectroscopy (AES) spectra of HOPG obtained after the thermal treatment displayed features characteristic of graphitic carbon with a small amount of oxygen. After the cell had been assembled and the temperature reached 55°C, a series of cyclic voltammograms was acquired. The currents associated with the intercalation of Li in HOPG were observed at potentials more negative than 1.25 V *vs.* Li[C/R] with no evidence for staging. This behavior is characteristic of HOPG both in liquid and solid electrolytes. The prominent peak obtained in the scan in the positive direction upon reversing the cycle at 1.4 V can be attributed to the deintercalation of Li from the HOPG lattice. Essentially identical features were found in parallel experiments conducted with a sandwich-type cell involving the same constituents in the glove box. This provides unambiguous evidence that the electrochemical behavior observed in UHV is indeed characteristic of the Li/LiClO₄(PEO)/HOPG system and is not affected in any discernible way by the ultralow pressures.

Regardless of whether Li⁺-intercalation into HOPG from ultraclean PEO/LiClO₄ films was performed in UHV or in a glove box, the very first linear voltammetric scan in the negative direction (initiated at the open circuit potential) yielded no features at potentials more positive than the onset of Li intercalation. This provides evidence that the films are free of adventitious water, oxygen and/or carbon dioxide. The charge associated with the first scan in the negative direction, for the HOPG/PEO(LiClO₄) system in both environments, was always larger than that observed upon reversing the scan at the negative limit, an effect that became less pronounced as the cycling was continued. For example, experiments performed in the glove box at 5 mV/s in the potential range 0.03–3.0 V *vs.* Li/Li⁺ with a three-electrode cell, yielded values of $g = Q_{\text{deint}}/Q_{\text{int}}$, where Q_{int} and Q_{deint} represent the charge during intercalation and deintercalation, respectively, of 7.5% in the first cycle ($Q_{\text{int}} = 26.8 \text{ mC/cm}^2$, $Q_{\text{deint}} = 74 \text{ mC/cm}^2$) up to 71.5% in the ninth cycle ($Q_{\text{int}} = 171 \text{ mC/cm}^2$, $Q_{\text{deint}} = 475 \text{ mC/cm}^2$). For much faster

scan rates, such as 80 mV/s, g values as high as 92.5% were observed in the third cycle.

A charge imbalance during the first charging cycle, also known as irreversible capacity loss, is almost universally found in the case of Li intercalation in a variety of high-area carbons in liquid electrolytes. Such a phenomenon, which adversely affects battery performance, has been attributed to, among other factors, the formation of a film at the interface derived from irreversible reactions between intercalated Li and the electrolyte, including both the salt and the solvent. Based on the *in situ* attenuated total reflection-Fourier transform infrared spectroscopy (ATR/FTIR) experiments, film formation in PEO/LiClO₄ solutions is not likely to be responsible for the observed charge imbalance; instead, this effect appears to originate from kinetic hindrances during discharge, which prevent the complete deintercalation of Li from the HOPG in the time scale of the cyclic voltammetry experiments. Measurements aimed at elucidating this interesting phenomenon are currently in progress.

Li UPD on Au. The AES spectrum of a Au foil never exposed to Li acquired after heavy Ar⁺-sputtering without subsequent thermal annealing showed the characteristic Au peaks and minor contributions from C (271 eV), N(392 eV), and O (511 eV). The first cyclic voltammogram obtained for this surface immediately after transferring the PEO/Li counter electrode to the UHV chamber and assembling the electrochemical cell yielded a curve resembling those reported in nonaqueous liquid electrolytes. Particularly noteworthy, however, is the rather featureless character of the scan in the negative direction in the range between 1 and 2 V, suggesting that under the UHV conditions in which these experiments were performed and to the level of sensitivity of cyclic voltammetry, the PEO films are free from water and/or dioxygen impurities.

The peak centered at 0.76 V in the scans in the negative direction may be attributed to the UPD of Li on Au(poly) which is followed by an increase in the current at more negative potentials from incipient Li/Au alloy formation. Finally at ca. 0.1 V, Li bulk deposition occurs, as signaled by the characteristic nucleation/growth loop.

The results obtained provided conclusive evidence (except for impurity effects) that the electrochemical behavior observed in UHV is indeed characteristic of the systems selected for these studies, and, therefore, is not affected in any discernible way by the ultralow pressures. In the case of Li UPD on polycrystalline Au, the voltammetric curves were found to be similar to

those reported in liquid nonaqueous-solvent electrolytes, displaying deposition and stripping

peaks with a charge equivalent to the adsorption and desorption of a single Li^+ per surface site.

Polymer Electrolyte for Ambient Temperature Traction Batteries: Molecular Level Modeling for Conductivity Optimization

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Objectives

- Analyze properties of polymer electrolytes by molecular dynamics and Monte Carlo simulations.
- Develop a microscopic understanding of the stability, structure and conduction properties of polymer electrolytes.
- Suggest modified materials with optimized conduction properties, based on mechanistic insight.

Approach

- Apply molecular dynamics and Monte Carlo simulations using high-speed computers to analyze the properties of polymer electrolytes

Accomplishments

- Demonstrated conclusively using hopping models within a relaxing environment that polymer electrolytes will generally exhibit higher mobilities than polyelectrolytes, although the transference properties are less attractive.
- Introduced novel cluster analysis method showing conclusively that although few free ions exist in concentrated polymer electrolytes, modified single-particle motions remain responsible for conduction.

Future Direction

- Analyze modified polyelectrolytes, in which unit transference numbers assure reduced cell polarization. Investigate possible roles of interfaces on mobilities, and develop methods for analysis of compatibility between electrodes and electrolytes.
-

Substantial progress was made towards understanding both the mechanism and the limitations for ion transport in neat polymeric materials. Several important results have been obtained using our simulation studies.

(1) Molecular-dynamics simulations of the parent polymer electrolyte, that have appeared from many groups, have been inadequate in ignoring polarization caused by the presence of the ions. This polarization results in substantially varied potentials, and therefore substantially varied diffusivities and conductivities, compared to the usual picture of a rigid unpolarized electronic behavior in the polymer host. We have developed a self-consistent molecular-dynamics scheme for

including polarization; this gives much better information on the dielectric, viscosity, density and dipole moment of the host material, and therefore provides much more accurate understanding of precisely how particular structures within the polymer host produce better polymer electrolytes. This is an issue of substantial experimental importance: preparing new polymeric electrolytes and characterizing them is complex and costly, and without the design criteria offered by modeling, this activity may not proceed effectively.

(2) Our dynamic hopping models, which can produce results for direct comparison with experimental measurements of conductivities, have been extended to examine the difference between

polyelectrolytes and polymer electrolytes. In polyelectrolytes, the anionic charge is functionalized on the polymeric backbone, assuring unit transference number for the cation. Our dynamic-simulation results show clearly that polymer electrolytes will be more conductive because the intrinsic mobility of the cation is higher and because of the additional contribution to the conductivity arising from the anions. These simulations also place theoretical limits on the conductivity of Li polyelectrolytes; it suggests that their activation processes should be of the usual WLF type, and that polyelectrolyte viscosity limits conduction.

These results are in accord with the experimental results of Shriver and Armand. Indeed, Armand's advanced, imide-based polyelectrolytes confirm quite nicely the results of this simulation: the conduction, in optimal cases, is roughly half that of the comparable polymer electrolytes, with similar temperature dependence.

(3) Molecular-dynamics simulations of concentrated salt solutions in oligomeric models for polymer electrolytes have shown quite clearly that large clusters exist, so that the simple notion of independent ions moving, with a conductivity given by the sum of individual particle conduction, is incorrect. For characteristic conditions (one molar solution of a uni-univalent salt), a substantial fraction of the ions is in clusters of one sort or another; this is in complete accord with experiments by Raman spectroscopy as well as dielectric relaxation and infrared spectroscopy.

Figure 15 shows the computed number of free ions and ion pairs from simulation studies of NaI in dimethyl ether and in diglyme at 300 K. Note that the percentage of free ions drops fairly sharply with an increase in salt concentration. Nevertheless, the dominant effect limiting the conduction, as our dynamic percolation picture suggested, is solvent friction slowing of ion flow. Conduction occurs largely by single-ion motions. This apparent contradiction is understood in terms of the trajectories obtained from the molecular-dynamics simulations. We see that ions moving from one end of a large cluster, or ion motion between clusters, is in fact responsible for most of the conduction process. This suggests that, while clustering is certainly present in these materials, it may not significantly reduce the conduction at high concentration. Exactly such conditions are obtained

in the ionic rubbers studied by Angell and his collaborators, and may offer an entirely new route to obtaining high-conductivity solid-state electrolytes.

Figure 15. The percent composition of free ions and neutral pairs at different salt concentrations in dimethyl ether or glyme. Note that the percentage of free ions drops significantly with salt concentration, suggesting that in this stoichiometry range, increasing salt content will not necessarily increase conductivity.

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The Performance of New Materials for Polymer-Electrolyte Batteries

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Objectives

- Synthesize polymer electrolytes based on aluminosilicate-polyether hybrid polyelectrolytes with improved low-temperature performance and higher cation transport number.
- Develop improved polymer electrolytes for rechargeable Li/polymer batteries.

Approach

- Synthesize polymer electrolytes based on aluminosilicate-polyether hybrid electrolytes and evaluate in electrochemical cells.

Accomplishments

- Synthesized polymer electrolytes based on aluminosilicate-polyether hybrid electrolytes, (amorphous PEO)₂₅LiTf and (amorphous PEO)₃₈Li[Al(OSiEt₃)₄], which yielded 135 mAh/g active positive-electrode material in Li/Li_xMn₂O₄ cells.

Future Directions

- Synthesize new polymer electrolytes and polyelectrolytes.
- Evaluate the performance of cells containing the polymer electrolyte and electrode composite materials such as V₂O₅.

The objective of this research project is to synthesize polymer electrolytes with improved low-temperature performance, higher cation transport number and useful performance in rechargeable Li/polymer batteries.

Tests were performed with cells containing simple polymer-salt electrolytes, such as (amorphous PEO)₂₅LiSO₃CF₃ and (amorphous PEO)₃₈Li[Al(OSiEt₃)₄], MEEP-LiSO₃CF₃ and an aluminosilicate polyelectrolyte network. The test cells contain Li-metal negative electrodes and composite positive electrodes (70% Li_xMn₂O₄, 15% carbon, and 15% of the respective electrolyte). The cells were charged/discharged at different rates.

The high bulk resistance of the aluminosilicate polyelectrolyte at room temperature (1×10^{-5} S/cm) prevents this material from use at room temperature, however this polyelectrolyte could be used in cells at 70°C where its conductivity is higher than 1×10^{-4} S/cm (Fig. 16). Cells with the simple polymer-salt electrolytes gave acceptable cell capacity at low discharge current at room temperature. The utilization of positive-electrode material dropped significantly when the discharge current was increased, because AC impedance showed that a high-resistance interfacial layer is formed during cell fabrication (Fig. 17). The resistance increase is not very significant after cell

fabrication (Fig. 18). Practical cells with polymer electrolytes may be developed when bulk and interfacial resistance are reduced.

Figure 16. Charge/discharge of Li/aluminosilicate polyelectrolyte network[2,2,2]/LiMnO₂ cell at 20 mA/cm² and 70°C.

The emphasis of this project for the next year will be to continue the synthesis of new polymer electrolytes and polyelectrolytes. Emphasis will be placed on comparison of the cell performance of polymer-salt complexes versus polyelectrolytes. Battery tests of aluminosilicate polyelectrolytes and modified clays, where the aluminosilicate

anion is covalently bonded to the polymer and therefore less exposed to the electrodes, will be performed. Also, xerogel composites of V_2O_5 and polymers will be explored as positive electrodes in the cell tests.

Figure 17. AC impedance spectra of Li/MEEP-LiSO₃CF₃/Li cell at 25°C.

Figure 18. Evolution of bulk and interfacial resistance in Li/MEEP-LiSO₃CF₃/Li cell at 25°C.

Novel Polymer Electrolytes for Rechargeable Lithium Batteries

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Objectives

- Synthesize and characterize polybenzimidazole-base materials for polymer electrolytes.
- Develop advanced SPEs for rechargeable Li batteries.

Approach

- Completed a study of the synthesis of phosphonated poly(2,6-dimethyl phenylene oxide).

Accomplishments

- PBI was successfully sulfonated by heating with sulfuric acid to yield a maximum of 0.95-SO₃H groups per PBI unit. When PBI was dissolved in H₂SO₄ containing either SO₃ or P₂O₅ and heated to 150°C, it reached 2.1 to 2.2 sulfonic acid/per PBI unit.
- Two point conductivities of 7.1×10^{-8} and 2.3×10^{-8} S/cm, respectively, were measured at 150°C for PBI/PEO films with weight ratios of 1/1 and 2/1.

Future Direction

- Project was completed.

The objective of this research is to develop advanced novel polymer electrolytes for rechargeable Li batteries. These polymer films

should have high T_g and high Li-ion conductivity in the membrane. Two approaches were studied concurrently:

i) Sulfonated and phosphonated commercial polymers. The labile protons can be replaced by Li to make a salt that should be stable to Li metal and could conduct well since it would have many ions per repeat unit. The Li transference number should be 1, since the anions are fixed on the polymer. After some experimentation, two polymers were chosen to study in detail. These were poly(m-phenylene bibenzimidazole (PBI) for sulfonation, and poly(2,6-dimethylphenylene oxide) (PPO) for phosphonation.

ii) Novel imidazole-containing polymers. These are acidic and have a very low equivalent weight per Li. However, such polymers had not been previously made, so a study of their syntheses was necessary. Most of the effort was expended on the synthesis of poly(4,5-dimethylene imidazole) and its hydroxy analogue. More recently the synthesis of poly(2,5-imidazoimidazole) was started.

Phosphonated PPO. A consideration of the final film properties of the phosphonated PPO has led to the following conclusions. There is probably some backbone cleavage during the bromination reaction. The final chain length is too small to have a film with good physical properties. Doping with a plasticizer would only exacerbate the problems, since that tends to make films even more brittle. The only solution is to make high-molecular-weight poly(2,6-di(chloromethyl)phenylene oxide) from the starting monomer, 2,6(di(chloromethyl)4-bromo phenol), and phosphonate that moiety. Because of the long time required for the synthesis, this effort was ended.

Sulfonated PBI. Elemental analyses and Fourier transform infrared spectroscopy (FTIR) spectra were taken on a series of PBIs sulfonated under various conditions. The combination showed that PBI sulfonated at 150°C with $\text{H}_2\text{SO}_4/\text{P}_2\text{O}_5$ for 5 h had only sulfonic acid groups. Harsher conditions produced sulfone groups with a net loss in acidity.

Doped films of Li sulfonated PBI salts were cast from ethanol solutions. Many were too brittle to be handled but several were useful for study. They were gold shadowed and run on a TK Instruments Dielectrometer as a function of temperature and frequency. The conductivity was taken at the frequency where the phase angle was zero. With this more-elegant approach compared to the initial technique, the conductivities behave normally with respect to temperature and had an activation energy of 1.1 eV. They were also higher than those reported initially, up to 10^{-6} S/cm at 150°C. Doping with lithium triflate (9×10^{-7} at 100°C) seemed to increase the conductivity the most, but this may be due to anion mobility as well as the larger concentration of cations. Even the highest conductivity was still low compared to the target values of $>10^{-4}$ S/cm at room temperature.

Polyimidazoles. While the initial idea to generate poly(4,5-dimethylene imidazole) and its 2-hydroxy analogue may have validity, it could not be demonstrated in the laboratory. The work was therefore terminated and the results have been written up for publication.

Novel Solid Polymer Electrolytes for Advanced Secondary Batteries

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Objectives

- Synthesize and characterize new polymer electrolytes that contain crown ethers to provide improved Li-ion transport.
- Develop advanced SPEs with high conductivity and better dimensional stability for rechargeable Li batteries.

Approach

- Synthesize and characterize new doped polymer electrolytes with side chains having the ability to form liquid-crystalline mesophases which are terminated with crown-ether groups.

Accomplishments

- Three liquid-crystalline monomers terminated by benzo-12-crown-4, benzo-15-crown-5 and benzo-18-crown-6 were synthesized by a multistep synthetic route, and the pertinent liquid crystalline properties determined. A procedure for preparation of films polymerized between indium/tin oxide (ITO) glass slides was developed and equipment for aligning the liquid crystal monomers with both an electric field and a magnetic field was assembled.

Future Direction

- Complete characterization of polymerized films with respect to properties pertinent to the solid polymer electrolyte application.
-

The objective of this research program is to develop new polymer electrolytes which will have a fundamentally different mode of ion transport than those currently under investigation. The systems under investigation are doped polymers with side chains that have the ability to form liquid crystalline mesophases. The side chains are terminated with crown-ether groups which can complex with the Li salt dopant. It is hypothesized that these materials will create highly ordered liquid-crystalline structures, thereby forming paths through which ions can easily move. Consequently, the polymer will conduct ions through a different mechanism which will not rely on the segmental motion of large portions of the polymer chains for ion transport as do the current systems.

Three analogous liquid-crystalline monomers terminated by benzo-12-crown-4, benzo-15-crown-5 and benzo-18-crown-6 have been synthesized by a multistep synthetic route based on similar work reported in the literature. These monomers were based on the 4-[(11-acryloylundecan-1-yl)oxy]-4'-(4'-carboxybenzo-X-crown-Y)biphenyl structure. Some of the individual steps have been improved to give the purified products in higher overall yields than the yields reported in the literature.

The yield of the critical intermediate, 4-[(11-hydroxylundecan-1-yl)oxy]-4'-hydroxybiphenyl, has been increased from a literature value of 27% to 65% of pure product. The mesophase transitions of the monomers and combinations with photoinitiator and lithium triflate are shown in Table 2. Similar transitions for some polymers are also shown. The mesophase ranges for the 12-crown-4 and 15-crown-5 based monomers provide a very convenient working range for carrying out alignment and polymerization studies. The lack of a mesophase for the 18-crown-6 based monomer was unexpected.

The monomers showing nematic mesophases were readily photopolymerized at 350 nm in a photoDSC cell. The photopolymerization was complete within 6 min as evidenced by the absence of residual reactivity as determined by DSC. Clear, colorless films were obtained when the polymerization was carried out using a mercury vapor lamp.

A process was devised for preparation of films between ITO glass slides using a silicone spacer to control the thickness at 125 μm . The process allows formulations to be melted under vacuum to degas the mixtures followed by photopolymerization while controlling the temperature of the system in

the nematic range. This allows the preparation of films that adhere to the ITO glass so that intimate contact is maintained for conductivity measurements.

Two techniques have been developed to carry out the alignment of molten liquid-crystal formulations. Equipment has been assembled that

will permit the use of a magnetic field for alignment using a 2 Tesla field. In addition, a system for generating an ac electric field has been assembled utilizing high-frequency, low-voltage fields in an attempt to prevent the occurrence of hydrodynamic instability that is typically caused by the presence of ionic species.

Table 2. Mesophase Transition Temperatures for Monomers Containing Crown Ethers.

Crown Ether Group	Mesophase Cooling Transition Temperatures °C			
	Isotropic	Nematic	Sematic	Crystalline
benzo-12-crown-4	> 110	110	77	54
benzo 15-crown 5	> 113	113		92
benzo-18-crown-6	> 116			116
benzo-12-crown-4/pi ^a	> 104	104	82	55
benzo-12-crown-4/Li ^b	none observed			
benzo-15-crown-5/pi	> 120	120		92
benzo-15-crown-5/Li	> 108	108		94
benzo-15-crown-5/pi/Li	> 103	103		84
polymer of benzo-15-crown-5/pi	> 194	194		161
polymer of benzo-15-crown-5/pi/Li	none observed			

^a pi = photoinitiator, ^b Li = lithium triflate

New Cathode Materials

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Objectives

- Synthesize and evaluate oxides of transition metals for alkali-metal intercalation electrodes.
- Identify new intercalation compounds for positive electrodes in advanced nonaqueous secondary batteries.

Approach

- Synthesize metal oxides that have an appropriate crystallographic structure to permit facile intercalation of Li ions.
- Characterize the metal oxide structures by XRD analysis and evaluate materials in electrochemical cells.

Accomplishments

- The mild hydrothermal aqueous decomposition reaction of potassium permanganate at 170°C produces a layered structure.
- Electrochemical intercalation and deintercalation of Li into the dehydrated potassium manganese oxide lattice shows a continuous curve indicative of single-phase behavior, $\text{Li}_x\text{K}_{0.25}\text{MnO}_2$ where $0 \leq x \leq 0.6$.

Future Direction

- Continue synthesis and electrochemical studies of vanadium and manganese oxides.

The objective of this project is to synthesize and evaluate oxides of W, Mo, and first-row transition metals for alkali-metal intercalation electrodes in advanced nonaqueous rechargeable batteries. Mild hydrothermal techniques are being used for the synthesis of molybdenum oxides or, in cases where the hydrothermal technique does not lead to compounds in the highest oxidation states, electrochemical oxidation will be used to drive the transition metal to its highest oxidation state.

Vanadium oxides were synthesized by mixing V_2O_5 powder with 25% tetramethyl ammonium (TMA) aqueous solution and LiOH crystals in a 1:2:1 molar ratio, respectively. This mixture was then acidified with 3 M HNO_3 to pH values ranging from 2-5. The resulting solution was transferred to a 125-ml Teflon lined autoclave (Parr bomb), sealed, and reacted hydrothermally for 3 days at 200°C. The resulting greenish black crystals, Fig. 19, contained no TMA ion but in its absence no crystallites were formed.

Figure 19. Photomicrograph of lithium vanadium oxide crystallites, showing their lamellar nature.

In the case of manganese we attempted to form a layered compound analogous to the layered titanium disulfides. We found that the mild hydrothermal aqueous decomposition reaction of potassium permanganate at 170°C produces a layered structure. This decomposition reaction may be represented by:

The structure of this manganese oxide is indicated in Fig. 20. It is layered, and exactly like the disulfides, the alkali ions can be hydrated by either one or two layers of water molecules. The water may be driven out by heating to 150°C; thus all water will be removed on cathode preparation.

We have performed Rietveld analysis, both X-ray and neutron, on the vanadium oxide phase. Its tetragonal structure is layered, and contains water between the vanadium oxide sheets. The chemical composition can be represented by the formula:

The X-ray pattern of this phase is shown in Fig. 21; the tetragonal lattice parameters are $a = 3.705 \text{ \AA}$ and $c = 15.80 \text{ \AA}$. The structure is shown in Fig. 22, where the layers between the vanadium oxide square pyramids are very apparent, and the Li resides in the interlayer regions together with the water molecules. Gentle heating up to about 150°C causes the water to be lost and the structure contracts from 15.8 to 12.8 Å. In the preparation of electrodes for electrochemical evaluation, a mixture of the vanadium oxide, carbon and Teflon powder were heated to between 150 and 200°C; X-ray analysis of the formed electrode indicated that the lattice had contracted confirming that lattice water is not present.

Figure 20. Schematic of layered manganese oxides showing (a) anhydrous material, (b) one water layer, and (c) two water layers. $\odot = H_2O$; $\bullet = M$ ion.

Figure 21. X-ray powder pattern of tetragonal vanadium oxide phase.

Figure 22. Crystal structure of tetragonal vanadium oxide phase, shown perpendicular to the planes ($a=3.705\text{\AA}$, $c=15.804\text{\AA}$).

Reaction of dehydrated potassium manganese oxide with *n*-butyl lithium showed an uptake of 1.0 Li/Mn. The electrochemical intercalation and deintercalation of Li into the dehydrated potassium manganese oxide lattice is shown in Fig. 23. This plot shows a continuous curve

indicative of single-phase behavior, $\text{Li}_x\text{K}_{0.25}\text{MnO}_2$ where $0 \leq x \leq 0.6$, similar to that observed in the layered disulfides. The curve for the electrochemical intercalation of Li into $\text{Li}_x\text{K}_{0.25}\text{MnO}_2$ also suggests that the oxidation state of the Mn is around 3.5, as the initial cell open-circuit voltage is 3.6 V, close to the value reported for Li insertion into LiMn_2O_4 . The extended cycling behavior of this hydrothermally formed manganate is now underway. A systematic study is required of the role of Mn defects, crystallinity, water, and other alkali metals in the electrochemical behavior of these layered manganese oxides.

Figure 23. The electrochemical reduction of manganese oxide in a Li cell; the Li anode was also used as the reference electrode.

The lattice of the dried $\text{Li}_{0.6}\text{V}_{2-8}\text{O}_{4-8} \cdot \text{H}_2\text{O}$ compound reacts to about 1.2 Li/V with n-butyl lithium. In electrochemical cells this compound has an initial emf of 3 V and readily takes up two Li atoms in well-defined voltage plateaus as shown in Fig. 24. On recharge all this Li is removed in a single continuous curve. Moreover, it appears that the Li originally in the structure is also removed on recharge. This vanadium oxide material is now being systematically evaluated. Rather than discharge first we have found that it is possible to first charge the vanadium cell, i.e., to remove the Li from the phase, $\text{Li}_{0.6}\text{V}_{2-8}\text{O}_{4-8}$. The results are shown in Fig. 25.

Figure 24. The electrochemical reduction of the $\text{Li}_x\text{V}_{2-8}\text{O}_{4-8}$ material in a Li cell; the cell was discharged first.

Figure 25. The electrochemical reduction of the $\text{Li}_x\text{V}_{2-8}\text{O}_{4-8}$ material in a Li cell; the cell was charged first.

During the next year, the electrochemical lithiation and cyclability of these vanadium and manganese oxides will be pursued. In particular we will explore the use of other electrolytes that are more stable than the LiClO_4 -dioxolane system now being used. The dioxolane is tending to polymerize at the high potentials found with these electrode materials. We will also optimize the composition of the electrode materials, and will in particular attempt to incorporate additional oxygen into the vanadium oxide lattice thus raising its electrochemical potential.

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Development of High-Energy Electrodes for Sodium/Polymer Cells

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Objectives

- Develop high-performance organic polydisulfide positive electrodes for low-temperature (ambient to 100°C) Na/polymer batteries.
- Improve the rate, capacity, and cyclability of polydisulfide electrodes through improved electrolyte and electrode formulations and improved electrode fabrication techniques.

Approach

- Synthesize polydisulfides based on hexathiobenzene (C_6S_6 , HTB) which has up to six reducible S centers and an equivalent weight of 44 g/eq.
- Evaluate electrode performance using standard electrochemical techniques, including DC charge/discharge cycling, cyclic voltammetry, and electrochemical impedance spectroscopy to screen potential materials to identify those with the highest sustainable current densities and practical specific energy.

Accomplishments

- Prepared HTB-based electrodes for evaluation in Na/PEO/polyorgano-disulfide cells.
- Evaluated the effectiveness of different techniques used to fabricate the polydisulfide electrodes.

Future Direction

- Project was completed.
-

The major objective of this research is to develop high-specific-energy organic polydisulfide positive electrodes for use in ambient-temperature (ambient to 100°C) Na/polymer cells. A number of candidate compounds was synthesized and evaluated as positive electrodes in the Na/polydisulfide cell system. The most promising material evaluated was polyhexathiobenzene (PHTB) which has a theoretical capacity of 600 mAh/g, however, the best performance realized in an actual cell was 160 mAh/g, a little over 25% of theoretical.

The stability of the Na/electrolyte interface was examined by assembling cells having configuration Na/SPE film/Na. SPE films studied were of the type EC:PC:NaPF₆:PVDF. The two solvents comprised 74 wt% of the total film weight, the salt was 10 wt% and the balance, 16 wt%, was PVDF (Kynar 741). Impedance spectra measured prior to cycling the cells were dominated by a capacitive relaxation which was probably due to a resistive film on the electrode surface. The radius of this loop was initially 12 k Ω cm². However,

after applying a small amount of charge to the system, the impedance dropped by almost an order of magnitude, and the cells cycled normally. The initial high impedance was probably due either to initially poor contact between the separator and the Na surface or to a film which formed on the Na surface during cell assembly and was subsequently reduced on cycling the cell. The conductivity of various SPE films was measured by placing the film between two blocking electrodes (Ni or Al) and measuring the AC impedance of the cell. The conductivity calculated from the series resistance was 0.8 mS/cm to 1.0 mS/cm, typical of films of this type.

Cold-pressing a mixture of 60 wt% PHTB, 30 wt% acetylene black, and 10 wt% PVDF binder directly onto the Ni current collector produced an electrode that did not adhere to the current collector or form a cohesive electrode. Neither hot-pressing the mixture nor reducing the amount of carbon first to 20 wt% (PHTB 70 wt%) and then to 10 wt% (PHTB 80 wt%) gave viable electrodes. At the lowest carbon composition (10 wt%), the

electrode had good internal cohesion; however, these electrodes did not adhere to the Ni current collectors. This problem of poor adhesion was later solved by using Ni or Al mesh as the current collector. In the revised solution-casting method, cathodes were cast onto the Ni current collectors from a slurry of PVDF (10 wt%), PHTB (80 wt%), and carbon (10 wt%) in cyclohexanone. Electrodes made in this manner had good cohesion and appeared to adhere well to the current collector.

Electrode construction appears to be the most critical factor affecting utilization. The best results were achieved using thin, solution-cast electrodes, but impedance spectroscopy showed that hot-pressed electrodes had a lower impedance. Reducing the amount of binder from 10 to 5 wt% while increasing the amount of active material to 75 wt% produced a 15% increase in utilization. Presumably, in addition to holding the electrolyte together, the binder coats the surface of the active material and the carbon, thereby

reducing the surface area available for reaction. Reducing the amount of carbon in the electrode to 15 wt% and increasing the active polymer to 80 wt% had no major effect on utilization, although the impedance of the cell was reduced.

The goal of the synthesis task is to synthesize sodium thiolate polyaniline and to investigate the use of this material as a high-capacity polydisulfide electrode combining intrinsic electrical conductivity with charge-storage capability. The synthetic route chosen was, first, to polymerize aniline using acidic ammonium peroxydisulfate; second, to convert polymer to its basic form; and third, to sulfonate the polymer using fuming sulfuric acid. This procedure gave a polyaniline with one sulfonate group for every two phenyl rings. Finally, the sulfonated polyaniline was reduced to the corresponding thiolate polyaniline *via* its acid chloride.

Synchrotron Radiation Studies of Structure, Rechargeability and Corrosion in Li/SPE/FeS₂ Battery System

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Objectives

- Investigate the relationship between the structure and rechargeability of FeS₂ electrodes by utilizing synchrotron-radiation-based XAS and EXAFS and other *in situ* methods.
- Evaluate the performance of Li/FeS₂ cells.

Approach

- Utilize the synchrotron radiation source at the Center for Advanced Microstructures and Devices (CAMD) for *in situ* EXAFS studies of structure and electronic properties of Li/FeS₂ battery system.

Accomplishments

- EXAFS system has been built using the double-crystal monochromator beam line (port 5B) at CAMD, and electrochemical studies of Li/FeS₂ were conducted.

Future Direction

- Project has been completed.
-

The objective of this project is to understand the structural integrity and rechargeability of FeS₂ electrodes in Li/FeS₂ cells using EXAFS. An electrochemical cell for *in situ* EXAFS measurements of the FeS₂ electrode was designed. The cell consists of a pyrite electrode, three layers of filter paper as an electrolyte separator and a thick carbon (Grafoil) electrode. The design

configuration for the test cell is Al (0.25 μ m), Mylar (1.5 μ m), pyrite (10 μ m), PEO (6 μ m), Li (250 μ m) layers sandwiched between support screens. It is a prismatic cell with the electrode/electrolyte interface exposed to the X-ray radiation to study the absorption as a function of energy at both the Fe edge and S edge. An allotment of synchrotron

beamtime to perform EXAFS is reserved for the experiments.

The X-ray absorption and emission spectra of S and electronic structure of disulfide anion in FeS_2 were investigated by measuring the *in situ* Fe and S K-edge absorption fine structure spectra of FeS_2 , Li/ FeS_2 and Li/SPE/ FeS_2 systems using the EXAFS system at CAMD. The UWXAFS and FEFF software packages are used for the analysis of

EXAFS and NEXAFS spectra of various battery materials. These packages are useful to determine the changes in the structure of the complex materials, in particular the proposed structural changes during cycling process. Natural pyrite samples were obtained from the Pittsburgh Energy Center for the XAFS work. Analysis of Li/ FeS_2 cells showed the presence of Li_2S .

Lithium Polymer Rechargeable Batteries with Lithium Manganese Oxide Cathodes

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Objectives

- Identify low-cost, high-performance Mn-based electrode material for Li rechargeable batteries.
- Demonstrate charge/discharge cycling of Mn-based electrodes in LiPF_6 and Li methide in solution and polymer electrolytes.

Approach

- Investigate process control and chemical analyses of electrode materials to confirm single-phase product.
- Evaluate electrode performance using Li/ LiMn_2O_4 test cells.

Accomplishments

- Established a preparation route that yields LiMn_2O_4 with an initial reversible capacity above 120 mAh/g, improved fade characteristics, and enhanced capacity at higher rates.
- Determined that both particle size classification and low levels of admatal stabilizer can benefit performance.

Future Directions

- Continue to synthesize and optimize new electrode materials with improved cycling performance.
 - Fabricate and evaluate polymer electrolytes in test cells, utilizing preferred electrode material and LiPF_6 /Li methide salt.
-

The major objective of this research is to develop an improved LiMn_2O_4 spinel electrode material for rechargeable Li batteries. A new protocol for LiMn_2O_4 synthesis that consistently yields material with the following physical attributes was developed:

Tap density:	1.5-1.6 g/cm ³
Surface area:	2.7-3.2 m ² /g
Particle size distribution:	98% 10-75 μm 33% 25-45 μm 42% 10-25 μm mean 25 μm
Li:Mn (molar):	1.00-1.005

In addition, SEM photomicrographs revealed particles with unusually high porosity.

Electrochemical testing of this material revealed >80% utilization during cycling (initial reversible capacity >120 mAh/g), but fade was governed in part by the choice of electrolyte salt. With Li methide, cells operated to 480 cycles still retained 45 mAh/g capacity, while those cells that contained LiPF_6 lost all capacity in 230 cycles. In fact, cells containing LiPF_6 were more susceptible to dendrite growth and premature failure, exhibited more-rapid capacity fade, and had lower coulombic efficiencies than cells employing Li methide (or even LiAsF_6).

Variable-rate studies of Li/Li methide: EC:DEC/LiMn₂O₄ cells showed little reversible capacity difference between 0.5 ("standard") and 1.0 mA/cm² charge/discharge rates, especially after 100 cycles. Cells run at a very slow 0.05 mA/cm² for 15 weeks showed near theoretical capacity for the first few cycles, but a fairly rapid decline thereafter; very poor coulombic efficiencies indicated electrolyte decomposition. At 2.0 mA/cm², initial capacities were 100 mAh/g, but remained surprisingly stable, slipping to 80 mAh/g at the 130th cycle. Test cells operated at 55°C faded from 122 mAh/g initial capacity to 65 mAh/g at the 50th discharge, clearly faster than under ambient conditions, but an improvement over published results. Storing a fully charged cell at 55°C for 10 days caused the OCV to drop from 4.13 to 3.98V.

While Cr-doped LiMn₂O₄ is a single-phase spinel and improves the stability of the electrode,

this is accomplished at the expense of initial capacity. For example, LiCr_{0.14}Mn_{1.86}O₄ (7 mol% Cr) starts at 85 mAh/g, but actually improves to 92 mAh/g after 120 cycles, and 2.5 mol% Cr material has a nearly constant discharge of 100 mAh/g over the first 85 cycles. In addition, preliminary results indicate that the presence of the Cr admetal delays performance loss in 55°C cells. Finally, sieve-classified 38-45 µm LiCr_{0.08}Mn_{1.92}O₄ particles were found to have roughly 10% greater capacity than either the as-prepared or 25-38 µm material, whereas the <25 µm electrode particles were 20% below the performance norm.

Future efforts on this project will be directed primarily at polymer electrolytes containing ceramic fillers to enhance Li⁺ mobility. Work will include further refinements on rate effects at ambient and elevated temperatures, and electrochemical characterization by cyclic voltammetry and electron impedance spectroscopy.

D. CROSS-CUTTING RESEARCH

Cross-cutting research is carried out to address fundamental problems in electrochemistry, current-density distribution and gas evolution, solution of which will lead to improved electrode structures and performance in batteries and fuel cells.

Analysis and Simulation of Electrochemical Systems

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Objectives

- Improve the performance of electrochemical cells used in the interconversion of electrical energy and chemical energy by identifying the phenomena that control the performance of a system.
- Identify important parameters which are crucial to the optimization of an advanced secondary battery.

Approach

- Utilize electrochemical engineering principles and advanced computation techniques to develop mathematical models

Accomplishments

- Mathematical models were developed to explore the design and optimization of Li and Li-ion batteries, the discharge behavior of LaNi₅/KOH/nickel oxide battery systems and electrochemical capacitors, based on pseudohomogeneous porous-electrode theory.
- The solid-state diffusion coefficient of protons in nickel oxide insertion compounds has been experimentally determined.

Future Directions

- Transport properties of different SPE systems will be measured as a function of salt concentration.
- A porous electrode model with a side reaction will be utilized to predict the behavior of a composite LiMn_2O_4 electrode.
- The capacitor model will be extended to include thermal effects, impedance and varying capacitance.

This program involves fundamental investigations of the transport and interfacial phenomena important in electrochemical systems. Results of this work are used to analyze experimental data, to identify important system parameters, and to aid in the design and scale-up of electrochemical systems. The approach taken is to develop a detailed mathematical model of the electrochemical device using the principles of transport phenomena, reaction kinetics, and thermodynamics. The mathematical models are developed to be as general as possible without unnecessary mathematical or physical approximations. The resulting sets of coupled equations are then solved numerically, which permits the complex interactions between phenomena to be treated. Experimental work may then be used to confirm and refine the mathematical models and to determine the physical parameters necessary for a complete, quantitative understanding of the system.

Lithium-based rechargeable batteries have been explored in detail using mathematical modeling. The first-generation model has been expanded to treat film formation on the electrode surfaces and temperature rise during nonisothermal discharge. The model is also able to simulate charge/discharge schemes more complicated than galvanostatic ones, for example, potentiostatic taper charges, power pulses, and extended cycling. The specific Li systems that are being explored include a Li-foil cell consisting of a polymer electrolyte and a manganese-oxide-spinel positive electrode. This system has been studied in detail to determine the tradeoffs in system performance that occur as the transport properties of the polymer electrolyte, especially ionic conductivity and Li-ion transference number, are varied.

The necessary transport properties are rarely available for even the most common Li salt and solvent combinations. This problem is even worse for SPEs where the methodology to measure the Li-ion transference number without the assumption of an ideal solution does not exist. Motivated by this situation, a novel method to measure the transference number has been developed. This method is not only easy to carry out, but also

involves no assumption about the ideality of the solution. To demonstrate the generality and validity of this method, it is being applied to the measurement of the potassium-ion transference number in aqueous potassium chloride solutions of several different concentrations. The experimentally determined transference numbers are found to be within 1% agreement with the literature values. This method has also been used to measure the Na-ion transference number in a concentrated SPE solutions.

Experiments have shown that an electrochemical cell having a composite positive electrode containing lithium manganese oxide and carbon black, a lithium perchlorate in propylene carbonate electrolyte, and a Li-foil negative electrode exhibits behavior indicative of a side reaction at the positive electrode. Such a cell will cycle with a coulombic efficiency of less than 100% and will completely self-discharge if left at open circuit for a long time. This behavior is expected to affect the performance and safety of Li batteries. A model of this system is being developed which will consider the main insertion reaction in the positive electrode as well as a side reaction occurring predominantly on the conductive filler. This model will be used to guide experiments into the nature and significance of the side reaction.

The variable diffusivity in intercalation materials is also being studied. A theoretical approach for estimating a "best" constant diffusion coefficient to use in an electrode model is being developed. We are considering the case where experimental data on the diffusion coefficient as a function of the state of charge for an intercalation material are available. This method uses a model of diffusion in a single particle as its basis. From examining the surface concentration *vs.* average concentration curve for diffusion in a single particle, we can determine a diffusion coefficient that is a function of the dimensionless flux rate of material into the particle. This diffusion coefficient function can then be used in a model of a porous electrode.

The solid-state diffusion coefficient of protons in nickel oxide insertion compounds has been experimentally determined using an intermittent galvanostatic method. The diffusion coefficient of

protons was found to range between 8×10^{-14} to $8 \times 10^{-13} \text{ cm}^2/\text{s}$ for approximately $1 \mu\text{m}$ thick sol-gel deposited nickel oxide. The range of diffusion coefficients obtained demonstrates the dependence of the diffusion coefficient on the state of charge of the nickel oxide. The film preparation, characterization, and diffusion coefficient measurement methods used in this work are generally applicable to most insertion materials. The accurate determination of proton diffusion coefficients is important for the optimization and design of devices which employ insertion materials. The dependence of the diffusion coefficient on temperature, electrolyte concentration, and film thickness is under investigation.

A fairly comprehensive model of electrochemical capacitors has been developed. The model is based on pseudohomogeneous porous-electrode theory. Concentrated-solution theory is used to predict the mass transfer. The capacity to treat multiple faradaic reactions, including side reactions and those leading to faradaic pseudocapacitance, is incorporated. Simulations allow us to identify the physical processes that govern the behavior of these systems, as well as to investigate the dependence of performance on various design parameters. The model is being used to test the potential of different systems; the specific systems being modeled include carbon electrodes in aqueous sulfuric acid, ruthenium oxide electrodes in aqueous sulfuric acid, and carbon electrodes in propylene carbonate with a suitable salt. The influence of side reactions on the behavior of the carbon electrodes in aqueous sulfuric acid system has been shown to be fairly important. With consideration of side reactions, the model predicts some of the anomalous behavior seen in experiments on similar devices. The model is fairly general and can be extended to treat other systems and effects.

A mathematical model of the discharge behavior of the $\text{LaNi}_5/\text{KOH}/\text{nickel oxide}$ battery system has been developed. The model shows great sensitivity to the kinetic parameters of the nickel oxide active material. The electrode thickness and porosity of the battery system are optimized in terms of the specific energy and power of the system.

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Heat Transport and Thermal Management in Advanced Batteries

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Objectives

- Investigate by mathematical modeling and experimental measurement, heat generation and transport properties in advanced secondary batteries for EV applications.
- Evaluate the management of operating temperature in solid oxide fuel cells for EV applications.

Approach

- Utilize mathematical models to analyze the thermal conduction properties of rechargeable Li batteries.
- Measure the thermal conduction properties of cell components with a heat-flow meter.

Accomplishments

- The mathematical modeling results indicate that during normal operation, the temperature of a Li-ion battery is unlikely to reach the onset temperature for thermal runaway, however if a battery is continuously cycled under high-rate charge and discharge, significant heat accumulation may occur.

Future Directions

- Determine the thermal conductivities of polymer electrolytes and other cell components.
 - Determine the heat generation rates in MH/NiOOH cells by conducting charge/discharge studies under different operating conditions, and analyze the thermal performance of the batteries.
-

The objective of this project is to examine the thermal behavior of advanced rechargeable batteries by use of mathematical modeling and experimental measurements. In addition, this study is expected to lead to the identification of suitable thermal management systems, to evaluate battery energy efficiency and the effects of thermal runaway from battery abuse. A similar approach is also being applied to solid oxide fuel cells (SOFC).

A three-dimensional model was developed to simulate and compare the heat generation and transport rates in a Li/polymer-electrolyte battery during galvanostatic discharges and the Simplified Federal Urban Driving Schedule (SFUDS) dynamic power profile. Emphasis has been placed on maintaining the operational temperature constant and the temperature uniform in a battery by designing a suitable thermal

management system. The results indicate that, on the one hand, because of the low effective thermal conductivity across a laminated cell stack, steep temperature distributions may occur if cooling channels or electric heaters are placed at the two ends of a cell stack. On the other hand, the relatively large average thermal conductivity along the width and height directions allows more-efficient heat removal or addition, and thus facilitates the maintenance of a uniform operating temperature. The thermal model has been applied to study the effectiveness of different arrangements of cooling channels, electric heaters and suitable insulating materials.

Calculations of temperature rise in the conceptual battery designs (SNL) for the Ford Van and GM Impact operating at constant-current discharges and a Dynamic Stress Test (DST)/Fast Charge/DST/Full Charge cycle were conducted using the three-dimensional thermal model. Also, a comparison of heat generation rates in a Li/polymer-electrolyte battery during the DST and SFUDS dynamic power profile was carried out.

A major concern with the room-temperature Li-ion batteries is the significant temperature increase which may occur during thermal runaway. The modeling results indicate that, during normal battery operation, the battery temperature is unlikely to reach the onset temperature for thermal runaway, although heat may not be completely dissipated from a large cell stack during high-rate discharge (e.g., during the short periods of high-pulse power discharge). However, if a battery is continuously cycled under high-rate charge and discharge, significant heat accumulation may occur in the battery. The analysis of heat transfer from highly localized heat sources that arise by battery abuse (e.g., short circuit) indicates that localized heating may increase the battery temperature, within one minute, to the temperature at which thermal runaway occurs. Above this temperature, the battery temperature may keep increasing rapidly because of exothermic side reactions.

A thermal analysis of a SOFC stack used for transportation applications was carried out to address concerns as to how quickly the temperature will decrease during vehicle idle or standby. Because of the high operating temperature of SOFC stacks, it is important to select suitable thermal insulations to reduce heat loss. The results indicate that a high-performance, vacuum-multifoil

thermal insulation can be applied to significantly reduce heat loss and to maintain temperature uniformity across a cell stack. Consequently, the cool-down time from 1000 to 800°C is extended from 2 h (with a 5-cm thick conventional material) to about 31 h (with a 1-cm thick high-performance material).

A systematic investigation of the thermal conductivity of cell components and the effective thermal properties of cell stacks for Li/polymer-electrolyte batteries is underway. The total energy efficiency of the Li/polymer-electrolyte battery will be evaluated by including the energy consumption for heating the battery before vehicle start-up or during vehicle stand-by, and by taking into account statistical data on the commute length. In addition, the thermal models will also be extended to examine the thermal behavior of MH/NiOOH batteries.

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Electrode Surface Layers

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Objectives

- Apply advanced *in situ* and *ex situ* characterization techniques to study the structure, composition and mode of formation of surface layers on electrodes used in rechargeable batteries.
- Identify film properties that improve the rechargeability, cycle-life performance, specific power, specific energy, stability and energy efficiency of electrochemical cells.

Approach

- Apply sensitive techniques such as spectroscopic ellipsometry and Raman spectroscopy to monitor the formation of surface layers on secondary battery electrodes.
- Incorporate foreign ions in porous nickel oxide electrodes to improve cycle-life performance in alkaline electrolytes.
- Incorporate conductive surface layers on Li electrodes to increase cycle life in nonaqueous electrolytes.

Accomplishments

- The co-precipitation of Co^{2+} ions into the $\text{Ni}/\text{Ni}(\text{OH})_2$ electrode reduced the drop in charge efficiency to ~25% after long-term cycling, compared to ~50% drop in electrodes without Co.

Future Directions

- Complete research to modify the Ni electrode.
 - Initiate a new effort to characterize film formation on carbonaceous materials in nonaqueous electrolytes using ellipsometry and infrared spectroscopy.
-

Advanced *in situ* and *ex situ* characterization techniques are being used to study the structure, composition and mode of formation of surface layers on electrodes used in rechargeable batteries. The primary objective of this research is to identify film properties that improve the rechargeability, cycle-life performance, specific power, specific energy, stability and energy efficiency of electrochemical cells. The present research seeks to characterize the transformation of surface phases that accompanies the charging and discharging of Ni electrodes in alkaline electrolytes and Li electrodes in nonaqueous electrolytes.

Nickel Electrodes. The formation and growth of oxide/hydroxide films on Ni electrodes remain poorly understood, partly because of the complex environment in which the growth occurs, and partly because of experimental complications such as the presence of native oxide films. We have used *in situ* spectroscopic ellipsometry to study the films

formed on polycrystalline Ni electrodes in air and in 1.0 M NaOH electrolytes. Exposure of a Ni electrode to air resulted in the formation of a 2-nm-thick film of NiO, as well as significant roughness at the Ni/NiO and NiO/air interfaces. When the Ni electrode was exposed to the electrolyte and held at a potential corresponding to the initial formation and growth of $\text{Ni}(\text{OH})_2$ (-0.4 V vs. Hg/HgO), the surface layer was a ~1.4 nm thick mixture of 50 vol% NiO plus 50 vol% $\text{Ni}(\text{OH})_2$. When the electrode potential was held at 0.0 V for 2.0 h the surface layer thickness grew to ~15.6 nm and contained only $\text{Ni}(\text{OH})_2$. These data will be used in the interpretation of future experiments to characterize the formation of both pure and doped Ni electrodes.

We recorded the *in situ* Raman spectrum of a freshly oxidized Ni electrode (nominally NiOOH), and the spectrum was consistent with previously published data. We monitored the

changes in the spectrum as the Ni electrode was subjected to repeated oxidation and reduction during long-term cycling. We deconvoluted the recorded spectra to monitor the film structural transitions which accompanied electrode capacity loss during cycling. *In situ* surface-enhanced Raman spectroscopy (SERS) spectra of the reduced (discharged) film measured during long-term cycling experiments were characteristic of neither true β -phase material nor the pure α -phase form of the $\text{Ni}(\text{OH})_2$. It appears that long-term cycling leads to the formation of an unknown phase which may contribute to electrode capacity loss. We estimate that the Ni electrode charge efficiency dropped to ~50% of its initial value at the end of the cycling experiments. The co-precipitation of Co^{2+} ions into the $\text{Ni}(\text{OH})_2$ film reduced the drop in charge efficiency to ~25% after similar long-term cycling. Raman spectra of the Co-doped oxidized films showed that Co additions stabilize a structure that is γ -like, is characterized by a high average Ni valence state, and exhibits minimal changes upon cycling. Incorporation of Co^{2+} ions into the film appears to involve formation of a new phase in the surface layer, suggesting that Co doping occurs by substitution of Ni sites.

Lithium Electrodes. The high ionic conductivity and chemical stability of Li_3N suggest its use as a protective surface layer in rechargeable Li batteries, but prior attempts to form a compact, non-porous Li_3N have not succeeded because of the large difference between the molar volumes of Li and Li_3N . We have used the LBNL low-energy ion implantation and plasma-assisted deposition facility to form compact and homogeneous nitrided Li surface layers. We used ESCA to measure 3-6 at% nitrogen at the nitrided electrode surface.

SEM images of as-grown nitrided Li surfaces showed island structures with characteristic sizes of ~20 μm , and no macroscopic cracks or other inhomogeneities were detected.

We fabricated Li/PC/stainless-steel and Li/PC/ MnO_2 cells with and without protective Li_3N layers on the Li electrodes. Cells with protective Li_3N layers could be operated in a stable manner up to ~4.4 V, which is comparable to the behavior of Li-ion cells. We also prepared 3-electrode cells and measured the cell capacity as a function of current density over the range 0.2 to 2.0 mA/cm^2 . The polarization characteristics of the nitrided Li electrode were quite different from those observed in cells with untreated Li electrodes. Features associated with unwanted Li dendrite growth that accompany the repeated charging and discharging of Li/PC cells were absent in the cells with protective Li_3N layers. These preliminary tests with unoptimized electrodes clearly demonstrate the beneficial effects of using protective Li_3N layers in rechargeable cells with liquid organic electrolytes.

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IV. AIR SYSTEMS RESEARCH

The objectives of this program element are to identify, characterize, and improve materials for air electrodes; and to identify, evaluate, and initiate development of metal/air battery systems and fuel-cell technology for transportation applications.

A. FUEL CELL RESEARCH

Fuel cell research includes projects in several areas of electrochemistry: fuel-cell testing, fuel processing, fuel-cell component characterization and theoretical studies.

Electrode Kinetics And Electrocatalysis

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Objectives

- Develop an atomic level understanding of the processes taking place in complex electrochemical reactions at electrode surfaces.
- Determine the relationship between the kinetics of electrode processes and the atomic structure of the electrode surface by using a variety of surface- or bulk-sensitive techniques.

Approach

- Employ low-energy electron diffraction (LEED) to study single crystals; high-energy electron microscopy (HREM) in the case of carbon electrode materials; and EXAFS for organometallic catalysts.
- Utilize low-energy ion scattering (LEIS) and Auger electron spectroscopy (AES) to study the composition of sputtered and UHV-annealed polycrystalline Pt-Ru and Pt-Sn bulk alloys for methanol and CO oxidation electrocatalysis.

Accomplishments

- It was found that both the structure sensitivity and the high catalytic activity of the Pt₃Sn surface to CO oxidation is attributed to an adsorbed state of CO unique to this alloy and occurs at relatively high coverage on the (111) surface.

Future Direction

- Continue the study of CO tolerance in low-temperature acid fuel cells and in parallel begin the examination of methanol oxidation on one or more new Pt alloy systems.
-

The objective of this project is to develop an atomic-level understanding of the processes taking place in complex electrochemical reactions at electrode surfaces. Physically meaningful mechanistic models are essential for the interpretation of electrode behavior and are useful in directing the research on new classes of materials for electrochemical energy conversion and storage devices.

The electrooxidation of pure hydrogen and carbon monoxide on Pt-Ru alloy surfaces was

studied as a prelude to a companion study of the electro-oxidation of CO/H₂ mixtures such as those produced by steam reforming of hydrocarbon fuels. The rotating disk electrode (RDE) technique was uniquely combined with characterization of the electrode surface composition in UHV by LEIS. Whereas hydrogen oxidation was found to be a very fast reaction on both pure Pt and Pt-rich Ru alloy surfaces (an exchange current density on the order of 0.1 A/cm²), it is orders of magnitude slower on a pure Ru surface at room temperature. However,

unlike pure Pt, the reaction is thermally activated on pure Ru, such that at 60°C the reaction occurs at both Pt and Ru sites of the alloy surface at practical rates. The onset potential for CO oxidation is inversely related to the Ru content of the surface and is the lowest for pure Ru. However, the maximum current density, equal to the diffusion-limiting current, occurs on the 50% alloy surface. The results are consistent with the previously proposed mechanism for the oxidation of adsorbed CO on these same surfaces when the effect of a continuous flux of CO from the electrolyte is taken into account. According to this mechanism, Ru sites nucleate oxygenated species at low potential, but the species formed on Pt-Ru site pairs are uniquely reactive towards adsorbed CO.

The electrooxidation kinetics of mixtures of carbon monoxide and hydrogen were studied on well-characterized surfaces of Pt, Ru and two Pt-Ru alloys, Pt₅₀Ru₅₀ and Pt₁₀Ru₉₀ in 0.5 M H₂SO₄ at 62°C. The electrooxidation of CO/H₂ mixtures on Pt₅₀Ru₅₀ or Pt₁₀Ru₉₀ alloy surfaces is characterized by two states of activity: a state of low but finite activity at potentials below ca. 0.3-0.4 V and a highly active (mass-transfer limited) state at potentials above ca. 0.3-0.4 V. The exact potential of the transition depends on the gas mixture and the surface composition. The transition to the active state occurs at a slightly (ca. 50-100 mV) lower potential on the Ru-rich surface, and at about 0.1 V lower potential with 0.1% CO *vs.* 2% CO. In contrast, pure Pt surfaces have no measurable activity below 0.4 V and a transition to a highly active state at potentials above 0.5-0.7 V. On all three surfaces, the transition to the highly active state coincides with onset of oxidation of adsorbed CO, while the reaction at potentials below 0.4 V on the alloy surfaces appears to be the oxidation of hydrogen *via* transient holes in the CO ad-layer on these surfaces. Such transient holes do not appear to occur or be as numerous on a pure Pt surface. The absolute activity of the Pt-Ru alloys at potentials below the transition potential is too low to be of practical use in proton-exchange membrane (PEM) fuel cells. We have concluded that if one uses Pt, Ru, or any of the Pt-Ru alloys as electrocatalysts, there appears to be little or no reduction of the anode overpotential by steam reforming methanol and using the reformat as a fuel *vs.* direct electrooxidation of methanol unless rather complex additional CO removal processes are added to reduce the CO level well below 0.1%.

The electrochemical oxidation kinetics of carbon monoxide (CO) in sulfuric acid electrolyte was studied on different surfaces of the ordered

alloy Pt₃Sn in single-crystal form. Characterization of the surface composition and structure was determined in UHV using LEED, AES, and LEIS prior to determining the electrode kinetics using the classical RDE method with CO dissolved in the electrolyte. Clean annealed and sputter-cleaned but not-annealed surfaces of (110) and (111) orientation were studied. A remarkable difference in activity was observed between the annealed (111) surface and the sputtered but not-annealed (110) surface, with both surfaces having the same nominal surface composition, 20-25% Sn, but different local structures. The onset potential for CO oxidation on the (111) surface was shifted cathodically by 130 mV relative to that for the sputtered (110) surface, and the onset comes remarkably close to 0 V on the hydrogen potential scale. Relative to pure Pt surfaces (of any crystal structure), the potential shift is more than 500 mV, corresponding to a catalytic activity that is higher by more than 4 orders of magnitude. Both the structure sensitivity and the high catalytic activity of the Pt₃Sn surface is attributed to an adsorbed state of CO unique to this alloy and occurs at relatively high coverage on the (111) surface.

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Fuel Cell Electrocatalyst and Electrolyte Studies

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Objectives

- Obtain information on the nature of the poisoning intermediate(s) in CH₃OH electrooxidation on Pt-based electrocatalysts by nuclear magnetic resonance (NMR) and photothermal deflection spectroscopy (PDS).
- Evaluate novel electrode-electrolyte combinations.

Approach

- Apply NMR and PDS to obtain information about surface poisoning on Pt supported on graphite and Pt anodes in electrolytes containing methanol.
- Carry out gas-diffusion electrode studies in model fuel cells.

Accomplishments

- An *in situ* probe beam deflection (PBD) study of anion adsorption at polycrystalline Pt electrode surfaces showed that the onset of anion adsorption began at ~200 mV in 0.1 M solutions of H₃PO₄, H₂SO₄ and HClO₄.

Future Direction

- Establish the feasibility of NMR and PDS to detect surface poisons during methanol electrooxidation.
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The performance of the electrodes employed in direct methanol fuel cells (DMFCs) is typically limited by slow electrochemical kinetics. The goals of research performed on these electrodes are to characterize their kinetic and mechanistic behavior and to identify electrode structures, electrocatalysts, and electrolyte compositions that lead to improved cell performance.

We are using NMR spectroscopy to study surface poisoning of carbon-supported Pt and Pt-alloy DMFC anodes in operating electrochemical cells. We constructed a glass 3-electrode electrochemical cell for use in a narrow-bore (5 cm) spectrometer operating at a proton frequency of 270 MHz. The working-electrode material is commercial 20% Pt/Vulcan XC-72 supported on thin carbon cloth. The cloth is rolled tightly to form a cylindrical porous plug, filling the volume of the NMR coil

with an active catalyst surface area of ~3 m². The electromagnetic coupling of the conductive electrode material with the coil presents a special problem for these experiments. To minimize this effect, a porous separator is wound with the cloth to electronically insulate adjacent layers of the plug. We have carried out preliminary studies of the model system of CO adsorbed on Pt, because prior *in situ* IR studies of smooth Pt electrodes suggested CO as the main poisoning adsorbate in the CH₃OH electrooxidation reaction. We used a circulation system for adsorption of ¹³C-enriched CO from saturated aqueous H₂SO₄. As an indirect monitor we used voltammetry to observe the displacement of adsorbed H₂ from the Pt surface by the irreversibly adsorbed CO, and we detected the ¹³C NMR signal arising from ¹³CO adsorbed on the electrodes under open-circuit conditions.

The rate and extent of anion adsorption on electrocatalyst surfaces can have a major effect on the electrochemical kinetics of important fuel cell reactions such as H_2 oxidation, CH_3OH oxidation and O_2 reduction. Anion adsorption isotherms are difficult to measure, and few reliable data have been reported in the literature. We have now used *in situ* PBD to study anion adsorption at polycrystalline Pt electrode surfaces as a function of electrode potential. We carried out a series of PBD experiments to detect the proton and anion fluxes that accompany oxidation and reduction processes on Pt electrode surfaces in 0.1 M solutions of H_3PO_4 , H_2SO_4 and $HClO_4$. The measured beam-deflection signals exhibited a strong dependence on electrode potential and anion identity. We found that in all three electrolytes the onset of anion adsorption began at ~ 200 mV (*vs.* the dynamic hydrogen reference electrode), *i.e.*, within the potential range wherein adsorbed H_2 is oxidized. We also confirmed that the presence of PO_4^{3-} anions shifts

the Pt oxidation reaction towards more positive potentials.

A model fuel cell was designed and fabricated to accommodate 20-cm² electrodes. The electrodes have a bi-layered structure, consisting of a semi-hydrophilic reaction layer which is hot-pressed onto a hydrophobic gas diffusion layer. Electrodes of various catalyst loadings (0.3-1.0 mg/cm²) and polytetrafluoroethylene content (15-40 wt%) have been prepared and tested in half- and full-cell configurations, utilizing both H_2SO_4 and Cs_2CO_3 as electrolytes with H_2 and CH_3OH feeds. Thus far, the full-cell performance has been lower than expected, because of problems with the design of the complete cell.

PUBLICATION

B.R. Rauhe, F.R. McLarnon and E.J. Cairns, "Direct Anodic Oxidation of Methanol on Supported Platinum/Ruthenium Catalyst in Aqueous Cesium Carbonate," *J. Electrochem. Soc.* **142**, 1073 (1995).

Fuel Cells for Renewable Applications

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Objectives

- Identify, evaluate and initiate development of fuel cell technology for transportation applications.
- Conduct basic research in electrochemistry to explore and improve the potential of fuel cell systems for use in transportation applications.

Approach

- Apply electrocatalysis and heterogeneous catalysis principles to develop improved electrode materials for polymer electrolyte fuel cells (PEFCs).
- Utilize experimental techniques to determine the transport properties of polymer electrolyte membranes.
- Test laboratory-scale fuel cells to obtain information on the performance of cell components.

Accomplishments

- Improved performance of a DMFC was obtained with Pt-RuO_x ("unsupported") anode catalysts and unsupported Pt cathode catalysts.
- An analysis of the characteristics of a DMFC and PEM fuel cell with a methanol steam reformer reformat/air fuel cell (RAFC) indicated that the key issue to improving the performance of DMFCs is to reduce the methanol cross-over.

- A new type of ultra-thin composite ionomeric membrane developed by W.L. Gore showed encouraging results, power densities of 0.9 W/cm^2 were achieved in hydrogen/air cells and 3000 h of cell life were demonstrated.

Future Direction

- Continue tasks to improve the performance and life of PEM fuel cells, and to identify new low-cost components for these fuel cells.

The primary focus of this program is to develop efficient and cost-effective PEFC for transportation applications. The specific goals of the program are to: *i*) reduce the cost of the Pt catalyst and ionomeric membrane, *ii*) increase the efficiency and power density of the PEFC, *iii*) optimize the system for operation on reformed organic fuels and air, *iv*) achieve stable, efficient, long-term operation, and *v*) solve key technical issues that impede the development of the DMFC.

DMFCs. To date, the DMFC has not been considered a serious option for transportation applications because of its limited performance (low power density) compared to the RAFC. However, recent advancements in DMFC R&D have been quite dramatic, with the DMFC achieving power densities which are a significant fraction of that obtained with the RAFC. The use of established Pt-Ru anode electrocatalysts and Pt cathode electrocatalysts in conjunction with a polymer electrolyte in DMFCs has resulted in very significant enhancements in performance when the cells are operated at temperatures as high as $120\text{--}140^\circ\text{C}$, and particularly when the catalyst-layer composition and structure are optimized. Operation at elevated temperatures is facilitated in these PEFCs when the anode is continuously in contact with liquid methanol/water mixtures.

To maximize performance, we have employed Pt-RuO_x ("unsupported") anode catalysts as well as unsupported Pt cathode catalysts. Their higher performance is due to high catalyst utilization, enabled by effective access of protons, electrons and methanol to a large number of active sites in optimized, thin catalyst layers of high site density. The overall loadings in such layers of unsupported Pt-Ru catalysts are higher than those typical for carbon supported Pt alloy catalysts ($1\text{--}4 \text{ mg/cm}^2$ vs. $0.1\text{--}0.5 \text{ mg/cm}^2$). However, the high performances of DMFC anodes is not just a result of the higher loading, but also the dense thin-film catalyst layer structure which permits high transport rates to a large number of active sites. This type of thin-film catalyst layers that is bonded directly to the polymer electrolyte was developed earlier for use in H₂/air fuel cells. It has proven very effective in PEM DMFCs.

A significant improvement in DMFC performance can be achieved by operating at somewhat elevated temperatures. Figure 26 illustrates the DMFC performances for various Nafion membranes with LANL-type thin-film catalyst layers, as a function of cell temperature. As the cell temperatures are increased, significantly better cell performances are obtained, primarily due to the substantial improvement in anode kinetics. The important point to realize is that, by slight pressurization, a liquid methanol/water mixture is maintained next to the anode, and this liquid film in polymer-electrolyte cells permits operation for prolonged periods at temperatures well above 100°C .

Figure 26. The increase in DMFC current density at 0.5 V with temperature for thin-film catalyzed Nafion™ 112, 115, and 117 membranes. Anodes: 2.2 mg/cm^2 Pt-RuO_x, 1 M methanol at 2 ml/min and 3 atm. Cathodes: 2.3 mg/cm^2 Pt-black, 5 atm O₂ at 0.6 l/min.

Figures 27 and 28 show the highest performances achieved to-date with polymer electrolyte DMFCs based on membrane/electrode assemblies with thin-film catalyst layers, for oxygen and air cathodes, respectively. The exact conditions are specified in the captions. Figure 29 shows the power densities achievable in a DMFC under such conditions.

Figure 27. Polarization curves for 130°C, oxygen cathode DMFC based on thin-film catalyzed Nafion 112, 115 and 117 membranes. Anodes: 2.2 mg/cm² Pt-RuO_x, 1 M methanol at 2 ml/min and 3 atm. Cathodes: 2.3 mg/cm² Pt-black, 5 atm O₂ at 0.6 l/min.

Figure 28. Polarization curves for 110°C, air cathode DMFC based on thin-film catalyzed Nafion 112, 115 and 117 membranes. Anodes: 2.2 mg/cm² Pt-RuO_x, 1 M methanol at 2 ml/min and 1.8 atm. Cathodes: 2.3 mg/cm² Pt-black, 3 atm air at 0.6 l/min.

Figure 29. Power density curves for the thin-film catalyzed Nafion 112 assembly operating at 130°C on oxygen and at 110°C on air as depicted in Figs. 26 and 27.

Comparative Evaluation of Fuel Cells for Transportation Applications. The significant increase in demonstrated DMFC performance, as shown above, has brought the peak power density of the polymer electrolyte DMFC to a level which is only three times lower than that of the RAFC. Because of this improvement in performance, an analysis was made to compare the overall system characteristics for the following two options: *i*) a DMFC stack and, *ii*) a methanol reformer + RAFC stack. The overall energy conversion efficiencies, methanol chemical energy to DC power, of the two systems was found to be comparable (43%) when the DMFC is operating at 0.55 V and the RAFC is operating at 0.70V. This result assumes: (a) fuel efficiencies of 90% can be reached in the DMFC, (b) the methanol reformer efficiency (hydrogen energy out/methanol energy in) is 72% (data from reformer manufacturer), (c) the overall efficiency of the PROX (hydrogen energy out/hydrogen energy in) is 97%. (The fuel efficiency in the RAFC assumed here is 100%).

The key DMFC parameter that needs significant improvement to reach the level assumed above is the fuel efficiency, which is low because of methanol cross-over. There are, however, some encouraging new results which show that the cross-over flux may possibly be decreased significantly (particularly at higher temperatures) by the use of modified membranes and of lean methanol feeds to the anode, without sacrificing cell performance significantly. A analysis of the energy and power densities and estimated cost of the two systems are presented in Table 3, based on the most recent DMFC results obtained at LANL. From the comparative evaluation made above, albeit based on very rough estimates, we conclude that, based on recent performance levels attained, the DMFC could become a serious candidate for transportation applications, provided the following requirements are also met: *i*) Catalyst loadings are further reduced (or alternative anode catalysts developed); *ii*) Long-term stable performances (1000 h time scale) are demonstrated; *iii*) Fuel efficiencies are actually increased to the 90% level.

Evaluation of a New Membrane for PEM Fuel Cells. A new type of ultra-thin composite ionomeric membrane from W.L. Gore was examined for PEM fuel cells. This membrane has enhanced mechanical properties which enable handling of and operation with very thin fuel-cell membranes. Membranes 5-10 μm thick have been fabricated and compared with a minimum thickness of 50 μm for other perfluorosulfonic acid ionomeric membranes. Such very thin membranes promise high

performance because of the lower cell resistance, provided other properties such as gas cross-over is minimized and long-term mechanical integrity does not suffer excessive deterioration.

Table 3. Projected DMFC and RAFC Stack and Systems Characteristics

	DMFC ^a	RAFC ^b
Stack Power Density (kW/kg)	0.25	1.0
Stack Materials Cost (\$/kW)		
• Projected ^c	200	45
• Today	2500	1500
System Specific Energy ^d (Wh/kg)	450	450

^a Advanced fuel cell stack is 50-75% of total weight. ^b Advanced fuel cell stack is 10-30% of total weight. ^c Assuming drop in membrane cost by an order of magnitude. ^d Assuming (1) Similar overall conv. efficiency of 40%, and (2) Range of 240 mile @ 20 kW, 40 mph. Results of (1) and (2) are: DMFC system: 55 kg MeOH, 100 kg stack, 100 kg BOP; RAFC system: 55 kg MeOH, 20 kg stack, 180 kg BOP

To evaluate the potential of this new material, the Gore membrane was catalyzed at LANL by the thin-film (ultra-low Pt loading) technique and tested in laboratory-scale fuel cells. The results have been encouraging: power densities of 0.9 W/cm² were achieved in hydrogen/air cells and 3,000 h of cell life have been demonstrated in one cell with an ultra-thin membrane. Various membrane transport properties have also been measured at LANL to correlate with cell performance.

These results prompted W.L. Gore to develop a new commercial product for PEM fuel cells. The new membrane product was described in detail for the first time in the form of a joint, LANL/W. L. Gore paper, delivered at the Electrochemical Society meeting in Chicago, October 1995.

PUBLICATIONS

The first 5 papers are included in: "Proton Conducting Membrane Fuel Cells I," S. Gottesfeld, G. Halpert and A. Landgrebe, Eds., the Electrochemical Society, Oct. 95, *Proceedings* Volume 95-23.

- (a) "Alternative Flow-Field and Backing Concepts for Polymer Electrolyte Fuel Cells," by M.S. Wilson, T.E. Springer, J.R. Davey and S. Gottesfeld (pp. 115-126).
- (b) "Diagnostic Information from AC Impedance Measurements on Polymer Electrolyte Fuel Cells," by T.E. Springer, T.A. Zawodzinski, M.S. Wilson, and S. Gottesfeld (pp. 137-151).
- (c) "On Direct and Indirect Methanol Fuel Cells for Transportation Applications," by X. Ren, M.S. Wilson and S. Gottesfeld (pp. 252-260).
- (d) "Methanol Cross-Over in Direct Methanol Fuel Cells," by X. Ren, T.A. Zawodzinski, F. Uribe, H. Dai and S. Gottesfeld (pp. 284-288)
- (e) "Advanced Composite Polymer Electrolyte Fuel Cell Membranes," by J.A. Kolde, B. Bahar, M.S. Wilson, T.A. Zawodzinski and S. Gottesfeld (pp. 193 - 201).

T.A. Zawodzinski, J. Davey, J. Valerio and S. Gottesfeld, "The Water Content Dependence of Electro-osmotic Drag in Proton-Conducting Polymer Electrolytes," *Electrochim. Acta* **40**, 297 (1995).

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