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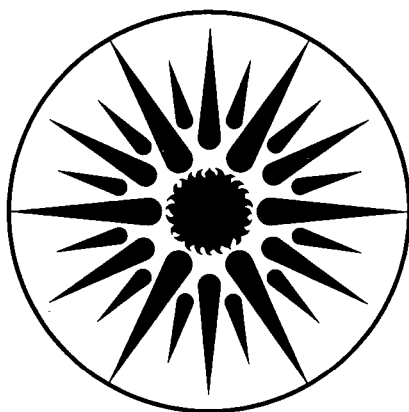
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

**Exploratory Technology Research Program
for Electrochemical Energy Storage:
Annual Report for 1993**

K. Kinoshita, Editor

September 1994



**ENERGY & ENVIRONMENT
DIVISION**

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**EXPLORATORY TECHNOLOGY
RESEARCH PROGRAM
FOR
ELECTROCHEMICAL ENERGY STORAGE**

**ANNUAL REPORT
FOR 1993**

Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Edited by Kim Kinoshita, Technical Manager

September 1994

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EXECUTIVE SUMMARY

The U.S. Department of Energy's Office of Propulsion Systems 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). The program centers on advanced 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 Electrochemical Energy Storage Program is divided into two projects: the Electric Vehicle Advanced Battery Systems (EVABS) Development Program and the Exploratory Technology Research (ETR) Program. The EVABS Program management responsibility has been assigned to Sandia National Laboratories (SNL); Lawrence Berkeley Laboratory* (LBL) is responsible for management of the ETR Program. The EVABS and ETR Programs include an integrated matrix of R&D efforts designed to advance progress on selected candidate electrochemical systems. The United States Advanced Battery Consortium (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 consumer EVs. The role of the ETR Program is to perform supporting research on the advanced battery systems under development by the USABC and 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 the EVABS Program for further development and scale-up. This report summarizes the research, financial and management activities relevant to the ETR Program in CY 1993. 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 air-system (fuel cell, metal/air) 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 LBL scientists: E. Cairns, K. Kinoshita, F. McLarnon and J. Newman of the Energy and Environment Division; and L. Dejonghe, J. Evans, P. Ross and C. Tobias of the Materials Sciences Division.

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 advanced battery and electrochemical performance goals. Research was conducted on new versions of the Zn/NiOOH cell, a novel Na/polymer cell, and an all-solid state Li/Mn oxide cell. Each of these cells is considered to be an attractive candidate for EV applications, and should provide high performance at ambient or near-ambient temperatures. A Zn/NiOOH battery would exhibit higher performance and lower costs, compared to the MH/NiOOH battery; and a Na/polymer battery would be lower cost, compared to a Li/polymer battery.

- LBL has applied X-ray photoelectron spectroscopy (XPS) and found that the NiOOH electrode in Zn/KOH/NiOOH cells does not react chemically with Zn species under cell cycling conditions with a KOH-KF-K₂CO₃ electrolyte.
- The Advanced Energy Systems Division of Acme Electric Corporation has completed 175 charge/discharge cycles with a 20-Ah starved-electrolyte Zn/NiOOH cell that contains the KOH-KF-K₂CO₃ electrolyte developed at LBL.
- LBL has found that the most promising manganese oxide so far in Na/polymer cells is Na_{0.44}MnO₂, first synthesized by Parant and Hagemuller in 1971. Tests on Na/polymer cells with Na_{0.44}MnO₂ positive electrodes indicate that this material can insert 0.55 Na/Mn over a voltage range of 3.4-2.0 V at 0.1 mA/cm² (x ranges from 0.2-0.75 in Na_xMnO₂). This corresponds to a capacity of 160 mAh/g, a theoretical specific energy of 440 Wh/kg and theoretical energy density of 1450 Wh/L.
- Oak Ridge National Laboratory (ORNL) has fabricated all-solid-state Li/Li_xMn₂O₄ cells that contain a solid electrolyte of amorphous lithium phosphorus oxynitride (1-mm thickness). These cells can be cycled between 4.5 and 2.8 V at current densities of 10-20 mA/cm² at room temperature. Efforts are underway to reduce the impedance of the cell to operate at higher current densities.
- PolyPlus Battery Co. was awarded a subcontract on the basis of a Request-for-Proposals (RFP) to demonstrate the viability of Na/organosulfur (Na/SRPE) cells as practical components in batteries for EV applications. Components for Na/SRPE cells have been fabricated and evaluated in preliminary cycle-life tests.

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 — alkaline, metal/air, flow, solid-electrolyte and nonaqueous. 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 determine the role of surface morphology on mass transport which may affect the morphology of electrodeposits and to evaluate the performance of cells utilizing Li intercalation electrodes. Advanced spectroscopic techniques are utilized to investigate the chemical state of electrode materials during charge/discharge cycling.

- LBL has designed and constructed new cells and improved experimental facilities for the study of the effect of protrusions on mass transport to electrodeposited surface layers, and the coalescence of electrolytic gas bubbles which may affect the morphology of electrodeposits. A hemispherical protrusion as small as 50- μm radius was successfully attached to the surface of a micromosaic electrode. A mathematical model has been completed that uses the Boundary Integral Element Method (BIEM) to understand the hydrodynamics of flow over protrusions. Improvements in the experimental apparatus have led to the observation of the coalescence of electrolytic gas bubbles (about 0.1-cm diameter) with a resolution of 10^{-5} s.
- A new thrust was initiated at LBL to identify the physicochemical properties of carbonaceous materials that control the intercalation of Li in nonaqueous electrolytes. Analysis of existing data suggests that no unified theory that links the physicochemical properties of carbon to the reversibility and amount of Li intercalation that occurs is available.
- Brookhaven National Laboratory (BNL) has used extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge spectroscopy (XANES) to study nickel oxide electrodes that were cycled in Zn/NiOOH cells at LBL. EXAFS showed a substantial amount of Zn is present in the nickel oxide electrodes, and the Zn EXAFS was different for the electrodes obtained from three vendors. Doping of manganese oxides with Group VIB metal oxides (CrO_3 , MoO_3 , WO_3) was found to improve the rate capabilities of the electrode in an electrolyte consisting of $\text{LiClO}_4/\text{PC-DME}$.

- Lawrence Livermore National Laboratory (LLNL) is evaluating the performance characteristics of Li-ion cells manufactured by Sony Corporation. Using the USABC Dynamic Stress Tests (DST), the capacity and specific energy of cells charged to 4.2 V were observed to be about 1 Ah and >94 Wh/kg, respectively. The cell voltage at the DST high-power-step (150 W/kg) decreased approximately linearly with cycle number and run time from about 250 to 200 minutes after 310 cycles.

Corrosion Processes in High-Specific-Energy Cells are under investigation, and the aim is to develop low-cost container and current-collector materials for use in nonaqueous, alkali/sulfur and molten-salt cells.

- Illinois Institute of Technology (IIT) has undertaken a theoretical study of the evaporation process of Mo(CO)_6 to improve the quality of Mo_2C coatings obtained by plasma-enhanced chemical vapor deposition. The kinetic-gas theory was used to derive an equation that correlates the evaporation rate and the equilibrium pressure of Mo(CO)_6 .
- The Environmental Research Institute of Michigan (ERIM) has prepared TiN-coated Al containment materials by sputter-deposition techniques which were corrosion-resistant for 500 h in Na_2S_4 at temperatures up to 390°C. Another series of coatings, applied by ion plating, showed no evidence of corrosion after 500 h in Na_2S_4 at 345°C.

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

- Case Western Reserve University (CWRU) has used *in situ* spectroscopic techniques and thermal analysis to study the Li/organic electrolyte interface. Temperature programmed desorption (TPD) studies with Li exposed to propylene carbonate (PC) suggested that the thermal desorption peaks are characteristics of a reaction that produces Li carbonate. Evidence was also found by TPD to indicate that Li hydride may be formed with deuterated PC.
- Northwestern University (NU) was awarded subcontracts on the basis of a RFP to synthesize polymer electrolytes based on aluminosilicate-polyether hybrid electrolytes with improved low-temperature performance and to apply molecular dynamics and Monte Carlo simulations to understand the conduction process in polymer electrolytes. A new hybrid polymer electrolyte has been synthesized and will be tested shortly. Theoretical models are being developed to determine the influence of temperature, ion species, polymer chain basicity, and interionic correlations on conduction and Li transport number in polymer electrolytes.

- CWRU was awarded a subcontract on the basis of a RFP to develop novel polymeric materials for polymer electrolytes in rechargeable Li batteries. Effort is underway to synthesize sulfonated and phosphonated polybenzimidazole (PBI) polymers, and poly(4,5-dimethyleneimidazole and hydroxy imidazole) polymers.
- The University of Dayton was awarded a subcontract on the basis of a RFP to synthesize and characterize new polymer electrolytes that contain crown ethers which could have a fundamentally different mode of ion transport than those currently under investigation. The systems proposed are doped polymers with side chains that are terminated with crown ether groups which will complex with a Li salt. It is hypothesized that these materials will create highly ordered structures, thereby forming paths through which ions can move easily. The synthesis of the three polymers involving a seven-step procedure has been initiated. A common monomer intermediate is produced at step four; synthesis of this intermediate has been started following published procedures.
- Rutgers University was awarded a subcontract on the basis of a RFP to optimize the synthesis of polymer electrolytes by sol-gel processing of alkali silicate components. Various lithia-silicate compositions have been prepared which were found to have ionic conductivities over the range from room temperature to 400°C that show some promise for testing in Li batteries.
- The State University of New York (Binghamton) was awarded a subcontract on the basis of a RFP to synthesize molybdenum oxides for positive electrodes in rechargeable Li cells. Molybdenum oxides ($M_x\text{MoO}_{3+x/2}$, where M = cation) were synthesized using the hydrothermal method at 150-200°C. Layered structures were obtained which should allow for rapid diffusion of Li ions.
- SRI International was awarded a subcontract on the basis of a RFP to develop high-performance hexathiobenzene-based organosulfur electrodes for Na cells. Electrodes and polymer electrolytes for Na/PEO/ polyorganosulfide cells have been fabricated.

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.

- The important physical processes taking place in the galvanostatic charge and discharge of a Li/polymer/insertion cell have been identified by LBL. A mathematical model has been developed that elucidates the dynamic changes in the cell with charge or discharge, and this model has been extended to examine the behavior of the "Rocking Chair" configuration, which is based upon two materials which insert Li at different potentials. A thermal model has been developed which predicts the rate of heat generation of a Li/polymer battery during cycling.

- A new LBL project was started on mathematical modeling of heat transport in Li/polymer batteries. A two-dimensional mathematical model for the thermal behavior of Li-polymer batteries was developed, and the results demonstrate that thermal management may not be a serious problem for these batteries under low discharge rates. However, under high discharge rates, the temperature of a battery may increase significantly if the thickness of a cell stack exceeds a certain value.
- A newly developed technique at LBL for low-energy ion implantation known as Metal Plasma Immersion Ion Implantation (MPIII) was used to implant Co, Zr and Pb in nickel oxide electrodes. Co-implanted Ni electrodes appear to have a higher coulombic storage capacity than comparable electrodes without the addition of Co. However, a similar beneficial effect of doping with Zr or Pb in nickel oxide was not observed.
- LBL utilized low-energy ion-scattering spectroscopy (LEIS) and Auger electron spectroscopy (AES) to study the composition of sputtered and ultrahigh vacuum (UHV)-annealed polycrystalline Pt-Ru bulk alloys that were used for methanol electrocatalysis. Annealing at 800°C in UHV causes a strong surface enrichment in Pt for equilibrated Pt-Ru alloys. The alloy with a hcp bulk lattice (9.5 at% Pt) exhibited a larger segregation than the fcc alloys (>35 at% Pt), which was rationalized with the lattice mismatch between the bulk and the surface face structure, resulting in a loosely packed surface. The Pt surface enrichment of annealed bulk alloys was contrasted with the segregation observed for bimetallic supported clusters of Pt and Ru.
- LBL has observed that the highest activity for the methanol electrooxidation on Pt-Ru alloys shifts from a surface composition of 10 at% Ru at 25°C to about 30 at% Ru at 60°C. This change is attributed to the change in the adsorptive nature of the Ru sites with temperature.
- LBL is exploring the use of nuclear magnetic resonance (NMR) to obtain information about surface poisoning on Pt-based electrocatalysts for electrochemical oxidation of methanol. Experiments are underway to detect and characterize the signal from ^{13}CO adsorbed on the electrodes from ^{13}CO -saturated 0.5 M aqueous H_2SO_4 under open-circuit cell conditions.

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.

Metal/Air Cell Research projects address bifunctional air electrodes that are needed for electrically rechargeable metal/air (Zn/air, Fe/air) cells; and novel alkaline Zn electrode structures that could be used in either electrically-recharged or mechanically-recharged cell configurations.

- Eltech Research Corporation is investigating the viability of bifunctional air electrodes that contain two electrocatalysts – one for oxygen evolution and the other for oxygen reduction. Electrodes with a graphitized acetylene black for the support and NiCo_2O_4 and either CoTMPP or $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ as electrocatalysts have operated for over 100 cycles in 35 wt% KOH at room temperature.

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 1993 are listed below:

- LANL was awarded U.S. Patents describing the developments in membrane catalyst layers for fuel cells (No. 5,211,984, issued May 18, 1993, and No. 5,234,777, issued Aug 10, 1993) and the use of the thermoplastic (TBA⁺) form of the ionomer (No. 5,234,777, issued Aug 10, 1993).
- The first licensing agreement has been signed with a U.S. industrial company to utilize LANL technology for membrane/electrode assemblies in polymer electrolyte fuel cells (PEFC).
- LANL has investigated the use of Pt-Ru anodes and their tolerance to CO and CO₂. The study showed that the advantage of Pt-Ru is not to enhance the oxidation of CO, but rather to minimize the extent of the CO₂ reduction process(es).
- Freeze-thaw cycle tests of proton-exchange membrane (PEM) fuel cells at LANL demonstrated no deleterious effect on performance. These results suggest that the direct application of a thin-film catalyst to the membrane generates a very good bond between catalyst and membrane to effectively prevent delamination under the demanding freeze-thaw cycling conditions.
- A new flow-field design was introduced by LANL for PEM fuel cells which contains a macroporous flow field for the reactant gases. Higher limiting currents were obtained than in cells with ribbed flow fields.
- LANL observed that removal of the gas diffusion anode backing layer dramatically improved the performance of a direct-methanol fuel cell (DMFC) at 80°C, with both liquid and vapor feeds.
- BNL is utilizing X-ray absorption spectroscopy (XAS) to study the adsorbed Pb on Pt catalysts. The results suggest that the electrocatalysis of small organic molecules on Pb-modified Pt cannot be attributed to adsorption of oxygen species on Pb, rather it must be attributed to the disordered nature of the Pb adlayer.

MANAGEMENT ACTIVITIES

During 1993, LBL managed 20 subcontracts and conducted a vigorous research program in electrochemical energy storage. LBL staff members attended project review meetings, made site visits to subcontractors, and participated in technical management of various ETR projects. LBL staff members also participated in the following reviews, meetings, and workshops:

- USABC/DOE Review Meeting, Dearborn, MI, January 12-13, 1993
- CALSTART Strategic Planning Meeting, Sacramento, CA, February 5, 1993
- Project California Planning Meeting, Irvine, CA, February 11, 1993
- Zinc/Air Review Meeting, Washington, D.C., February 18-19, 1993
- IAPG Chemical Working Group Meeting, White Oak, MD, March 23-25, 1993
- 183rd Meeting of the Electrochemical Society, Honolulu, Hawaii, May 16-21, 1993
- Fuel Cells for Transportation Strategic Planning Meeting, Leesburg, VA, April 6-8, 1993
- Lithium Polymer Battery Meeting, Washington, D.C., June 22-23, 1993
- 28th IECEC, Atlanta, GA, August 8-13, 1993
- 144th International Society of Electrochemistry Meeting, Berlin, Germany, September 5-10, 1993
- Progress in Electrocatalysis, Ferrara, Italy, September 12-15, 1993
- LANL Exploratory Fuel Cell and Capacitor Research for Transportation Review Meeting, Washington, D.C., October 6, 1993
- 184th Meeting of the Electrochemical Society, New Orleans, Louisiana, October 10-15, 1993
- Annual Automotive Technology Development Contractors' Coordination Meeting, Dearborn, MI, October 18-21, 1993
- US/DOE Fuel Cell Microgeneration Workshop, Alexandria, VA, October 21-22, 1993
- Symposium on the Science of Advanced Batteries, CWRU, Cleveland, OH, November 8-9, 1993
- Zn/Air Battery Review and Strategic Planning Meeting, Albuquerque, NM, December 1-2, 1993

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1. Exploratory Technology Research Project for Electrochemical Energy Storage – Annual Report for 1992, LBL-34081 (October 1993).
2. Exploratory Technology Research Project for Electrochemical Energy Storage – Annual Report for 1991, LBL-32212 (June 1992).
3. Technology Base Research Project for Electrochemical Energy Storage – Annual Report for 1990, LBL-30846 (June 1991).
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5. Technology Base Research Project for Electrochemical Energy Storage – Annual Report for 1988, LBL-27037 (May 1989).
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11. Technology Base Research Project for Electrochemical Energy Storage – Annual Report for 1982, LBL-15992 (May 1983).
12. Technology Base Research Project for Electrochemical Energy Storage – Report for 1981, LBL-14305 (June 1982).
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LIST OF ACRONYMS

AES	Auger electron spectroscopy
ATR	attenuated total reflectance
BIEM	Boundary Integral Element Method
BNL	Brookhaven National Laboratory
CRADA	Cooperative Research and Development Agreement
CV	cyclic voltammetry
CVD	chemical vapor deposition
CWRU	Case Western Reserve University
DME	dimethoxyethane
DMFC	direct methanol fuel cell
DOD	depth of discharge
DOE	Department of Energy
DST	Dynamic Stress Test
EIS	electrochemical impedance spectroscopy
EMD	electrolytic manganese dioxide
EMF	equilibrium electromotive force
EPRI	Electric Power Research Institute
ERIM	Environmental Research Institute of Michigan
ETR	Exploratory Technology Research
EV	electric vehicle
EVABS	Electric Vehicle Advanced Battery Systems
EXAFS	extended X-ray absorption fine structure
fcc	face centered cubic
FIDAP	finite element package, Fluid Dynamics International
FT	Fourier transforms
FTIR	Fourier transform infrared reflectance
hcp	hexagonal close packed
HTB	hexathiobenzene (C_6S_6)
HREM	high-resolution electron microscopy
IAPG	Interagency Power Group
IECEC	Intersociety Energy Conversion Engineering Conference
IIT	Illinois Institute of Technology
ISE	International Society of Electrochemistry
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory

LEED	low energy electron diffraction
LEIS	low-energy ion-scattering spectroscopy
LLNL	Lawrence Livermore National Laboratory
MEEP	polybis(methoxyethoxyethoxide) phosphazene
MES	Mossbauer Effect Spectroscopy
MPIII	Metal Plasma Immersion Ion Implantation
NSLS	National Synchrotron Light Source
NMR	nuclear magnetic resonance
NU	Norwestern University
ORNL	Oak Ridge National Laboratory
PBI	polybenzimidazole
PC	propylene carbonate
PDS	photothermal deflection spectroscopy
PEEK	polyether ether ketone
PEFC	polymer electrolyte fuel cells
PEM	proton-exchange membrane
PEO	poly(ethylene oxide)
PFSA	polyfluorosulfonic acid
PPE	polypropylene
PTFE	polytetrafluoroethylene
RFP	Request for Proposal
SEM	scanning electron microscopy
SERS	surface-enhanced Raman spectroscopy
SFUDS	Simplified Federal Urban Driving Schedule
SNL	Sandia National Laboratories
SPE	solid polymer electrolyte
SPL	Silent Power Ltd., Salt Lake City
TBA	tetrabutyl ammonium
TDF	perdeuterated tetrahydrofuran
THF	tetrahydrofuran
TPD	temperature programmed desorption
UHV	ultrahigh vacuum
UPD	underpotential deposition
USABC	United States Advanced Battery Consortium
XANES	X-ray absorption near edge spectroscopy
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy

SUBCONTRACTOR FINANCIAL DATA - CY 1993

Subcontractor	Principal Investigator	Project	Contract Value (K\$)	Term (months)	Expiration Date	Status in CY 1993*
<u>EXPLORATORY RESEARCH</u>						
Advanced Zn/NiOOH Cells						
Acme Electric Corp.	M. Anderman	Secondary Zn/NiOOH	193	12	6-94	T
Solid-State Cells						
Oak Ridge National Laboratory	J. Bates	Rechargeable Li Batteries	150	18	9-94	C
PolyPlus Battery Company	M.-Y. Chu	Na/SRPE EV Batteries	184	12	10-94	C
<u>APPLIED SCIENCE RESEARCH</u>						
Lawrence Berkeley Laboratory	E. Cairns, L. DeJonghe, J. Evans, K. Kinoshita, F. McLarnon, J. Newman, P. Ross and C. Tobias	Electrochemical Energy Storage	1865	12	9-94	C
Electrode Characterization						
Brookhaven National Laboratory	J. McBreen	Battery Materials	105	12	9-94	C
Lawrence Livermore National Lab.	S. Mayer	Li-Ion Battery Testing	55	12	6-94	T
Corrosion Processes in High-Specific Energy Cells						
Illinois Institute of Technology	R. Selman	Corrosion Resistant Coatings	132	12	5-93	T
Environmental Research Institute of Michigan	T. Hunt	Secondary Batteries	100	13	1-94	T
Components for Ambient-Temperature Nonaqueous Cells						
Case Western Reserve University	D. Scherson	<i>In Situ</i> Studies	125	12	9-94	C
Northwestern University	M. Ratner	Polymer Electrolytes	145	12	9-94	C
Northwestern University	D. Shriver	Polymer Electrolytes	121	12	9-94	C
Case Western Reserve University	M. Litt	Polymer Electrolytes	158	12	9-94	C
University of Dayton	G. Glasgow	Polymer Electrolytes	95	12	9-94	C
Rutgers University	L. Klein	Sol-Gel Electrolytes	95	12	9-94	C
SUNY at Binghamton	S. Whittingham	Cathode Materials	125	12	9-94	C
SRI International	S. Smedley	Na/Polymer Cells	156	12	9-94	C
<u>AIR SYSTEMS RESEARCH</u>						
Metal/Air Cell Research						
Eltech Research Corporation	E. Rudd	Oxygen Electrodes	104	18	3-94	T
Fuel Cell R&D						
Los Alamos National Laboratory	S. Gottesfeld	Fuel Cell R&D	1000	12	9-94	C
Brookhaven National Laboratory	J. McBreen	Fuel Cell Research	0	12	9-93	T

* 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 1993. The primary objective of the ETR Program, which is sponsored by the U.S. Department of Energy (DOE) and managed by Lawrence Berkeley Laboratory (LBL), 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 (*e.g.*, SNL's Electric Vehicle Advanced Battery Systems Development Program, EVABS) for further development and scale-up.

Besides LBL, 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 electric vehicles (EVs). Exploratory research was carried out on Zn/NiOOH and Na/polymer cells, and novel components for various versions of these cells were also investigated, as described in the Applied Science section of this report.

A. ADVANCED ZINC/NICKEL OXIDE CELLS

New approaches to extend the cycle life of Zn/NiOOH cells by modifying the electrolyte composition are underway. There is a strong incentive to develop a long-lived Zn/NiOOH battery, because it would exhibit superior performance and lower life-cycle costs, compared to Cd/NiOOH and MH/NiOOH batteries.

Zn/NiOOH Cell Studies

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Objectives

- Investigate the behavior of Zn electrodes in alkaline Zn/NiOOH cells and improve their lifetime and performance.
- Improve NiOOH electrode performance without compromising the lifetime of the Zn electrode.

Approach

- Determine the performance and cycle life of alkaline Zn/NiOOH cells using realistic cell components and operating conditions.
- Utilize analytical instruments such as X-ray diffraction analysis and XAS to understand changes to cell components resulting from charge/discharge cycling.

Accomplishments

- XPS was used to determine that the NiOOH electrode in Zn/KOH/NiOOH cells does not chemically react with Zn species under cell cycling conditions with a KOH-KF-K₂CO₃ electrolyte.

Future Directions

- Evaluate lightweight and low-cost NiOOH electrodes in model Zn/NiOOH cells.
 - Evaluate novel separator and wick materials that may provide better wetting characteristics.
 - Establish a CRADA with Energy Research Corporation to further technology transfer.
-

The purpose of this project is to investigate the behavior of Zn electrodes in alkaline Zn/NiOOH cells to improve their lifetime and performance. Earlier work at LBL demonstrated that KOH-KF-K₂CO₃ electrolytes greatly extend the cycle life of 1.35-Ah Zn/NiOOH cells. The rate of Zn-electrode shape change is much slower in these cells, and cell cycle life is increased to 500-800 deep-discharge cycles, compared to 100-200 cycles in traditional 7 M KOH - 0.5 M LiOH electrolytes. Zn/NiOOH cells employing these novel electrolytes now tend to be life-limited and performance-limited by the NiOOH electrode rather than the Zn electrode. Therefore, increased emphasis is being placed on improving NiOOH electrode performance without compromising the excellent lifetime of the Zn electrode.

NiOOH Electrode. Various types of NiOOH electrodes were evaluated in KOH-KF-K₂CO₃ electrolytes by cycling pairs of NiOOH electrodes to assess electrode performance without the complicating effects of a Zn electrode. The NiOOH electrodes employed sintered-Ni plaque, Ni-plated plastic fiber, and Ni foam-metal current collectors. The KOH concentration was varied from 3 to 6 M, and F⁻ and CO₃²⁻ ionic concentrations were fixed at 2 M. Increasing the KOH concentration above 4.5 M afforded no improvement in the NiOOH electrode capacity. All NiOOH electrodes suffered a 10-20% decrease in capacity when the electrolyte was saturated with ZnO, which is consistent with the results of prior Zn/NiOOH cell cycle-life tests.

Lithium hydroxide is traditionally added to KOH electrolyte to promote efficient operation of the NiOOH electrode in rechargeable alkaline batteries. Fluoride ions in the KOH-KF-K₂CO₃ electrolyte precipitate any added Li⁺ ion as insoluble LiF, which prevents the Li⁺ from reaching the interior pores of the NiOOH electrode and results in a ~10% decrease in electrode capacity. A novel technique was developed for preparing a very fine suspension of LiF particles, which when added to KOH-KF-K₂CO₃ electrolytes results in a full recovery to the expected NiOOH electrode capacity. Life-cycle testing is underway to define an upper limit for KOH concentration and lower limits for F⁻ and CO₃²⁻ ionic concentrations that result in improved lifetimes of Zn/NiOOH cells.

Various techniques are being employed to characterize NiOOH electrodes recovered from Zn/NiOOH cells cycled using the novel KOH-KF-K₂CO₃ electrolyte, in an effort to better define the reason(s) for the gradual capacity loss that is observed in these cells. X-ray photoelectron spectroscopy (XPS), vibrational

spectroscopies (IR and Raman) and X-ray diffraction techniques were used to determine the chemical composition of Ni and Zn species in cycled NiOOH electrodes. Only XPS gave high-quality results. Figure 1 compares the Ni 2_{p3/2} XPS spectrum of a discharged NiOOH electrode cycled in 3.5 M KOH - 2 M K₂CO₃ - 2 M KF electrolyte with that of chemically prepared β-Ni(OH)₂. The spectra substantially agree with each other, which suggests that the NiOOH electrode does not chemically react with Zn species under cell-cycling conditions.

Similar experiments indicated that the Ni 2_{p3/2} spectrum of discharged NiOOH electrode material cycled in 3.5 M KOH - 2 M K₂CO₃ - 2 M KF electrolyte agreed with the spectrum of discharged NiOOH material cycled in 6 M KOH-1 M LiOH electrolyte, which suggests that CO₃²⁻ and F⁻ species do not react with Ni under cell-cycling conditions. Measured Zn spectra indicated that the Zn deposited in cycled NiOOH electrodes is in the form of ZnO. This result is consistent with BNL data presented on page 16 of this report.

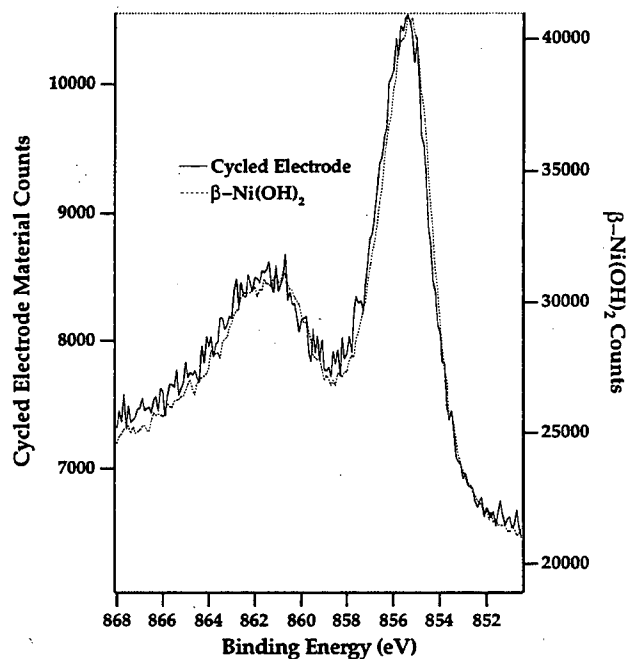


Figure 1. Comparison of the photoelectron spectrum of a porous NiOOH electrode harvested from a Zn/NiOOH cell with that of chemically prepared β-Ni(OH)₂.

There is a possibility that various chemical or mechanical processes may degrade the sintered-Ni current collector, leading to loss of electronic contact and poor utilization of the NiOOH active material. To explore this issue further, four-point conductivity measurements were carried out on various NiOOH-electrode samples harvested from a 21-Ah Zn/NiOOH cell which was subjected to 200 deep-discharge cycles. The measured resistivity varied significantly with position in the cycled NiOOH electrodes, which implies that a mechanical degradation process is at least partially responsible for electrode capacity decline.

Zinc Electrode. Steady-state and potential-step polarization measurements were conducted to characterize the behavior of Zn-electrode reactions in alkaline electrolytes with and without K_2CO_3 additions. The objective of these studies is to determine if the beneficial effect of the K_2CO_3 additions is associated with fundamental changes in the Zn-electrode kinetics.

Because the Zn electrode is always covered by an oxidized surface layer in alkaline electrolytes, it is critically important to establish a reliable electrode pretreatment procedure to obtain reproducible electrode surface conditions. We demonstrated that reproducible Zn electrode surfaces can be achieved by using a square-wave potential pulse (-5 mV cathodic polarization for 60 s followed by holding the Zn electrode at its rest potential for 60 s) pretreatment procedure. Figure 2 shows typical steady-state polarization curves for the Zn electrode in 2.5 M KOH-0.15 M ZnO electrolytes with and without the addition of 2.5 M K_2CO_3 . The current densities in the carbonate-containing electrolyte are generally lower than those in the carbonate-free electrolyte, as is the derived exchange current density. The region of low overpotentials (<10 mV) is of greatest interest in this study, because that is the region wherein practical battery electrodes operate. The transient current response to potential steps in this region was measured, and a phenomenological model to describe the detailed mechanisms of the Zn-electrode reaction in these electrolytes is being developed. In this model, a chemical reaction step is followed by two consecutive charge-transfer reactions on the Zn electrode surface in the presence of a porous surface layer.

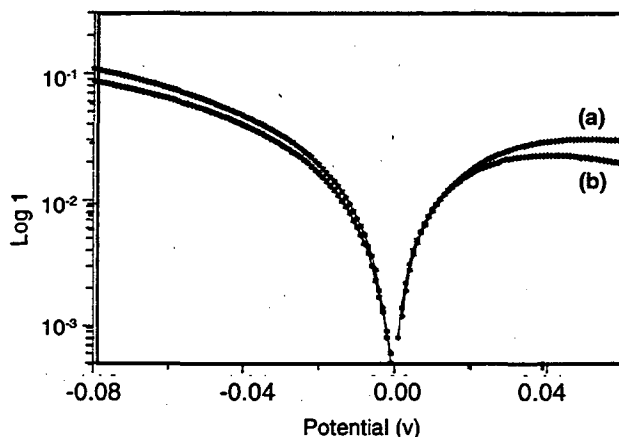


Figure 2. Polarization curves for Zn electrodes in alkaline electrolyte. The ordinate is the absolute value of the current density (A/cm^2) and the abscissa is the electrode potential measured against another Zn electrode at its rest potential. The curves show the current-potential response for a Zn electrode in 2.5 M KOH - 0.15 M ZnO electrolyte (a) without and (b) with the addition of 2.5 M K_2CO_3 .

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Applied Research on Secondary Zn/NiOOH Battery Technology

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Objectives

- Evaluate the LBL electrolyte composition in Zn/NiOOH cells and to demonstrate long cycle life.
- Develop Zn/NiOOH cells for EV applications.

Approach

- Utilize cell hardware available at Acme and fabricate Zn/NiOOH cells that contain the LBL electrolyte.
- Evaluate the performance of Zn/NiOOH cells that contain nickel fiber electrodes.

Accomplishments

- Completed 175 charge/discharge cycles with a 20-Ah starved-electrolyte Zn/NiOOH cell containing a low-alkaline electrolyte developed at LBL.

Future Direction

- Continue efforts to achieve performance with 20-Ah cells that is comparable to that obtained by LBL.

The objectives of this project are to evaluate the LBL electrolyte composition ($\text{KOH} + \text{KF} + \text{K}_2\text{CO}_3$) for extending the cycle life of Zn/NiOOH cells, and to develop these cells for EV applications. The effort in the past year was directed at technology transfer involving: *i*) LBL plastic-bonded ZnO electrode fabrication process, *ii*) cell assembly, *iii*) assembly and testing 20-Ah cells of various configurations, *iv*) verification of improved cycling characteristics and drastic reduction in shape change of the Zn electrode in the LBL electrolyte, and *v*) study of capacity fading of the NiOOH electrode in ZnO-saturated low-alkaline electrolytes.

After several start up problems related to cell assembly and cell formation, reproducible cells were built that did not experience internal short circuits. Figure 3 displays cycle life characteristics of a 20-Ah cell that was subjected to changes in operating conditions. The general picture is that cells yield 90 to 105% of the theoretical nickel oxide limited capacity in the flooded configuration. On the other hand, in a starved-electrolyte environment, the capacity of these electrodes dropped immediately to ~80% of theoretical capacity. Upon continued 100% depth-of-discharge (DOD) cycles, the capacity faded at a rate of

1 to 1.5% per cycle. However, when the cell is driven below 0.3 V to hydrogen evolution, the Ni electrode capacity recovers to its initial level. After 95 cycles, the cell was fully discharged to 0.0 volt. The Zn electrode capacity was 35 Ah compared to 40 Ah during

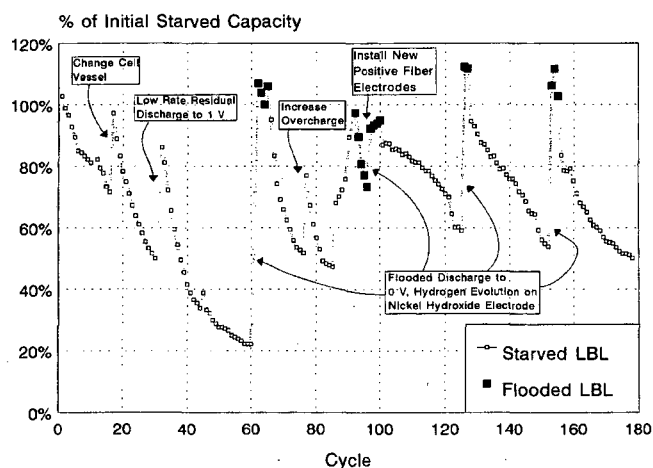


Figure 3. Variation in the capacity of a fiber Ni electrode in a 20-Ah Zn/NiOOH cell containing the LBL electrolyte

cell formation. This result also indicated that the cycle life of the Zn electrode is increased in the LBL electrolyte.

The results of the cell testing can be summarized as follows. A 20-Ah starved Zn/NiOOH cell, comprised of fiber Ni and plastic-bonded Zn electrodes, and LBL low-KOH electrolyte, completed 175 cycles. The cell maintained between 75 and 100% of initial capacity by applying light reconditioning cycles every 20 to 30 cycles. A visual examination of the electrodes from cells cycled in LBL low-KOH electrolytes showed a drastic improvement (reduction) in elec-

trode shape change compared to electrodes cycled in the standard, highly-alkaline electrolyte. The NiOOH electrodes appear to suffer from reversible capacity loss in the ZnO-saturated, starved electrolyte environment using the LBL electrolyte composition. This capacity loss is fully recoverable upon reversing the electrode into hydrogen evolution.

The emphasis of this project will be to continue building and testing Zn/NiOOH cells (Zn limited) cells of different configuration to determine the cause of capacity fading and to develop a practical sealed cell design that will achieve long cycle life.

B. 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 and a metal oxide positive in a rechargeable cell.

Electrochemical Properties of Solid-State Sodium/Polymer Cells

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Objectives

- Investigate the viability of all-solid-state cells based on a Na or Na-alloy negative electrode, polymeric electrolytes, and a metal oxide positive electrode for EV applications.
- Develop a suitable cathode material for use in Na/polymer cells.

Approach

- Synthesize and characterize manganese oxides for use as a cathode in Na/polymer cells.
- Employ AC and DC techniques (e.g., galvanostatic charging and discharging, four-probe techniques, impedance spectroscopy and pulse testing) to characterize solid state batteries, as well as the properties of the individual components and interfaces.

Accomplishments

- The most promising manganese oxide found so far for Na/polymer cells is $\text{Na}_{0.44}\text{MnO}_2$, first synthesized by Parant and Hagemuller in 1971. Tests on Na/polymer cells with $\text{Na}_{0.44}\text{MnO}_2$ cathodes indicate that this material can insert 0.55 Na/Mn over a voltage range of 3.4-2.0 V at 0.1 mA/cm² (x ranges from 0.2-0.75 in Na_xMnO_2), corresponding to a capacity of 160 mAh/g, a theoretical specific energy of 440 Wh/kg and a theoretical energy density of 1450 Wh/L.

Future Direction

- Continue work on the synthesis, characterization and testing of manganese oxides with large tunnels to accommodate Na ions, measurement of transport properties in Na/polymer cells, and Na/polymer cell testing to optimize its performance.
-

The objective of this project is to investigate the viability of all-solid-state cells based on Na or Na-alloy negative electrodes, polymeric electrolytes, and metal oxide positive electrodes. Emphasis is placed on developing a suitable cathode material not only in terms of performance but also in terms of cost and environmental impact. Fundamental investigations of bulk- and thin-film elastomeric electrolytes furnish information on the electrochemical and mechanical properties of these polymers, and provide the basis for advanced design of batteries, as well. Characterization of the various interfaces in solid polymer batteries is crucial to the successful development of these advanced systems. AC and DC techniques (e.g., galvanostatic charging and discharging, four-probe techniques, impedance spectroscopy and pulse testing) are used to characterize these solid-state batteries as well as the properties of the individual components and interfaces.

Sodium manganese oxides are synthesized by a variety of techniques depending upon which phase is desired. A solid-state reaction of sodium peroxide or sodium carbonate with Mn_2O_3 in the appropriate stoichiometries leads to $\text{Na}_{0.44}\text{MnO}_2$, which has a tunnel structure, or $\text{Na}_{0.7}\text{MnO}_2$, which has a layered structure analogous to that of the P2 phase sodium cobalt bronze. These materials can also be made by a combustion synthesis technique in which glycine, manganese nitrate and sodium nitrate starting materials are reacted by heating them together in an aqueous solution. The resultant fine powders are then calcined to obtain the desired phase. This technique (glycine-nitrate method) is advantageous in that it consistently produces very fine (1 μm), high quality powders. "Chimie douce" or wet chemistry techniques are also used to produce several phases of manganese dioxides. Treatment of spinel LiMn_2O_4 or $\text{Na}_{0.44}\text{MnO}_2$ with aqueous hydrochloric acid at room temperature for 24 hours removes the mobile alkali metal ions, producing $\lambda\text{-MnO}_2$ in the first case and $\text{Na}_{0.2}\text{MnO}_2$ with the $\text{Na}_{0.44}\text{MnO}_2$ structure in the second case. Reaction of KMnO_4 with H_2O_2 in water yields cryptomelane, a potassium-intercalated $\alpha\text{-MnO}_2$ after calcination.

The extent of intercalation of new manganese oxides was determined by galvanostatic charging and discharging of cells at low rates (0.05-0.1 mA/cm^2). This varied widely with type and structure, ranging from essentially no intercalation of Na for electrolytic manganese dioxide or $\gamma\text{-MnO}_2$ (EMD) to 0.55 Na/Mn for $\lambda\text{-MnO}_2$ and $\text{Na}_{0.44}\text{MnO}_2$. There is evidence for an irreversible phase change upon electrochemical insertion of Na ions into $\lambda\text{-MnO}_2$; the cell voltage at first drops and then rises as the discharge progresses. The

subsequent charge and discharge are completely different than the first discharge. While this new phase showed promising discharge characteristics with a high average voltage (3 V) and large extent of intercalation, corresponding to a theoretical specific energy of 420 Wh/kg, another irreversible phase change after a few cycles resulted in reduced cell capacity. This second phase change is probably temperature related and will become less problematic once the operating temperature is reduced. However, it does illustrate one characteristic typical of manganese dioxides: the propensity to undergo structural changes readily. Clearly thermodynamic stability as well as high capacity is an important feature in selecting new manganese oxides for Na cells.

The most promising manganese oxide studied so far in polymer cells is $\text{Na}_{0.44}\text{MnO}_2$, first synthesized by Parant and Hagenmuller in 1971. This material contains large irregularly shaped tunnels into which Na ions can insert readily. It is also the most thermodynamically stable phase in the Na-Mn-O system (for Na/Mn ratios below 0.5). In spite of these attractive features, it has never been tested in batteries before now. In fact, an electrochemical study of Na-intercalated manganese oxides by Hagenmuller et al. omitted this compound, stating that it would not undergo reductive intercalation. However, tests on Na/polymer cells with $\text{Na}_{0.44}\text{MnO}_2$ cathodes performed in this laboratory indicate that this material can insert 0.55 Na/Mn over a voltage range of 3.4-2.0 V at 0.1 mA/cm^2 (x ranges from 0.2-0.75 in Na_xMnO_2). The sloping voltage profile suggests that the structure is maintained throughout the discharge, and preliminary X-ray diffraction results confirm this observation. This corresponds to a capacity of 160 mAh/g , a theoretical specific energy of 440 Wh/kg, and a theoretical energy density of 1450 Wh/L. Cells can sustain current densities up to 0.5 mA/cm^2 although there is some capacity loss at the higher current densities. $\text{Na}_{0.44}\text{MnO}_2$ cells have undergone sixty cycles at 0.1 mA/cm^2 , although severe capacity fading was seen. Capacity fading was also seen when cells with the configuration $\text{Na}_{0.44}\text{MnO}_2/\text{P}(\text{EO})_8\text{NaCF}_3\text{SO}_3/\text{Na}_{0.44}\text{MnO}_2$ were cycled at the same rate. This indicates that this phenomenon is not associated with instability at the Na/PEO (polyethylene oxide) interface but rather with the cathode or interfaces at the current collectors or separator. *In situ* X-ray experiments may reveal structural changes in $\text{Na}_{0.44}\text{MnO}_2$ responsible for the cell failure, and are presently under way.

Several other manganese oxides have been investigated for use in Na polymer cells this year, including EMD or $\gamma\text{-MnO}_2$, spinel LiMn_2O_4 in which Li ions

have not been removed, $\text{Na}_{0.7}\text{MnO}_2$, a layered compound with the P2 structure analogous to the sodium cobalt bronze studied in this laboratory, and the defect spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ which has been acid oxidized. Neither EMD or spinel LiMn_2O_4 are electrochemically active in Na cells; the small 2×1 and 1×1 tunnels in these compounds are not large enough to accommodate the rather large Na ions ($0.97\text{\AA}$). (Contrast this to the results with $\lambda\text{-MnO}_2$, which reductively intercalates Na by changing structure; Li ions in LiMn_2O_4 serve to "pin" the spinel structure). The acid-treated defect spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ also inserts Na over a wide range of composition (up to 0.5 Na/Mn on the first cycle); as with $\lambda\text{-MnO}_2$ there is evidence of an irreversible phase change, and the capacity is reduced upon subsequent cycles. The P2 type $\text{Na}_{0.7}\text{MnO}_2$ undergoes reductive intercalation of Na ions only over a narrow composition range (from about $x = 0.5$ - 0.7 in Na_xMnO_2) and is very sensitive to over-discharge. Its poor performance contrasts sharply with the P2 Na_xCoO_2 analogue, which has a high specific energy in Na cells and is insensitive to overdischarge. These observations suggest that the most successful manganese oxides for use as intercalation electrodes are not the layered structures, but those with large tunnels that can accommodate ions readily; large tunnels are particularly important for Na insertion. Synthesis of $\alpha\text{-MnO}_2$, which has 2×2 tunnels, psilomelanes (2×3) tunnels, and other manganese oxides with even larger tunnels is presently underway.

Another aspect of this project concerns the measurement of the transport properties of sodium salt-PEO complexes, including conductivity, diffusion coefficients and transference numbers. The goal of this research is not only to provide data for modeling studies in conjunction with the Newman group (LBL) but also to optimize the performance of practical cells. In particular, lowering the operation temperature of cells below the present testing temperature of 85°C is considered to be of primary importance. AC impedance spectroscopy is used to measure conductivity of PEO-salt complexes as a function of salt concentration and type. For NaCF_3SO_3 -PEO complexes, a maximum conductivity is reached at a composition of $\text{P(EO)}_{20-40}\text{NaCF}_3\text{SO}_3$ (Fig. 4) and is approximately one order of magnitude higher than for the corresponding Li complexes. Diffusion coefficients for Na ions in polymer electrolytes are calculated using restricted diffusion theory. In short, Na/P(EO) $_x$ NaX/Na cells are galvanostatically polarized and the current is turned off at time $t = 0$. The cells are allowed to relax and the open circuit voltage is measured as a

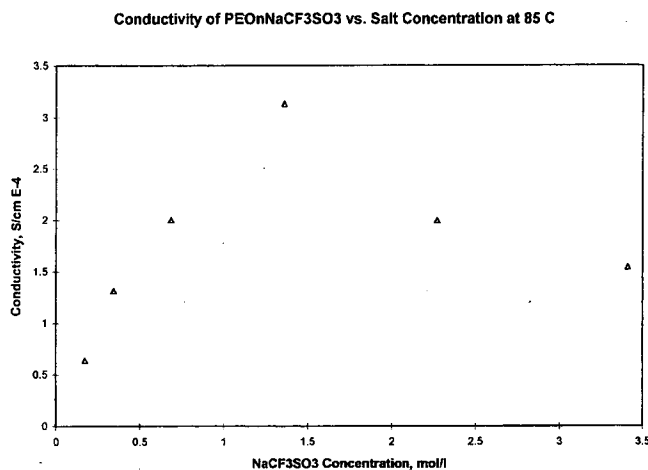


Figure 4. Ionic conductivity of $\text{P(EO)}_n\text{NaCF}_3\text{SO}_3$ at 85°C for various concentrations of NaCF_3SO_3 . Maximum corresponds to $n = 20$.

function of time. Near the end of the relaxation process, the following equation holds true:

$$\ln V = 2A_1 - \frac{\pi^2 D(c^0)}{L^2} \quad (1)$$

Where A_1 is a constant and L is the thickness. The highest diffusion coefficients are obtained for $\text{P(EO)}_{20-40}\text{NaCF}_3\text{SO}_3$ although there is little variation with composition.

Accurate measurement of transference numbers in polymer electrolytes is problematic. Many of the traditional methods cannot be applied, and assumptions using dilute solution theory lead to errors. A method in which junction potentials of Na/P(EO) $_x$ NaX/P(EO) $_y$ NaX/Na cells are measured as a function of ΔC and related to transference numbers has been described by Armand. This requires separate knowledge of the activity coefficients of NaX, however. A technique for the accurate determination of transference numbers is now being developed in this laboratory in conjunction with the Newman group. The concentration cell measurements described by Armand can be used to relate cell equilibrium electromotive force (EMF) to a certain concentration gradient. Na/P(EO) $_x$ NaTf/Na cells are then polarized slightly and the current turned off at time, t . The cell voltage is then measured immediately. The transference number is calculated from equation 2, developed from concentrated solution theory without any assumptions about activity coefficients.

$$t_+^0 = 1 - \left\{ \frac{FD^{1/2}\delta c}{2[\text{erfc}(0)]It^{1/2}} \right\} \quad (2)$$

Although this work is not yet complete, it is already clear that t_+ is non-unity for NaCF_3SO_3 and a strong function of the salt concentration in PEO, decreasing as salt concentration increases. At any rate, this work suggests that cell performance may improve if the NaCF_3SO_3 concentration in PEO is decreased to a ratio of 20-40 ethylene oxide units per Na ion, rather than the eight that has been used up until now. Conductivities, diffusion coefficients and transference numbers are also being measured for the PEO- NaClO_4 system as well, but this work is not yet complete.

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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 $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cathodes for rechargeable thin-film Li batteries.
- Develop solid-state $\text{Li}-\text{Li}_x\text{Mn}_2\text{O}_4$ rechargeable batteries for EV applications.

Approach

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

Accomplishments

- Fabricated $\text{Li}-\text{Li}_x\text{Mn}_2\text{O}_4$ cells in which the cathodes was deposited at temperatures below 150°C by rf magnetron sputtering. One of the cells delivered 3 W/g at a discharge rate of 13 C.
- Fabricated $\text{Li}-\text{Li}_x\text{Mn}_2\text{O}_4$ thin-film cells capable of sustaining current densities of several mA/cm^2 and having a specific power of 30 W/g at an 85 C discharge rate.

Future Direction

- Continue experiments to improve the performance of $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode films deposited at low temperatures and investigate the performance of a hybrid solid-state $\text{Li}-\text{Li}_x\text{Mn}_2\text{O}_4$ cell.
-

The objective of this research is to identify methods for depositing acceptable thin-film electrodes for rechargeable Li batteries. These methods are being applied to develop solid-state $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ rechargeable thin-film Li batteries for EV applications. These batteries are expected to have several important advantages as power sources: high specific energy and energy density, long cycle lifetimes, and a wide temperature range of operation. Because they are constructed of all-solid-state components, thin-film Li batteries are intrinsically safe. Much of the research is focused on depositing thin-film LiMn_2O_4 or $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x < 1$) films at ambient temperature which can sustain the same current densities as bulk materials.

Lithium cells are fabricated by the following procedures: a LiMn_2O_4 or $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode film from 0.2 to 2 μm thick, which is deposited (by electron beam evaporation of LiMn_2O_4 followed by an anneal in O_2 at 400°C) onto a metal current collector, is covered with about 1 μm of an amorphous lithium phosphorus oxynitride ("Lipon") electrolyte deposited by magne-

tron sputtering of Li_3PO_4 in N_2 . A Li anode film about 5- μm thick having the same geometric area as the cathode is deposited over the electrolyte film by evaporation of Li metal. In some cases, a protective coating is applied so that a cell can be exposed to air without damage to the Li electrode. The cells are tested by constant-current cycling at different discharge and charge current densities. Modules are fabricated in the form of cells deposited side-by-side at the same time and cells deposited as multilayers structures.

The impedance and intermittent galvanostatic pulse measurements are made at various stages of cycling to determine the sources of cell polarization. From analysis of the impedance data, the chemical diffusion coefficient of Li^+ ions in the cathode at a cell potential of 4 V was about $10^{-12} \text{ cm}^2/\text{s}$ at 25°C. This is considerably less than the value of about $10^{-9} \text{ cm}^2/\text{s}$ reported for bulk $\text{Li}_x\text{Mn}_2\text{O}_4$, but it is consistent with our findings that the Li^+ diffusion coefficients are several orders of magnitude lower in thin films compared to bulk material of the same nominal composition. At the present time, the

low Li diffusion in the cathode limits the practical current density to 100 $\mu\text{A}/\text{cm}^2$ or less in a thin-film Li battery.

Several $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ thin-film cells were fabricated using cathodes that were, for the first time, deposited by sputtering. The targets were prepared by cold pressing and sintering LiMn_2O_4 powder that was synthesized by reacting Li_2CO_3 with Mn_2O_3 . Films were deposited onto substrates at temperatures from near ambient to about 400°C by rf magnetron sputtering of 2.5-cm and 5.0-cm diameter targets in Ar + O₂ gas mixtures. The initial results were encouraging. The targets sputtered normally, with no apparent segregation or loss of Li that often occurs with sputtering of other Li

compounds. All of the films contained the spinel phase; the degree of crystallinity and the phase purity improved with the presence of oxygen in the process gas and with an elevated substrate temperature. Increased crystallinity with substrate temperature was also evident in the film microstructure: the grain structure coarsened and the film density decreased as the film deposition temperature increased. Thin film $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells were cycled between 4.5 and 2.8 V at current densities of 10 and 20 $\mu\text{A}/\text{cm}^2$. Cells with cathodes deposited below 200°C had capacities and polarization losses comparable to those of a cell in which the cathode was deposited by e-beam evaporation and annealed at 400°C.

Na/SRPE Electric Vehicle Batteries

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Objectives

- Demonstrate cycling capability of cells containing Na negative and organosulfur-based positive electrodes.
- Develop a low-cost high-performance Na/polymer cell that utilizes an organosulfur-based positive electrode.

Approach

- Fabricate and cycle test Na/organosulfur (Na/SRPE) cells.

Accomplishments

- Approximately 80 laboratory Na/SRPE cells have been constructed and tested.

Future Directions

- Formulate initial low-cost cell design.
 - Demonstrate performance scaling of cells at least 10 times larger than current test cells.
-

The overall objective of the project is to develop a low-cost high-performance secondary cell using Na as a negative electrode, a solid polymeric electrolyte separator, and organosulfur-based cathodes (SRPE). The energy density of practical, free-standing batteries are projected to be around 200 Wh/l (150 Wh/kg), while the steady power densities are projected to be, depending on design, around 200–300 W/l (150–220 W/kg). The pulse power densities (1 min) are expected to be several times these steady-state values. The proposed batteries will be mechanically sturdy, have reliable electrical performance, operate between

about 50 and 80°C, and are expected to be immune to thermal cycling. The current goals are to characterize and improve the cycling behavior of the above mentioned Na/SRPE cells. These studies will be followed by evaluation of a number of experimental cells with a capacity of about 100 mAh.

To date, processes for making the components necessary for the Na/SRPE cells and methods to assemble the cells without any internal shorts have both been successfully developed. About 80 Na/SRPE cells have been assembled with a variety of electrolyte salts and preliminary cycling tests have been initiated.

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: alkaline, flow, molten salt, nonaqueous and solid-electrolyte. 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.

Surface Morphology of Metals in Electrodeposition/Carbon Electrochemistry

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Objectives

- 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.
- Identify the critical parameters that control the reversible intercalation of Li in carbonaceous materials and determine their maximum capacity for Li intercalation.

Approach

- 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.
- Couple electrochemical studies with physical measurements to correlate the relationship between the physicochemical properties of carbonaceous materials and their ability to intercalate Li.

Accomplishments

- A hemispherical protrusion as small as 50- μm radius was successfully attached to the surface of a micromosaic electrode which will be used in a new cells to study of the effect of protrusions on mass transport to electrodeposited surface layers.
- A mathematical model has been completed that uses the BIEM to understand the hydrodynamics of flow over protrusions.

- Improvements in the experimental apparatus have led to the observation of the coalescence of electrolytic gas bubbles (about 0.1-cm diameter) with a resolution of 10^{-5} s.
- Analysis of existing data to identify the physicochemical properties of carbonaceous materials that control the intercalation of Li in nonaqueous electrolytes suggests that no unified theory that links the physicochemical properties of carbon to the reversibility and amount of Li intercalation that occurs is available.

Future Directions

- Extend numerical modeling using FIDAP to study mass transport for flows in the turbulent region.
- Evaluate the dynamics of bubble phenomena in electrolytic gas evolution to understand coalescence behavior and its impact on the hydrodynamics and mass transfer in gas evolving systems.
- Analyze carbonaceous materials by Raman spectroscopy, transmission electron microscopy and X-ray diffraction analysis to determine the relationship between the physical properties and the intercalation of Li.

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. A new effort has been initiated to identify the critical parameters that control the reversible intercalation of Li in carbonaceous materials and to determine their maximum capacity for Li intercalation. 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 LLNL to evaluate the intercalation of Li in carbonaceous materials for rechargeable Li batteries.

Surface Morphology of Metals in Electrodeposition. A new flow cell was designed and constructed for the study of the mass transfer around a protrusion using a newly designed micromosaic electrode. This electrode consists of 50- μ m square, electrically isolated, Pt microelectrodes arranged in a cross pattern. The cell can be rotated around the axis of symmetry of the protrusion enabling detailed mass transport information to be obtained at various angles around the protrusion. The cross section of the flow

cell is 3 x 3 mm, which is sufficiently large to minimize the influence of the cell wall, and has over 50 diameters of entrance length to ensure fully developed flow. Two micromosaic electrodes have been fabricated in the Microfabrication Laboratory of EECS on the Berkeley campus. One has a 50- μ m radius, hemispherical protrusion (316 stainless steel) at the center of a cross pattern of 22 microelectrodes. The other has no protrusion. Both of these microelectrodes will be inserted into the flow cell for the measurement of mass transfer coefficients to the individual microelectrode segments using a $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. Comparison of the coefficients will determine the effect of the protrusion on mass transfer in both the laminar and turbulent regimes ($0 < \text{Re} < 4000$).

A program using the Boundary Integral Element Method (BIEM) to solve for viscous flow around an axisymmetric protrusion was completed. To supplement BIEM, FIDAP, a finite element package written by Fluid Dynamics International, will be used to solve for high-Reynolds-number laminar flows. Solution of the Navier-Stokes equations at $\text{Re}=0$, using the BIEM for flow over an axisymmetric, hemispherical protrusion, was extended to include flow trajectories. The trajectories were generated along the direction of flow in the symmetry plane. Furthermore, refinements to the code allowed the trajectories to be resolved near the wall but not near the protrusion. This enabled the discovery of two vortex regions near the electrode surface. They were located 20% of the hemisphere's radius away from the front and back of the protrusion. Trajectories very close to the

protrusion are still difficult to resolve, and this deficiency is being investigated. The flow trajectories were also computed using FIDAP in the range of $0 < \text{Re} < 10$. As expected, trajectories in the range of $0 < \text{Re} < 1$ compared well to the BIEM solution, and slight deviations were noticed at higher Re . Trajectories from the BIEM, $\text{Re} = 0$, were nearly identical to flow trajectories generated by FIDAP in the range of $0 < \text{Re} < 1$. It should be noted that the BIEM is significantly easier to implement than FIDAP because the mesh is 1-dimensional instead of 3-dimensional. Mass transfer to the electrode surface is in the process of being solved with FIDAP. FIDAP will also be used to study laminar flows at $10 < \text{Re} < 2000$.

For the study of coalescence between electrolytically generated gas bubbles, a high-speed laser-illuminated photo-detector array and associated data acquisition system developed in this laboratory has been employed. The fast phenomena associated with the coalescence and separation from the surface of two electrolytically generated hydrogen bubbles, each of the order of 0.1 cm in diameter, are recorded with a resolution of 10^{-5} sec. In agreement with theoretical predictions, the coalescence event is completed in less than 10^{-3} sec. The electrolysis apparatus built for this purpose contains two opposing micro-electrodes on which identical or dissimilar gases may be generated at slow, controlled rates. Refinements have been made to the system including incorporation of a high-power (1 W) laser to increase the optical signal strength, redesign of the detector circuit to reduce the effects of electronic noise, rearrangement of lenses to reduce the influence of diffraction and optical aberrations, and installation of a video microscope monitor and recorder for accurate electrode positioning and bubble size measurement (to ± 0.001 cm). These improvements have increased the accuracy and reproducibility of coalescence measurements and extended the range of the experiments to include 0.025-0.1 cm diameter bubble pairs. The results to date indicate that, for coalescence of 0.05-0.1 cm diameter hydrogen bubbles, the intersection ring

of the two bubbles initially moves at a rate such that its position varies with the square root of time. For coalescence of 0.025-cm diameter hydrogen bubbles, position varies with time to the 0.4 power. The result for the large bubbles agrees with a simple theory which predicts that the excess surface energy of the two-bubble configuration is initially converted to kinetic energy upon spontaneous rupture of the interfacial film. The weaker dependence of position upon time for the smaller bubbles indicates the increased importance of viscous effects. Additional observations made with the apparatus are oblate/prolate oscillations of the resultant bubbles following coalescence. These oscillations are driven by the inertia of the surrounding electrolyte and damped by surface tension.

Carbon Electrochemistry. The major thrust to date has been to identify the physicochemical properties of the carbonaceous materials which should be considered in this study. Analysis of the published literature suggests that no consensus exists on the most relevant physicochemical parameter which can influence the degree of Li intercalation in carbon. It appears that several parameters such as the $d(002)$ spacing, crystallite size in the c - and a -axis directions (i.e., L_c and L_a , respectively) and surface area are important, but their role in influencing the reversibility and amount of Li intercalation also depends on the nonaqueous electrolyte that is used in the experiments.

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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* EXAFS to obtain chemical information on Bi-doped manganese oxides.
- Use *ex situ* EXAFS to study cycled nickel oxide electrodes from zinc-nickel oxide cells and lithium manganese oxides.

Accomplishments

- Doping of manganese oxides with Group VIB metal oxides (CrO_3 , MoO_3 , WO_3) was found to improve the rate capabilities of the electrode in an electrolyte consisting of $\text{LiClO}_4/\text{PC-DME}$.
- EXAFS showed a substantial amount of Zn is present in the nickel oxide electrodes, and the Zn EXAFS was different for the electrodes obtained from three sources.

Future Directions

- Continue EXAFS studies of additives in nickel oxide and zinc electrodes.
 - Continue EXAFS studies of molybdenum and tungsten oxide electrodes.
-

The objective of this research project 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. The effort during the year included *in situ* extended X-ray absorption fine structure (EXAFS) studies of Bi-doped manganese oxides and *ex situ* studies of lithium manganese oxides and nickel oxide electrodes that were cycled in Zn/NiOOH cells.

EXAFS Studies of Bi-Doped Manganese Dioxides. *In situ* transmission EXAFS studies were done at the Bi L_3 edge and the Mn K edge on Bi-doped manganese oxide electrodes in a 9 M KOH electrolyte. Spectra were recorded at several potentials during charge and discharge. The data clearly showed evidence for the reduction to Bi metal on deep discharge. On charge, the Bi is oxidized prior to the onset of oxidation of the manganese active material. In partially charged and fully charged electrodes, the Bi is Bi(III) but is not Bi_2O_3 . There is some evidence that in the initial stages of charge, the Bi(III) species are on

the surface of the manganese oxide particles. A complete set of experiments was run at the Mn K edge at various stages of charge and discharge. This was done both for Bi-doped material and MnO_2 that had been prepared by an identical method, but without the Bi additive. The electrochemical and X-ray absorption near edge spectroscopy (XANES) results indicate that the Bi additive inhibits the kinetics of the reduction of Mn(IV) to Mn(III) and catalyzes the kinetics of the reduction of Mn(III) to Mn(II). The result is that both reduction steps occur simultaneously in the same potential region. This apparently inhibits the formation of Mn_3O_4 , a major cause of electrode irreversibility. Figure 5 shows that the short-range order of the MnO_2 is completely restored on recharge when the electrode is doped with Bi. Figure 6 shows that the undoped material forms a completely different structure on recharge. These results elegantly confirm the reversibility of the Bi doped material, particularly with respect to structure changes.

EXAFS Studies of Cycled Nickel Oxide Electrodes. EXAFS studies were made on nickel oxide

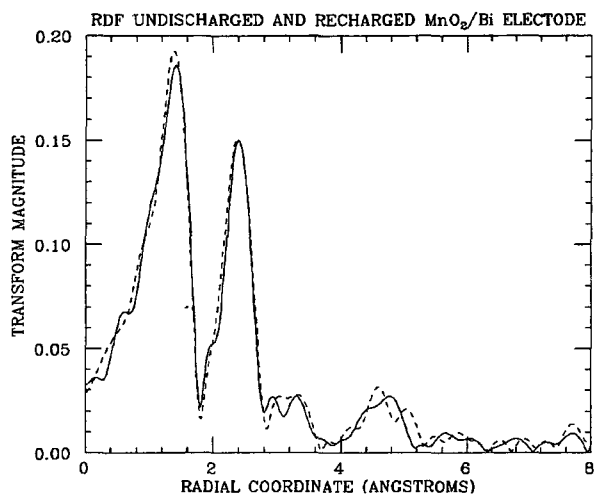


Figure 5. Fourier transform of the EXAFS for a Bi-doped MnO_2 electrode; before discharge (—), after recharge (---).

electrodes that had been cycled at LBL. The electrodes were obtained from three suppliers—Acme Electric, Eagle Picher and Johnson Controls. The EXAFS samples were prepared from electrodes that were taken apart at the end of charge and at the end of discharge of Zn/NiOOH cells. The electrodes were ground up and any Ni in the sintered electrodes was separated from the ground mix. The wet ground material was pressed into thin wafers, sealed between acrylic sheets, and sent to BNL where EXAFS data were obtained at the Co, Ni and Zn edges.

Excellent data were obtained at the Ni and Zn edges. All of the electrodes contained a substantial

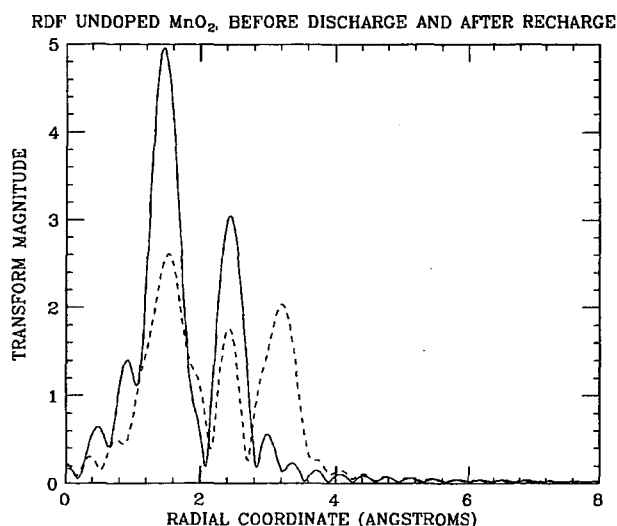


Figure 6. Fourier transform of the EXAFS for an undoped MnO_2 electrode; before discharge (—), after recharge (---).

amount of Zn. For instance, in the Eagle Picher material, the ratio of Ni to Zn was 1.68:1. The Ni active material in all of the electrodes was mostly in the discharged state, presumably because of the long time between sample preparation and the EXAFS studies (three months). The Zn data were interesting. In all cases there were differences between the Zn EXAFS in the charged and discharged electrodes. In some cases these were large. The Zn EXAFS in the charged material from Acme Electric was almost identical to that for ZnO. In the charged Eagle Picher material, the Zn EXAFS was similar to, but not identical to that for $\text{Zn}(\text{OH})_2$.

EXAFS Studies of Cr-Doped Manganese Oxides:

A series of manganese oxides mixed with Group VIB metal oxides (CrO_3 , MoO_3 and WO_3) was prepared and electrochemically characterized in an electrolyte consisting of 1 M LiClO_4 in propylene carbonate/dimethoxy-ethane (PC/DME). This electrochemical study was conducted using both potential sweep and galvanostatic techniques. All of the added oxides improved the rate capabilities of the electrode. The best results were found with an electrode that had the mol% composition of 85 MnO_2 – 15 CrO_3 , which was prepared by heating a mixture of MnO_2 and CrO_3 at 250°C for 72 h. X-ray absorption spectroscopy (XAS) measurements were made on this material at both the Mn and Cr K edges. XANES measurements at the Mn K edge indicated that some of the Mn(IV) sites were replaced with Mn(III) during thermal treatment of the mixed oxides. Similar measurements at the CrK edge indicated that the Cr(VI) was reduced to a valence state close to Cr(IV). The manganese EXAFS indicated that thermal treatment of the mixed oxides increased the number of corner-shared MnO_6 octahedra in the structure. The increased utilization and the faster kinetics for the Cr-doped electrodes was correlated with a higher Li^+ ion diffusion coefficient in these materials. The enhanced diffusion coefficient is apparently related to changes in the tunnel structure in the manganese oxide.

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Lithium-Ion Battery Testing

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Objectives

- Evaluate the performance of Li-ion cells
- Provide information on the cycle life, energy/power and impedance characteristics of the SONY Li-ion cell.

Approach

- Evaluate the performance of commercial SONY cells using the DST established by USABC by cycle testing.

Accomplishments

- Capacity and specific energy of cells that were charged to 4.2 V were about 1 Ah and >94 Wh/kg, respectively.
- Cycle life exceeded 300 cycles under DST at 100% DOD, 2800 cycles at 44% DOD.

Future Directions

- Project has been completed.
 - Final report "Electric Vehicles Dynamic-Stress-Test Cycling Performance of Lithium-Ion Cells," LLNL Report # UCRL-ID-116443.
-

The objective of this project is to evaluate the performance of Li-ion cells to determine their cycle life and energy/power characteristics under controlled conditions. In this study, cells manufactured by the Sony Corporation for use in portable electronic devices were tested. The capacity and specific energy of single cells were determined at both the 4.1 and 4.2 V charging conditions (0.45 A to voltage cutoff, followed by 3-h at constant voltage, discharge was at C/5 rate). The average capacity and specific energy of eight cells at 4.1 V charging were 0.943 Ah and 82.6 Wh/kg, respectively. The corresponding values for 4.2 V charging were 1.056 Ah and 93.9 Wh/kg, respectively. Two other cells with a more recent manufacturing date yielded average values at 4.1 V charging of 0.98 Ah and 86.3 Wh/kg, and at 4.2 V charging of 1.10 Ah and 98.0 Wh/kg.

Sony Corporation 20500 Li-ion rechargeable cells were cycled under the USABC Dynamic Stress Tests (DST) after they were received in November 1993. Initial screening was performed to determine the capacity, energy, and AC impedance of all cells under testing. Cycle life tests were then begun using the full mid-term

DST discharge "waveform" (peak power pulse 150 W/kg) with variable charging and DOD conditions.

Figure 7 shows the progression of the DST high-power-step (150 W/kg) voltage as a function of time in the given discharge for various recharge cycles for a 4.2 V charged cell (2.5 V and <100 W/kg cutoff). The run time decreases approximately linearly with recharge cycle number, and has decreased from about 250 to 200 minutes after 310 cycles (Fig. 8). Similar linear degradation has been observed under different charging and DOD conditions. It is interesting to note that the degradation rate does not appear to be a strong function of charging conditions or even the DOD (amortized for total run time). This implies that the stress of the DST is more cycle-life determining than these other factors.

The AC impedance of a new cell at various states of charge is shown in a Nyquist plot (Fig. 9). The radius of the semi-circle loop is seen to increase non-linearly with the state-of-charge, and shows a very large radius (>8 Ω) at near 100% discharge. Because of the large variance in results with state of charge, all AC impedance tests (made at various points in the cell's life) were run at

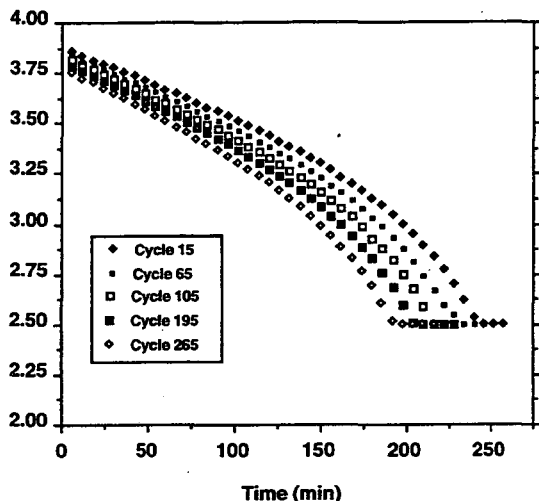


Figure 7. Change in the cell voltage with DST cycling at the high-power step.

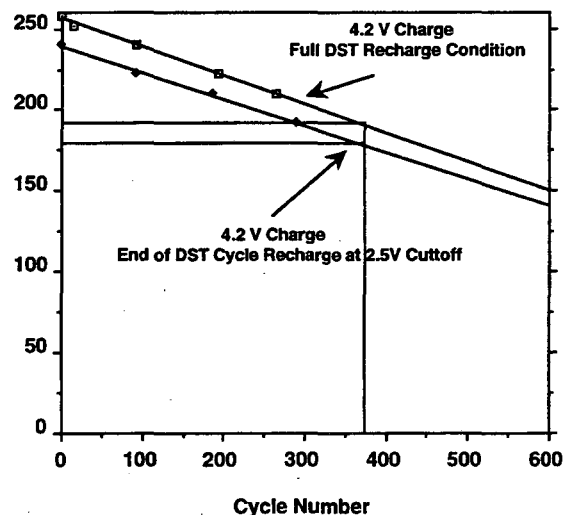


Figure 8. Variation in the run time with cycling.

3.50 V, to remove this variable from the response. Figure 10 shows the change in AC impedance for a cell cycled under full DST end-point conditions and a 4.2 V charge. Initially, the radius of the Nyquist semi-circle is almost unchanged, but the curve is shifted to the right, indicating an increasing pure-ohmic contribution. Later, the radius increases. Most cells (under less-stringent conditions) show only an increasing ohmic contribution at this point in the cycling.

More recently, some Li-ion cells which were sold as a battery for Toshiba's portable color computer were purchased and analyzed. After opening the battery casing, these cells were found to be also manufactured by Sony Corporation, though the cell design

was different than the 20500 cells (part no. US18650A). The 18650A has the same capacity and energy density as the 20500 series but are more slender in shape (thinner and longer). The most-notable difference in cell design appears to be the carbon anode. The 18650 consists of irregular-shaped carbon granules, whereas the 20500 anode uses carbon microspheres. The carbon anode "packing" density appears higher in the 18650 than in the 20500. State-of-the-art packaging technology, rather than superior chemical characteristics appear to be responsible for the excellent performance of this cell (*e.g.*, ultra-thin 0.4 mil Cu foil current collector and thin uniform films).

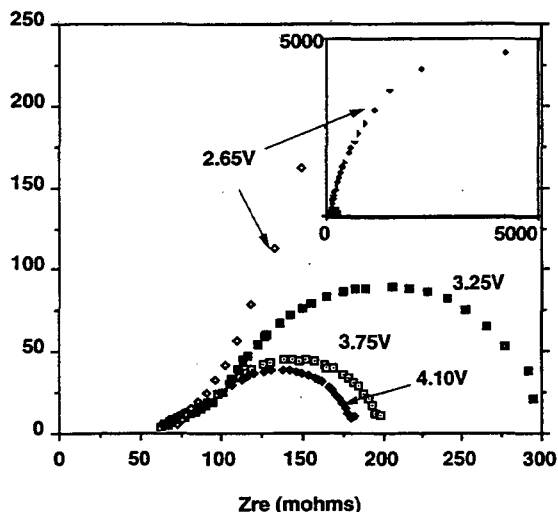


Figure 9. AC impedance of SONY cell.

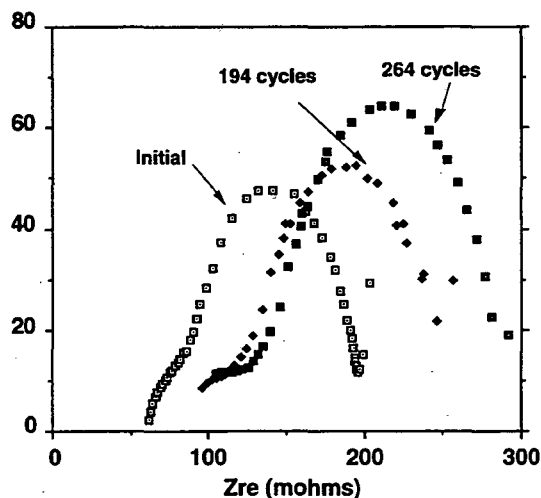


Figure 10. AC impedance for a cell cycled to DST end point and 4.2 V charge.

B. CORROSION PROCESSES IN HIGH-SPECIFIC-ENERGY CELLS

These projects aim to develop low-cost containers and current-collector materials for use in nonaqueous, alkali/sulfur and other molten-salt cells.

Corrosion-Resistant Coatings for High-Temperature High-Sulfur-Activity Applications

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Objectives

- Explore electrodeposition and CVD techniques to prepare corrosion-resistant coatings.
- Develop corrosion-resistant coatings for high-temperature batteries.

Approach

- Use molten salt electrodeposition and plasma-enhanced CVD techniques to prepare corrosion-resistant Mo-based coatings.
- Conduct theoretical studies to understand the deposition processes.

Accomplishments

- An equation that correlates the evaporation and deposition rates with the equilibrium pressure of $\text{Mo}(\text{CO})_6$ and other process variables was derived to aid in the understanding of CVD of Mo.

Future Direction

- Experimental measurements have been completed and a final report is being prepared.
-

The objective of this research is to develop corrosion-resistant coatings for cell components that are exposed to high-sulfur-activity environments in Na/S and Li/FeS₂ cells. This research is intended to assist in developing the technology for the production of Mo and molybdenum carbide (Mo_2C) coatings. Plasma-enhanced chemical vapor deposition (CVD) was employed as a new technique for preparation of thin protective films at much lower temperatures than by thermally driven CVD. A laboratory was set up for plasma-enhanced CVD and the current focus is to investigate the evaporation process for $\text{Mo}(\text{CO})_6$. The investigation of the evaporation rate in a vacuum has been carried out from a theoretical approach and experimental information concerning parameters such as the evaporation coefficient.

The application of the kinetic-gas theory to interpret the evaporation phenomena resulted in a specialized evaporation theory. As a result, the evaporation theory includes concepts of reaction kinetics, thermodynamics, and solid-state theory. Early attempts to express quantitatively the rates at which condensed materials enter the gaseous state are attributed to the research by Hertz, Knudsen and Langmuir. Generally, the theoretical maximum evaporation rate can be obtained only if as many evaporant molecules leave the surface as would be the case if the equilibrium pressure, p^* , on the same surface exists, while none of them return. The evaporation rate is equal to the impingement rate which, according to kinetic theory, is related to temperature as follows:

$$\Gamma = m (dN_e / A_e dt) \quad (1)$$

or

$$\Gamma = 5.834 \times 10^{-2} (M/T)^{1/2} p^* \quad (2)$$

Γ is the evaporation rate in g/cm²-sec and p^* is the pressure in torr.

Based on these considerations, the number of molecules, dN_e , evaporating from a surface area, A_e , during the time, dt , is equal to the impingement at the equilibrium (or saturation) pressure, p^* , minus a return flux corresponding to the partial pressure, p_i , in the evaporant of the bulk gas phase. The most general form of the evaporation rate equation is:

$$dN_e / A_e dt = \alpha_v (2\pi mkT)^{-1/2} (p^* - p_i) \quad (3)$$

This equation is commonly referred to as the Hertz-Knudsen equation, and α_v is the evaporation coefficient. There is a factor of driving force, which comes from the difference of equilibrium pressure and partial pressure of the bulk gas in the evaporation process. For $\alpha_v = 1$ and $p_i = 0$, the maximum evaporation rate results, as indicated by equation (1). The evaporation coefficient, α_v , was introduced into the Hertz-Knudsen equation to account for observed

evaporation rates that are smaller than those permitted by the equilibrium pressure. It may be referred to as the condensation coefficient and is defined as the ratio of molecules condensing to those colliding with the surface of the condensed phase.

By applying the Hertz-Knudsen equation, one can deduce the evaporation coefficient. If one assumes $p_i = 0$ under vacuum pumping condition, equation (3) can be simplified as following:

$$\Gamma = \alpha_v (2\pi mkT)^{-1/2} p^* \quad (4)$$

or

$$\Gamma = 5.834 \times 10^{-2} \alpha_v (M/T)^{1/2} p^* \quad (5)$$

The saturation pressure of $\text{Mo}(\text{CO})_6$ is $p^* = 0.12$ torr at 22°C. The change of $\text{Mo}(\text{CO})_6$ per unit area and per unit time can be obtained by weighing, which is equal to the mass evaporation rate, i.e., $\Delta W / A_e t = \Gamma$. Thus, one can calculate that the evaporation coefficient of $\text{Mo}(\text{CO})_6$, α_v , is about 10^{-3} at 22°C. Generally, α_v is strongly dependent on the surface condition. If surface contamination exists, or the pressure and temperature of the precursor is changed, the evaporation coefficient will be affected. Further analysis of $\text{Mo}(\text{CO})_6$ evaporation is in progress.

Improved Container Electrode Coatings for Na/S Battery Systems

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Objectives

- Explore sputter-deposition techniques to prepare TiN coatings.
- Develop corrosion-resistant coatings for high-temperature batteries.

Approach

- Prepare TiN coatings for corrosion studies by sputter deposition.
- Investigate ion-plating technique to prepare TiN coatings.

Accomplishments

- Prepared TiN-coated Al containment materials by sputter-deposition techniques that were corrosion-resistant for 500 h in Na_2S_4 at temperatures up to 390°C.

Future Direction

- Project has been completed.

The objective of this project is to develop improved corrosion-resistant coatings for high-temperature secondary batteries by sputter-deposition techniques. Research is underway to determine the utility of titanium nitride films as durable, corrosion protective, conductive coatings for the sulfur electrodes in Na/S batteries. Several series of sputter-deposited TiN coatings were applied to Al coupons and the resulting samples soaked in Na_2S_4 at temperatures up to 390°C for 500 h. The sputtering conditions were modified during the test series and the latter coatings showed essentially no visible signs of corrosion following the 500-h exposure tests. Electrical conductivity measurements of the films give some confirmation of their integrity following sulfide exposure. As expected it was found that proper cleaning of the Al surface was essential to achieve corrosion resistance and prevent spalling of the TiN coating. Glow discharge cleaning in the vacuum sputtering chamber produced the best film adherence.

Another series of coatings, applied by ion-plating by Balzers, Inc., was also tested by soaking in the sulfide melt. The initial test samples showed considerable flaking of the TiN coating after the exposure run. A second set of samples, however, showed no evidence of corrosion after 500-h in Na_2S_4 at 345°C .

After many and long delays, 10 Na/S battery electrode cores (aluminum) were received from Silent Power Ltd. (SPL) of Salt Lake City, UT. A TiN coating has been sputtered on one of the cores and four others are currently being prepared for deposition. When completed a set of five will be shipped to SPL for assembly into their standard sulfur core Na/S test cells.

Another four cores were shipped to Balzers for coating by their proprietary ion-plating method. This approach was stalled when it was discovered, during

preparation for their deposition, that the method by which these Al electrode cores (Fig. 11) were fabricated, incorporates a low melting, Zn-containing solder to attach the current mounting stud. The presence of this solder precludes the use of ion plating since the ion plating proceeds during both bake out and deposition with the substrate heated to $\sim 500^\circ\text{C}$. At this temperature the Zn has a vapor pressure so high that it can rapidly contaminate the deposition apparatus. This problem was discovered during their bake-out process when considerable distortion of the parts was observed. By agreement, we are presently fabricating, in-house, five additional Al electrode cores to SPL's standard dimensions, with the stud machined integrally with the core shaft. When completed these will be shipped to Balzers, coated with TiN and sent on to SPL for complete in-cell testing.

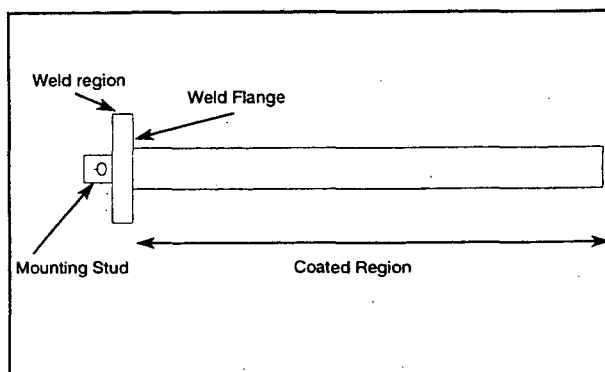


Figure 11. Aluminum electrode for sulfur core sodium sulfur battery. Shaft length = 10 cm.

C. COMPONENTS FOR AMBIENT-TEMPERATURE NONAQUEOUS CELLS

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

In Situ Spectroscopic Applications to the Study of Rechargeable Lithium Batteries

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Objectives

- Characterize reactivity of electrode/polymer and electrode/liquid electrolyte interfaces.
- Develop *in situ* spectroscopic techniques to investigate charge/discharge reactions of Li at Li/SPE interfaces.

Approach

- Conduct experimental studies under ultrahigh vacuum conditions to examine the reactivity of Li at the Li/polymer and Li/liquid electrolyte interfaces.
- Design and utilize advanced spectroscopic and thermal techniques to investigate Li/electrolyte interfaces.

Accomplishments

- TPD studies with ultra-clean Li exposed to PC suggested that the TPD peaks are consistent with a reaction that produces alkyl carbonate and lithium hydride as the main products.
- For short times of several hours, ATR/FTIR studies indicate that no reaction occurs at the Li/PEO interface.

Future Directions

- Continue experiments to investigate the interfacial reactions at Li/electrolyte interfaces with the newly constructed UHV/FTIR.
- Develop high-vacuum environmental chamber to conduct ATR/FTIR measurements of the Li/polymer interface.

The purpose of this project is to use *in situ* spectroscopic techniques to investigate the electrochemical phenomena that occur at Li/electrolyte interfaces during charge/discharge cycling. Two cell technologies are being investigated: Li/polymer electrolyte and Li/FeS₂.

***In Situ* Fe K-Edge X-ray Absorption Fine Structure Study of Lithium Insertion in Pyrite.** The effects of Li-ion insertion on the structural and elec-

tronic properties of FeS₂ (pyrite) have been examined by *in situ* Fe K-edge EXAFS using electrodes and electrolytes similar to those found in conventional, ambient-temperature Li/FeS₂ batteries. A substantial reduction in the amplitudes of the Fe-S and Fe-Fe backscattering was observed as the amount of intercalated Li in the FeS₂ lattice was increased from 0 to 2 Li⁺ equivalents, (Li⁺)_{eq}. After the insertion of two (Li⁺)_{eq}, the shells associated with the distant Fe-S

and Fe-Fe interactions were no longer discernible in the FT spectrum. Curve fitting analysis of the $k3v(k)$ EXAFS for this latter material employing *ab initio* phases and amplitudes (FEFF Version 3.25) yielded an average Fe-S distance, $d(\text{Fe-S}) = 0.229 \pm 0.002$ nm. In addition, XANES revealed a rounding of the otherwise highly structured region of FeS_2 as the amount of inserted Li was increased. This behavior is consistent with the formation of Fe_{1-x}S and thus supports the assignment made on the basis of *in situ* Mossbauer Effect Spectroscopy (MES) of the same system.

Surface Analytical Studies of Li Passive Layers in Ultrahigh Vacuum. The reactivity of metallic Li toward PC has been studied in ultrahigh vacuum (UHV) using Auger electron spectroscopy (AES) and temperature programmed desorption (TPD). All experiments were conducted with perdeuterated-PC (Icon Corp, PC-d) to avoid ambiguities in the interpretation of the TPD data derived from the presence of hydrogen in the UHV chamber. Prior to each series of measurement, the PC-d was degassed to remove products presumably originating from the reaction between PC and stainless steel. Lithium was vapor deposited from a carefully degassed SAES sources onto a clean polycrystalline Au foil substrate kept at a temperature of about 120 K. Immediately after the deposition was completed, AES spectra were recorded in selected energy regions to identify the possible presence of carbon and oxygen impurities. Lithium coverages are given in terms of percent of AES signal (%Li), where $\% \text{Li} = (I_{\text{Li}}/S_{\text{Li}})/(I_{\text{Li}}/S_{\text{Li}} + I_{\text{Au}}/S_{\text{Au}})$, I_i is the peak-to-peak height of the AES signal, and S_i is the sensitivity factor of element i . The equivalent thickness of the Li deposits can be estimated from the homogeneous attenuation of the Au AES signal by the equation $I = I_0 e^{-x/k}$, where k is the mean free path of AES electrons for Au, *i.e.*, about 1 nm. The density of Li is 0.53 g/cm^3 , which corresponds to an atomic density of $4.57 \times 10^{22} \text{ atoms/cm}^3$. Therefore a 78% Li layer has an equivalent thickness of about 1.6 nm. The PC dosing was effected immediately after deposition and AES analysis of the Li layer with all the filaments in the chamber turned off so as to reduce problems associated with PC decomposition induced by adventitious electrons.

The most significant results of TPD experiments in which either bare or Li-covered Au surfaces were exposed to 3 Langmuir (L) PC-d, while maintaining the substrate at 120 K may be summarized as follows:

- The TPD spectra of the largest mass fragment associated with the cracking pattern of PC-d ($m/e = 90$) obtained for bare Au surfaces exposed to 3-L PC-d at 120 K yielded a well-defined peak centered at about 230 K. Such a feature could not be detected when the Au surface was covered a thick Li layer (78% Li/Au) under otherwise identical experimental conditions. This clearly indicates that the interaction of PC with Li leads to the activation and further fragmentation of the molecular species on the surface.
- No evidence for any TPD peaks was found at temperatures above 240 K for PC-d adsorbed on bare Au at 120 K for all masses examined. In contrast, the $m/e = 44$ TPD spectra observed for 78% Li/Au displayed a very broad peak extending from about 260 to 520 K, and two smaller peaks centered at about 750 and 850 K. Although it is not possible to infer the structure of the adsorbed material(s) associated with the broad, low-temperature feature, the set of peaks at the higher temperature (*i.e.*, 750–850 K) are characteristic of Li carbonate.
- A very prominent $m/e = 4$ desorption peak at about 650 K, which corresponds to the thermal decomposition of Li hydride, was found in the TPD spectra of 3-L PC-d/78% Li/Au surfaces. This feature was also identified in earlier studies in this laboratory as one of the products of the reaction between condensed, perdeuterated THF (TDF) (which had been previously condensed on bare Ag at 130 K), and metallic Li, but was not observed for PC or TDF adsorbed on Au or Ag surfaces that were never exposed to Li. It may be noted that both H_2 and D_2 react with Li at room temperature to form the corresponding hydride or deuteride; therefore, it is conceivable that LiH or LiD could form by a reaction between H_2 and D_2 desorbed from the chamber walls during PC dosing. However, despite the fact that the partial pressure of H_2 in the chamber is two orders of magnitude larger than that of D_2 , and given that the chemical reactivity of the two species to produce the hydride (or deuteride) can be assumed to be the same, the $m/e = 2$ recorded during the same TPD run yielded only a very small peak at about the expected decomposition temperature of the hydride. It may thus be concluded that the D_2 originates from PC adsorbed on Li and not from other sources.

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 clearly the thermal instability of salt complex electrolytes at high temperatures.
- Predicted relatively weak ion correlation effects on conduction, due mostly to ion atmosphere (cluster hopping) processes.

Future Direction

- Continue the development of theoretical models to determine the influence of temperature, ion species, polymer chain basicity, and interionic correlations on conduction and Li transport number in polymer electrolytes.
-

The goal of this research is to apply molecular dynamics and Monte Carlo simulations to understand the conduction process in polymer electrolytes, and its modification by such parameters as temperature, density, ion species, polymer chain basicity, and interionic correlations. The results of this study should be beneficial in the development of improved polymer electrolytes for rechargeable Li batteries for EV applications.

The polymer electrolyte materials comprise single-phase dispersions of ions in an immobile solvent (a polymer host). From the point of view of optimizing the ionic conductivity, it is important to increase both the intrinsic mobility of the ions and the number of free ionic carriers. The mobility is largely fixed by the relaxation rate of the polymer host, as modified by the presence of ionic charge. This is reflected in the glass transition temperature, and in

such structural properties as the local microviscosity. Calculations of the viscosity, and its dependence upon the nature, both of the polymer host and the ion load, are now beginning. The analysis involves the use of nonequilibrium statistical mechanics (response to applied stress fields). This technique has not been previously used in our laboratory, and therefore coding is really just beginning.

We have, since the start of this research, gained some important insights and made some major strides in the area of interionic correlation, ion cluster formation and dynamics, and the static structure of the ionic environment in models for the polymer electrolyte materials. These have come both from Monte Carlo and molecular dynamics simulation.

In the Monte Carlo studies, a model is considered in which the ions are restricted to ion lattice sites, with variable density and variable temperature. The ions interact by full coulomb interactions, and appropriate periodic boundary conditions (Ewald) are used. An additional set of calculations has been completed on the identity of ions and clusters. The simulations permit (which, unfortunately, experiments do not) individual ions to be followed, and to see how they form clusters, both statically and dynamically. Figure 12 shows the identity of the cluster in which a particular cation finds itself as a function of time. In this simulation, which was run for a relatively high concentration of 5 vol% salt, the ions are very largely clustered. The identity of a particular cluster in which an ion finds itself changes dynamically and rapidly in time. This means that the notion of identifiable clusters moving (be they single ions, ion pairs, ion triples or large clusters) seems at substantial odds with the dynamics as predicted by these simple Monte Carlo hopping algorithms. This could be very important in considerations of transport numbers.

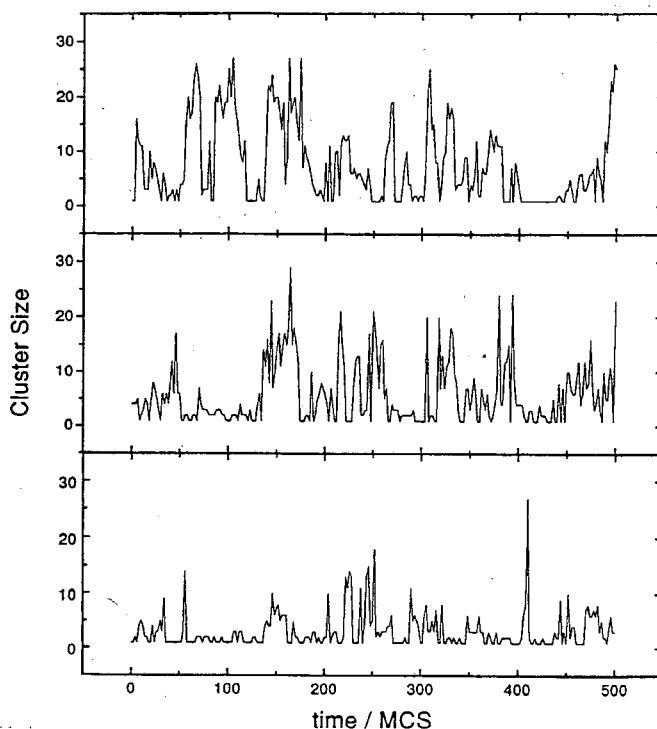


Figure 12. The time dependence of the cluster size (from Monte Carlo) to which a tagged particle belongs, for three randomly selected particles. Note the rapid change in cluster identity for any chosen ion.

These calculations show the importance of clusters, and of interionic interactions, in determining the static structure and transport dynamics in polymer electrolyte materials. The actual conductivity, which is determined both by interionic interactions and by dynamics of the solvent host, will be considered in the ongoing studies.

The Performance of New Materials for Polymer Electrolyte Batteries

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Objectives

- Synthesize polymer electrolytes based on aluminosilicate-polyether hybrid polyelectrolyte 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

- A new aluminosilicate-polyether hybrid polymer electrolyte has been synthesized and will be tested shortly.

Future Direction

- Cycle cells containing the new polyelectrolyte, a cathode consisting of 85% Li_xMnO_2 , 10% carbon and 5% binder, and a Li-metal anode.
-

The objective of this project is to synthesize polymer electrolytes based on aluminosilicate-polyether hybrid polyelectrolyte with improved low-temperature performance and higher cation transport number. These polymer electrolytes should be useful in rechargeable Li/polymer batteries. The initial effort has concentrated on the assembly of equipment and the preparation of materials. Specifically, an Ar-filled dry box was set up and tested. A bank of ten potentiostats was built and a computer interface was constructed. This interface can independently control each of the potentiostats through a LabView program that was written to log the data with typical battery testing protocols.

A new aluminosilicate-polyether hybrid polyelectrolyte material (Fig. 13) was prepared in sufficient quantity to permit battery assembly and testing. This polymer electrolyte was characterized by elemental analysis, variety of spectroscopic techniques, and temperature-dependent complex impedance. The current cell testing is performed with cells containing simple polymer-salt electrolytes. The electrolytes under investigation are amorphous $\text{PEO-LiSO}_3\text{CF}_3$ and

polybis(methoxyethoxyethoxide) phosphazene (MEEP) with LiSO_3CF_3 . The current test cells use a cathode consisting of 85% Li_xMnO_2 , 10% carbon, and 5% binder and Li-metal anodes. The data from these cells will provide a baseline for comparison with more advanced polyelectrolytes such as aluminosilicate-polyether hybrid polyelectrolyte.

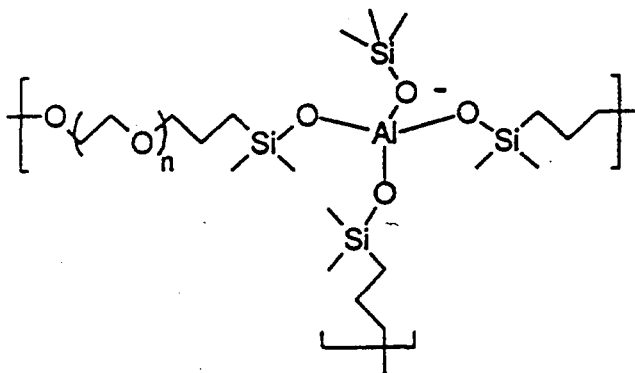


Figure 13. Aluminosilicate-polyether hybrid polyelectrolyte.

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

- Prepare sulfonated and phosphonated PBI polymers and poly(4,5-dimethyleneimidazole and hydroxy imidazole) polymers for electrochemical studies.

Accomplishments

- Precursor materials to prepare the polymer electrolytes have been synthesized.
- Preliminary conductivity measurements were conducted on poly benzimidazole films.

Future Directions

- Complete synthesis and electrochemical evaluation of novel polymer electrolytes.
 - Expand program to include sulfonated PEEK, sulfonated and phosphonated PPE and soluble polyphenylenes (Maxdem).
-

The objective of this research is to develop advanced novel polymer electrolytes for rechargeable Li batteries. Thin polymeric films will be cast and characterized by spectroscopic, nuclear magnetic resonance (NMR), thermal and electrochemical techniques. Two types of polymer materials are under investigation:

- Sulfonated and phosphonated polybenzimidazole (PBI) polymers. The labile protons will be replaced by Li to make a salt that should be stable to Li metal and should conduct well since it would have many ions per repeat. The Li transference number should be 1 since the anions are fixed on the polymer.
- Novel poly(4,5-dimethyleneimidazole and hydroxy imidazole) polymers; these are acidic and can have a very low equivalent weight per Li.

Polybenzimidazoles. PBI (Hoechst Celanese) was exposed to H_2SO_4 and H_3PO_4 at elevated temperatures (200 or 250°C) to form sulfonated and

phosphonated sites, respectively, in the films. For both H_2SO_4 and H_3PO_4 , the uptake was found to be linear with acid concentration. In H_2SO_4 , the uptake was 0.41 (gm acid/g film) in 2 M acid and 0.54 in 4 M acid. In H_3PO_4 , the uptake was 0.71 in 5 M acid and 1.02 in 9 M acid. These samples are being characterized by thermal gravimetric analysis.

Polyimidazoles. Two approaches are being used in the synthesis of polyimidazoles. In the first approach, the precursor monomer, 4,5-dimethylene ethylene carbonate was synthesized and polymerized. Experiments are underway to develop a better synthesis route for the monomer. In the second approach, a model compound for the polymer, 4,5-dimethyl vinylene carbonate, was synthesized following a literature procedure. This can be made easily in large amounts. It is easier to develop the synthesis procedures for making imidazole derivatives using this material, where the products can be isolated and analyzed, rather than working only on the polymer. Once such procedures are found, they will be refined using the polymer.

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

- Synthesis of three polymers that will contain crown ethers has been initiated.

Future Direction

- Complete synthesis of polymer electrolytes with attached crown ethers.
 - Conduct characterization studies of the polymers with respect to ionic conductivity, dimensional stability and interfacial stability.
-

The objective of this research program is to synthesize and characterize new polymer electrolytes that contain crown ethers which could have a fundamentally different mode of ion transport than those currently under investigation. The systems proposed are doped polymers with side chains having the ability to form liquid crystalline mesophases. The side chains are terminated with crown ether groups which will complex with a Li salt. It is hypothesized that these materials will create highly ordered structures, thereby forming paths through which ions can move easily. Furthermore, it is expected that these paths will decrease the distance an ion must traverse to migrate between electrodes. 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 the current systems do. The result is expected to be solid polymers with high conductivity and dimensional stability. The polymers will be prepared from Li-doped liquid crystalline monomers by conducting the polymerizations in a liquid mesophase. Acrylate-tipped liquid-crystalline monomers will be oriented and polymerized photochemically to produce these ordered polymers.

The synthesis of the three polymers required for this program has been initiated. The seven-step synthesis required to obtain these polymers share a common monomer intermediate at step four. The synthesis of this common intermediate has been started following published procedures.

Sol-Gel Electrolytes in Lithium Batteries

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Objectives

- Optimize the synthesis of solid electrolytes by sol-gel processing of alkali/silicate components.
- Develop improved solid electrolytes for rechargeable Li/oxide batteries.

Approach

- Identify suitable oxide components for our Li-ion conductors by thermodynamic analysis.
- Prepare candidate metal oxides and evaluate in electrochemical cells.

Accomplishments

- Various lithia-silicate compositions have been prepared that were found to have ionic conductivities over the range from room temperature to 400°C which show some promise for testing in Li batteries.

Future Direction

- Complete thermodynamic analysis and measure the ionic conductivity of selected metal oxides.
-

The objective of this research project is to optimize the synthesis of polymer electrolytes by sol-gel processing of alkali/silicate components, which involves combining the components in liquid form, prior to chemically reacting the solution with water to form a gel. These materials should produce solid electrolyte compositions that can be applied directly to electrode materials for rechargeable Li batteries. The approach used in this investigation is to select oxide components that are Li-ion conductors and are thermodynamically stable. Calculations will be conducted to determine the thermodynamic stability of various oxide materials. Compositions that are predicted to have increased stability will be selected from this analysis and prepared for evaluation.

The base composition in this study is lithia-silica. Various lithia-silica compositions have been pre-

pared which were found to have ionic conductivities over the range, room temperature to 400°C, that are high enough to meet the minimum values for Li batteries. Based on earlier thermodynamic calculations, alumina was selected to substitute for part of the silica. The calculations indicate that alumina has a beneficial effect in changing the conditions, relative to Li, from unstable (decreasing E) to stable (increasing E) over the temperature range RT to 400°C. Boria additions have a negative effect, whereas zirconia has a neutral effect. These predictions were used to guide the selection of initial compositions.

Lithium aluminosilicates with 5, 10 and 15% alumina substituted for silica were prepared. Facilities are being set up to measure ionic conductivity by the complex impedance method to evaluate performance of our selected compositions.

New Cathode Materials

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Objectives

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

Approach

- Synthesize Mo oxides that have crystallographic structure to permit facile intercalation of Li ions.
- Characterize the structure of the Mo oxides by X-ray diffraction analysis and evaluate materials in electrochemical cells.

Accomplishments

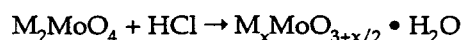
- Molybdenum oxides ($M_x\text{MoO}_{3+x/2}$, where M = cation) were synthesized using the hydrothermal method at 150-200°C.
- Layered structures were obtained which should allow for rapid diffusion of Li ions.

Future Directions

- Continue synthesis and evaluation of Mo oxides.
 - Perform electrochemical tests on new Mo oxides.
 - Expand synthesis and electrochemical studies to vanadium and manganese oxides.
-

The objective of this project is to synthesize and evaluate oxides of tungsten, Mo, and first-row transition metals for alkali-metal intercalation electrodes which are useful as positive electrodes in advanced nonaqueous rechargeable batteries. Mild hydrothermal techniques will be used for the synthesis of molybdenum oxides or, in cases where the hydrothermal technique does not lead to compounds with the highest oxidation state, electrochemical oxidation from an aqueous alkaline solution will be used to drive the cations to their highest oxidation state.

The synthesis of molybdenum oxides using the hydrothermal method at 150-200°C can be summarized by the following equation:



where M is a cation. For example, in the case where M = Na, the synthesis procedure was as follows. A 1 M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99.9%) solution was acidified with 3 M HCl to pH = 1.5 where a clear green solution resulted. This solution was then transferred to a 100-ml Teflon-lined autoclave (Parr 4744), sealed and reacted hydrothermally for days at 150°C and at autogenous pressure. The resulting pale yellow microcrystallites were collected by suction filtration, washed with water and air dried in a 50°C oven. This material was highly crystalline and consisted of hexagonal rods 30 μm in length and 5 μm in diameter. The water contained in the structure can be easily removed by heating. Similar structures were formed when Ag or ammonium was used instead of Na. The Na^+ ions can be readily ion-exchanged for hydrogen ions by immersion in nitric acid. These hydrogen ions

can subsequently be removed on gentle heating leaving a hexagonal "MoO₃".

When the tetramethyl ammonium ion was used in the synthesis, several different structures were found depending on the exact conditions of reaction. One of these clearly has a layered structure, and chemical analysis suggests the chemical formula (NMe₄)Mo_{4-d}O₁₂. This structure should allow for ready diffusion of Li ions in the interlayer regions and from one interlayer to the next. The other compounds formed with the NMe₄ cation appear to have Keggin-like structures and are not expected to be of electrochemical interest.

Rietveld analysis was performed on both molybdenum oxide phases. The chemical composition varies

slightly, but can be represented by the formula: Na_yMo_{6-x}O₁₈H_{6x-y} • H₂O, where y=1 and x=2/3. The hexagonal phase contains a large tunnel along the c-axis with a = 10.584 Å, c = 3.728 Å along the 001 axis.

Preliminary data have been obtained on the chemical lithiation of the above two classes of molybdenum oxides using n-butyl Li. This data indicates that all these phases readily react with Li, with the silver molybdate reacting with the largest quantity. This is consistent with the previous finding on the pyrochlore tungstates that the Ag compound reacted with the greatest amount of Li. Moreover, little change is seen in the lattice volume (<4%), suggesting that changes in structure should not be a cause of loss of charge on cycling; in comparison TiS₂ expands 10% on reaction with Li.

Development of High Energy Density Cathodes for Sodium/Polymer Cells

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Objectives

- Synthesize and test hexathiobenzene-based compounds and their derivatives for positive electrodes.
- Develop high-performance organic polydisulfide positive electrodes for low-temperature (ambient to 100°C) Na/polymer batteries.

Approach

- Synthesize polydisulfides based on hexathiobenzene (C₆S₆, HTB) which has up to six reducible S centers and an equivalent weight of 44 g/eq.
- Evaluate electrode performance using an array of standard electrochemical techniques, including DC charge/discharge cycling, CV, and EIS to screen potential materials to identify those with the highest sustainable current densities and practical energy densities.

Accomplishments

- Prepared HTB-based organosulfur electrodes for evaluation in Na/PEO/polyorganosulfide cells.
- Developed a rapid screening procedure for evaluation of candidate cathode materials in Na/PEO/polyorganosulfide cells.

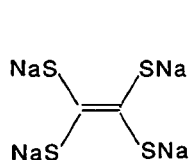
Future Directions

- Synthesize new cathode materials and evaluate electrochemical performance in Na/polymer cells.
 - Correlate electrochemical performance of cells with results of screening tests.
-

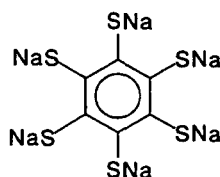
The major objective of this research is to develop high-performance organic polydisulfide positive electrodes for use in low-temperature (ambient to 100°) Na/polymer cells. This will be achieved by the synthesis and characterization of hexathiobenzene-based (HTB) compounds and their derivatives for positive electrodes. Specific parameters of investigation include the nature of any heteroatoms or side chains added to the base polymer, the structure of the polymer, the cathode thickness, the voltage stability window of the cathode, the degree of loading of the positive electrode material, the electrode construction technique, and the operating temperature of the cell. Electrodes will be judged on the basis of capacity density, energy density, discharge rate capability, and cyclability.

Polydisulfides based on HTB (C_6S_6) which has up to six reducible S centers and an equivalent weight of 44 g/eq were examined. The HTB will be modified by changing the number of S centers, by changing the ring structure, or by adding side chains to the benzene ring. The electrode performance will be tested using an array of standard electrochemical techniques, including DC charge/discharge cycling, CV, and electrochemical impedance spectroscopy (EIS) to screen potential materials to identify those with the highest sustainable current densities and practical energy densities.

The effort since the start of the project has concentrated on synthesis of electrode materials and on cell design and electrode construction techniques. Tetrasodium ethylenetetrathiolate (1) was synthesized, and hexathiolate hexasodium (sodium hexathiobenzene) (2) was purchased from an outside source. The electrochemical performance of these two materials will form a baseline for comparison with modified molecules.



(1)



(2)

A three electrode sandwich-type cell was designed which contains a organic polydisulfide positive electrode, a Na foil negative electrode, and two layers of polyethylene oxide-sodium triflate (PEO_8NaTf) electrolyte. A thin strip of Na-plated Ni foil that was placed between the layers of the electrolyte is used as a reference electrode. Nickel foil current collectors are used for both positive and negative electrodes. The cell components are pressed together using Ni backing plates secured by TFE screws. Glass plates insulate the cell from the backing plates. The cell is housed under an inert atmosphere (Ar) in a sealed, glass vessel contained in a secondary vessel which can be used to thermostat the cell. Electrical connections to the cell are made using TFE-coated Ni wires fed through Swagelok fittings at the top of the glass vessel.

The positive electrodes were fabricated from a slurry containing 45 wt% polysulfide polymer, 45 wt% PEO_8NaTf electrolyte and 10 wt% carbon black in acetonitrile (CH_3CN). Electrode films are cast directly onto Ni foil current collectors, air dried for 20 h, and then dried in a vacuum oven at 60°C for an additional 20 h. This technique gives electrodes with an active material loading of 4–8 mg/cm², and a total capacity of 10–20 mAh. The negative electrode is fabricated by rolling high-purity Na metal between polyethylene plates directly onto the Ni foil current collector. In both cases, the electrode area is 5 cm².

The electrolyte is fabricated by dissolving 67 wt% PEO and 35 wt% sodium triflate in CH_3CN . Films 0.12 to 0.17 mm thick are cast at room temperature, placed in a drying oven at 70°C overnight, and then vacuum dried for 2 h at 45°C. These films are cut slightly oversized with respect to the positive and negative electrodes to protect against shorting during cell assembly.

D. CROSS-CUTTING RESEARCH

Cross-cutting research is carried out to address fundamental problems in electrocatalysis, 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 computer techniques to develop mathematical models

Accomplishments

- The important physical processes taking place in the galvanostatic charge and discharge of a Li/polymer/insertion cell have been identified.
- A mathematical model has been developed that elucidates the dynamic changes in the secondary cells with charge or discharge, and this model has been extended to examine the behavior of the "Rocking Chair" configuration.

Future Direction

- Continue mathematical modeling to consider the behavior of electrochemical capacitors and metal hydride cells.
-

The object of this program is to improve the performance of electrochemical cells used in the interconversion of electrical energy and chemical energy by identifying the phenomena which control the performance of a system. These phenomena are incorporated into a mathematical model which can predict system behavior. The models aid in the recognition of important parameters that are crucial to the optimization of a given electrochemical system.

Although each electrochemical system has its own distinguishing features, all may be described by the fundamental principles of transport phenomena, reaction kinetics, materials science, and interfacial phenomena. The computer implementation of numerical methods permits the complex interactions of these phenomena to be treated without the need for gross mathematical and physical approximations. Experiments may then be used to confirm and refine the computer models and to determine the physical parameters necessary for a complete, quantitative understanding of the systems. The results of the computer models indicate what aspects of the system limit its performance, and can often suggest what

changes in the system might lead to its optimization.

The important physical processes taking place in the galvanostatic charge and discharge of a Li/polymer/insertion cell have been identified. A mathematical model has been developed that elucidates the dynamic changes in the cell with charge or discharge and provides guidelines for scale-up and optimization of such cells. This model has been extended to examine the behavior of the "Rocking Chair" configuration, which is based upon two materials which insert Li at different potentials. The model has also been used to study relaxation phenomena in the Li/polymer battery system, and the effort will be extended to provide experimental verification of the model by performing simulations of a well-characterized system which is the Na analog of the Li/cobalt dioxide cell. Along these lines, transport properties and thermodynamic data over a wide range of salt concentrations will be gathered for the polymer electrolyte: polyethylene oxide/sodium trifluoromethane-sulfonate. This will be the first measurement of a complete set of transport properties for a concentrated polymer electrolyte system in the Li battery field. A thermal model has been devel-

oped which predicts the heat generation of a Li/polymer battery during cycling.

A new mechanism explaining the phenomena of oscillations in electrochemical systems has been proposed and justified. Improvements on the basic model involve the inclusion of the possibility of salt precipitation inside of the separator. There is growing evidence that this is an important phenomenon in concentrated polymer electrolyte systems. Also, the model is being modified to predict the impedance response of the Li/polymer battery, and this will be compared to experimental data. This will provide insights into the measurement of important physical properties which govern the behavior of this battery system. The thermal model of this system will be extended to include prediction of thermal stability.

The important phenomena related to electrochemical double-layer capacitors and so-called "supercapacitors" have been identified, and work has begun on the modeling of these devices. The charge and discharge of electrochemical capacitors, including the effects of pseudocapacitance, is being modeled under various loads. Guidelines for the design of large-scale energy storage devices utilizing this principle will be identified.

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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 in advanced secondary batteries for EV applications.
- Evaluate the management of the temperature of Li/polymer batteries for optimum performance and to avoid temperature excursions that could damage the battery.

Approach

- Utilize mathematical models to analyze the thermal conduction properties of Li/polymer batteries.

Accomplishments

- A two-dimensional mathematical model for the thermal behavior of Li-polymer batteries was developed, and the results demonstrate that thermal management may not be a serious problem for these batteries under low discharge rates.

Future Direction

- Complete development of a three-dimensional mathematical thermal model of a Li/polymer battery and initiate experimental measurements of the thermal properties of cell components.
-

This new project was initiated in FY94 to investigate, by mathematical modeling and experimental measurement, heat generation and transport in advanced secondary batteries for EV applications. The objectives of this project are to evaluate the management of the temperature of the battery for optimum performance and avoiding temperature excursions damaging to the battery. The initial investigation is on Li/polymer batteries that are under development to operate in the temperature range of ~ 60 to 140°C which is needed to obtain sufficient polymer conductivity and to avoid overheating.

Mathematical modeling of heat transport in Li/polymer batteries is underway. A two-dimensional mathematical model for the thermal behavior of Li-polymer batteries was developed, and the results demonstrate that thermal management may not be a serious problem for these batteries under low discharge rates. However, under high discharge rates, the temperature of a battery may increase significantly if the thickness of a cell stack exceeds a certain value. Because of the low thermal diffusivity of the polymer, improvement of cooling around the stack is ineffective in large stacks.

The present work is being extended to consider a three-dimensional mathematical model to simulate

heat generation/transport under dynamic load conditions (Simplified Federal Urban Driving Schedule). The simulated results to date indicate that the major thermal management problems under practical driving conditions are to maintain battery temperature within a practical range and to keep temperatures uniform so as to achieve balanced utilization of active materials and avoid thermal stresses. The mathematical models will be employed to study the effectiveness of different arrangements of cooling channels and suggest suitable insulating materials.

The properties of battery materials, particularly the polymer(s) are not available in the open literature. An effort has been started to measure the thermal diffusivity and heat capacity of a representative polymer using facilities in the Thermophysical Properties Laboratory at Purdue University.

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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 ellipsometry, light scattering, Raman spectroscopy and scanning electron microscopy to monitor the formation of surface layers on secondary battery electrodes.
- Incorporate foreign ions in porous nickel oxide electrodes to improve the cycle performance in an alkaline electrolyte.

Accomplishments

- A newly developed technique for low-energy ion implantation, MP/III, was used to implant Co, Zr and Pb in nickel oxide electrodes. Co-implanted Ni electrodes appear to have a higher coulombic storage capacity than comparable electrodes without the addition of Co. However, a similar beneficial effect of doping with Zr or Pb in nickel oxide was not observed.

Future Direction

- Continue studies of the effect of ion-implantation on the performance of nickel oxide electrodes and the use of ellipsometry and Raman 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. Prior work on the evaluation of ion implantation as a means to improve the corrosion resistance of Pb battery electrode current-collector materials has been completed, and the present research seeks to characterize the transformation of surface phases that accompanies the charging and discharging of Ni electrodes in alkaline electrolytes.

Ellipsometric-Electrochemical Study of Oxide Film Formation on Nickel Electrodes. To examine the electrochemical interconversion between $\text{Ni}(\text{OH})_2$ (predominant species on a discharged Ni electrode) and NiOOH (predominant species on a charged Ni electrode), and search for an effective way to improve the utilization of active material in porous NiOOH battery electrodes, we have been studying the effects of foreign cations on the electrochemical behavior of solid Ni electrodes. Of special interest is to characterize the effects of Co additions on the film-forming properties of Ni electrodes, because Co additions are known to increase the charge-storage capacity of porous NiOOH battery electrodes. The exact mechanism by which substituted cations promote or

degrade the electrochemical interconversion between Ni(OH)_2 and higher-valent Ni oxides is not well understood, and the elucidation of this process is a primary focus of this research effort. Because the electrochemical oxidation of Ni^{2+} species is always accompanied by the unwanted (parasitic) O_2 -evolution reaction at the Ni electrode surface, there exists a strong motivation to modify the Ni electrode surface properties. Needed is an appropriate surface treatment that will not only improve the utilization of Ni active material (perhaps by promoting the formation of Ni^{4+} species during the charging process), but also suppress the O_2 -evolution reaction.

Electrode surface-modification experiments were conducted using Co, Zr and Pb additions to make the conductivities of both Ni(OH)_2 and NiOOH more equal to each other, and to decrease the electrocatalytic activity of the electrode surface for O_2 evolution. These elements were introduced into the surface layers of the Ni electrodes using a newly developed low-energy ion implantation technique known as Metal Plasma Immersion Ion Implantation (MPIII). The MPIII electrode bias potential and the duty cycle of the substrate bias pulser were controlled at -2 kV and 50%, respectively, to produce an ion-penetration depth of ~2-3 nm. The dose level of implanted ions was estimated to be $\sim 2 \times 10^{16}$ atoms/ cm^2 , and the atomic fraction of foreign atoms at the electrode surface was estimated to be 30-40%, which is a much higher level than that in electrodes implanted with medium-energy ions. Compared to Co-free Ni electrodes, the electrochemical potentials corresponding to the transformations between Ni(OH)_2 and NiOOH during both oxidation and reduction processes shifted to more-negative (reducing) values, and a higher coulombic capacity was obtained. This is the case for the electrodes prepared by using both low- and medium-energy Co implantation. In addition, *in situ* ellipsometric measurements detected a significant amount (up to 30% by volume) of inactive material (probably Co oxide) on the surface of the Co-implanted Ni electrodes.

It has been reported that Zr and Pb may suppress the O_2 -evolution reaction, however our initial experiments provided no evidence for such a beneficial effect when these elements were implanted into Ni electrodes. It is possible that passivating Zr or Pb compounds formed on the Ni electrode surfaces and inhibited NiOOH-Ni(OH)_2 interconversion. Experiments to further characterize ion-implanted Ni electrodes are underway.

Raman Spectroscopic Studies of the Electrochemical Behavior of Nickel Oxide Electrodes. A new Raman spectroscopic study of the surface films that form on Ni electrodes in alkaline electrolytes during charge-discharge cycling was initiated. The molecular sensitivity of Raman spectroscopy complements the ellipsometric study of Ni electrode surfaces described above. The goal of the Raman effort is to help determine the mechanism by which additives such as Co alter Ni-electrode film-formation processes and electrochemical properties. For example, if we can identify the chemical states of the Co and Ni species in the films, we can then determine whether Co forms a new surface phase, or instead modifies the properties of the NiOOH/Ni(OH)_2 surface layers. We will also seek molecular-spectroscopic evidence for Ni^{4+} species formation, and try to identify means to stabilize this highly oxidized form of Ni.

Three different experimental strategies will be employed to characterize film formation on pure and ion-implanted Ni electrodes: *i)* Normal *in situ* Raman spectra will be recorded during constant-current charge-discharge cycling, thereby providing data under the same experimental conditions used in the prior ellipsometric-electrochemical experiments. *ii)* Surface-enhanced Raman scattering (SERS) experiments will be attempted using a previously established method wherein a small amount of Ag is deposited onto the Ni electrode. In this case, the structure of the deposited Ag will enhance the Raman signal-to-noise ratio, however the presence of Ag may alter the chemical environment at the Ni electrode surface. *iii)* We will also try to develop a SERS technique in which an acceptable signal-to-noise ratio is obtained without relying upon Ag deposition. In all cases, the experimental regimen will not only replicate those under which ellipsometric data have been previously recorded, but also approximate the conditions in porous NiOOH battery electrodes.

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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 LEED to study single crystals; HREM in the case of carbon electrode materials; and EXAFS for organometallic catalysts.
- Utilize LEIS and AES to study the composition of sputtered and UHV-annealed polycrystalline Pt-Ru bulk alloys for methanol electrocatalysis.

Accomplishments

- Annealing at 800°C in UHV causes a strong surface enrichment in Pt for equilibrated Pt-Ru alloys. The alloy with a hcp bulk lattice (9.5 at% Pt) exhibited a larger segregation than the fcc alloys (>35 at% Pt), which was rationalized with the lattice mismatch between the bulk and the surface face structure, resulting in a loosely packed surface. The Pt surface enrichment of annealed bulk alloys was contrasted with the segregation observed for bimetallic supported clusters of Pt and Ru.

Future Direction

- Extend studies to consider methanol electrooxidation on Pt-Ru electrocatalyst particles.
-

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 relationship between the kinetics of electrode processes and the atomic structure of the electrode surface is being investigated. Processes under study include methanol oxidation electrocatalysis by ordered alloys, oxygen electrocatalysis by organometallic complexes, and the corrosion of carbon electrode materials. Atomic-level structure determination is made using a variety of techniques, depending on the material under study: low energy electron diffraction (LEED) in the case of single crystals; high resolution electron microscopy (HREM) in the case of carbon electrode materials; and EXAFS in the case of organometallic catalysts.

Low-energy ion-scattering spectroscopy (LEIS) and

AES were performed on sputtered and UHV-annealed polycrystalline Pt-Ru bulk alloys over the entire compositional range. LEIS spectra were acquired with an estimated sputter damage of less than 0.5% of a monolayer by employing 4 He⁺ ions with an energy of 2 keV and a current density of 20 nA/cm². The partial overlap of the scattering peaks of Pt and Ru made it necessary to devise a method to numerically fit the data. LEIS showed that sputter-cleaning with 0.5 keV Ar⁺ ions at 63° incidence does not effect any preferential sputtering. Annealing at 800°C in UHV causes a strong surface enrichment in Pt for equilibrated Pt-Ru alloys. The alloy with a hcp bulk lattice (9.5 at% Pt) exhibited a larger segregation than the fcc alloys (>35 at% Pt), which we rationalized with the lattice mismatch between the bulk and the surface face structure, resulting in a loosely packed surface. Second-layer compositions of annealed specimens were extracted from AES and LEIS data, utilizing a calibration method based on Auger signals of the continuously sputtered surface. A smooth decay of the enriched outermost layer composition towards the bulk

composition was assessed. The Pt surface enrichment of annealed bulk alloys was contrasted with the segregation observed for bimetallic supported clusters of Pt and Ru. Ideal solution thermodynamics, utilizing surface free energy data and molar surface area data from the literature, was able to predict the measured segregation for the UHV-annealed bulk alloys.

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Effect of Electrocatalyst and Electrolyte Composition on Methanol/Air Fuel Cell Performance

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Objective

- Elucidate the mechanism of methanol electrooxidation on electrocatalysts for DMFCs.

Approach

- Utilize well-characterized Pt-Ru alloy electrodes as electrocatalysts to investigate the electrooxidation of methanol.
- Employ LEIS and AES to study the composition of sputtered and UHV-annealed polycrystalline Pt-Ru bulk alloys.

Accomplishments

- The optimum surface composition of Pt-Ru varied with temperature, from ~10 at% at 25°C to ~30 at% at 60°C. The shift in optimum composition with temperature was attributed to a shift in the rate-determining step from CH₃OH adsorption/dehydrogenation at room temperature to the surface reaction between the dehydrogenated intermediate and surface oxygen at 60°C.

Future Direction

- Determine material balance for methanol electrooxidation in laboratory-scale fuel cells with Pt-Ru electrocatalyst.

There is a strong need to develop a fuel cell that can electrochemically oxidize liquid fuels, and the successful development of a direct-methanol fuel cell (DMFC) would represent a major advance for fuel-cell-powered vehicles. However, some major obstacles must be addressed before acceptable perfor-

mance can be attained with DMFCs. The oxidation rate of CH₃OH is several orders of magnitude lower than that of H₂ on a Pt catalyst, and oxidation products other than the expected H₂O and CO₂ were observed in some cases. The problem of the slow oxidation rate of CH₃OH has been partially addressed by

utilizing bimetallic catalysts. Previous work in this laboratory has confirmed that a Pt/Ru catalyst supported on graphitized carbon has a significantly higher catalytic activity for the oxidation of CH_3OH than supported Pt alone.

The electrooxidation of CH_3OH in H_2SO_4 electrolyte on well-characterized Pt-Ru alloy electrodes was studied over the temperature range from 25–60°C. The relationship between the bulk and surface compositions of annealed and sputter-cleaned alloy electrodes was determined definitively in UHV via LEIS and AES. The rate-limiting step in the electrooxidation of CH_3OH on sputter-cleaned Pt-Ru electrodes at 25°C was shown to be the initial adsorption/dehydrogenation of CH_3OH on Pt surface atom ensembles, resulting in an optimum Ru surface composition of ~10 at%; conversely, Ru-rich surfaces retard the CH_3OH oxidation reaction because Ru is inactive towards the dissociative adsorption of CH_3OH . However, the nucleation of O_2 -containing species on bare Ru atoms at low electrode potentials promotes the oxidative removal of CH_3OH dehydrogenation fragments, thereby preventing the long-term deactivation of Pt-Ru electrodes. This bifunctional character of Pt-Ru alloys was verified in measurements of their electrocatalytic activity toward the electrooxidation of CO. The nucleation of O_2 -containing species on Ru surface atoms significantly enhanced the oxidation rate of adsorbed CO, producing a catalytic shift of 0.25 V for an alloy with the optimum Ru surface composition of ~50 at%. The same optimum Ru surface composition was observed in the electrooxidation of HCOOH , which similar to CO interacts with both Pt and Ru surface atoms. For the CH_3OH electrooxidation reaction it was found that the activity of Ru toward the dissociative adsorption of CH_3OH is a strong function of temperature. This change in the adsorptive nature of the Ru sites with temperature produced a variation in the optimum surface composition with temperature, from ~10 at% at 25°C to ~30 at% at 60°C. The shift in optimum composition with temperature was attributed to a shift in the rate-determining step from CH_3OH adsorption/dehydrogenation at room temperature to the surface reaction between the dehydrogenated intermediate and surface oxygen at 60°C. Methanol oxidation current densities at 0.4 V in 0.5 M H_2SO_4 and 0.5 M CH_3OH for various temperatures are shown in Fig. 14 for an alloy with the optimum Ru surface composition under these conditions (~30 at%). The apparent activation energy for this surface was measured to be 60 kJ/mole as inferred from an Arrhenius plot of $\ln(i)$ vs $1/T$ (insert in Fig. 14). Current densities in terms of current per unit mass of exposed

metal for our smooth model catalysts are in good agreement with activities measured on supported high-surface-area electrodes, suggesting that there is no fundamental difference between these two types of catalysts, i.e., that there is no significant particle-size effect or metal-support interaction.

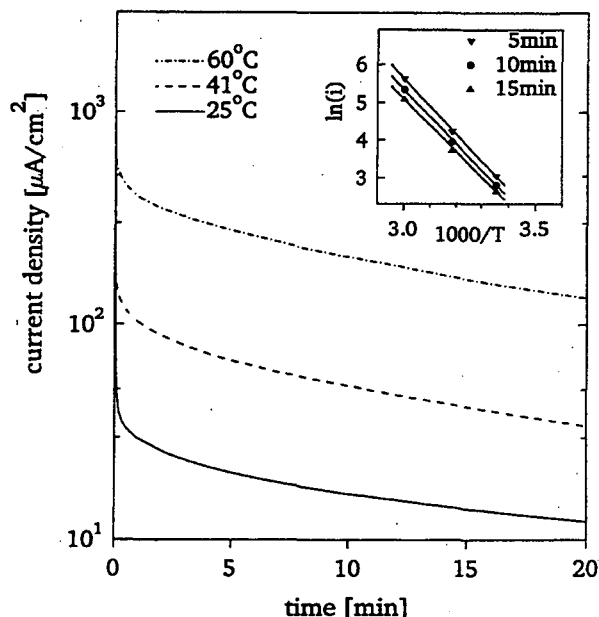


Figure 14. Transient CH_3OH oxidation current densities recorded at various temperatures. The inset illustrates the Arrhenius-type behavior of these data.

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Poisoning of Fuel Cell Electrocatalyst Surfaces: NMR Spectroscopic Studies

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Objective

- Obtain information on the nature of the poisoning intermediate(s) in CH_3OH electrooxidation on Pt-based electrocatalysts by NMR.

Approach

- Apply NMR spectroscopy to obtain information about surface poisoning on Pt supported on graphite and Pt anodes in sulfuric acid containing methanol.

Accomplishments

- Experiments are underway to detect and characterize the signal from ^{13}CO adsorbed on the electrodes from ^{13}CO -saturated 0.5 M aqueous H_2SO_4 under open-circuit cell conditions.

Future Direction

- Establish the feasibility of NMR to detect surface poisons during methanol electrooxidation.

Platinum is the most active single-component catalyst for CH_3OH electrooxidation in DMFCs; however, poisoning reactions at the surface render the anode ineffective under target operating conditions. Recently, a number of *in-situ*, on-line, and *ex-situ* techniques have been utilized to obtain information on the nature of the poisoning intermediate(s) in this system. Significant advances have been made towards this end, although no present technique can yield information on practical (supported, dispersed) electrocatalysts *via in-situ* analysis.

NMR spectroscopy is a quantitative, non-destructive, bulk method of probing the chemical environment of a specific nucleus and has been used successfully as a tool for identifying and characterizing chemisorbed species in gas-phase catalysis. To achieve high sensitivity, NMR requires large sample sizes, which translates into large surface areas for interfacial studies. NMR is therefore particularly well suited, and indeed limited to, studies of practical catalysts. Our research seeks to extend the application of NMR spectroscopy to obtain information about surface poisoning on graphite-supported Pt and Pt-alloy anodes in H_2SO_4 electrolyte containing CH_3OH .

Because CO has been postulated as the main poisoning adsorbate in the CH_3OH electrooxidation reaction, as suggested by *in-situ* IR studies on smooth

Pt electrodes, preliminary studies were conducted on a model system of adsorbed ^{13}CO . An electrochemical cell for use inside an NMR probe for the observation of ^{13}C magnetization in a 5-cm bore 63 kG magnet was designed and constructed (Fig. 15). The

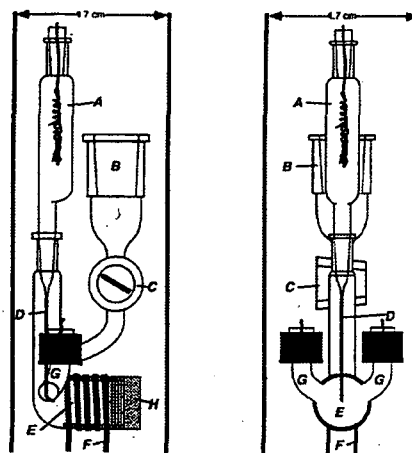


Figure 15. Side and rear views of a probe cell used for NMR studies of fuel cell electrocatalyst interfaces. (A) static H_2 reference electrode; (B) electrolyte fill port; (C) stopcock; (D) Luggin capillary; (E) working electrode chamber; (F) NMR coil; (G) sidearms for working electrode lead and counter electrode; (H) PTFE end cap.

working-electrode material is composed of 20 wt% metal on Vulcan XC-72 supported on a carbon cloth. This cloth is rolled tightly to form a cylindrical porous plug, filling the working electrode chamber inside the NMR coil with an active catalyst surface area of $\sim 3 \text{ m}^2$.

Preliminary experiments have detected the signal from ^{13}CO adsorbed on a 5% Pt/SiO₂ catalyst from the gas phase. Experiments are underway to detect

and characterize the signal from ^{13}CO adsorbed on the electrodes described above from ^{13}CO -saturated 0.5 M aqueous H₂SO₄ under open-circuit cell conditions. With these initial studies we hope to establish the feasibility of NMR for providing *in-situ* information on adsorption at the electrode-electrolyte interface. These studies are expected to provide a firm base for investigating the surface poisoning behavior of the CH₃OH electrooxidation reaction.

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. METAL/AIR CELL RESEARCH

Metal/air cell research addresses O₂ electrocatalysis; bifunctional air electrodes, which are needed for electrically rechargeable Zn/air cells; and novel alkaline Zn electrode structures.

Novel Concepts for an Oxygen Electrode in Secondary Metal-Air Batteries

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Objectives

- Investigate the electrochemical stability of graphitized carbons and metal oxides in bifunctional air electrodes.
- Provide improved bifunctional air electrodes for electrically rechargeable metal/air batteries.

Approach

- Fabricate bifunctional air electrodes using graphitized carbon and selected metal oxide electrode catalysts and evaluate their performance in half-cell tests.
- Determine the cycle life of these electrodes in Zn/air cells.

Accomplishments

- Electrodes with a graphitized acetylene black for the support and NiCo₂O₄ and either CoTMPP or La_{0.6}Ca_{0.4}CoO₃ as electrocatalysts have operated for over 100 cycles in 35 wt% KOH at room temperature.

Future Direction

- Complete evaluation of electrodes in both half and single cells in 1994.

The objective of this research is to develop improved bifunctional air electrodes for electrically rechargeable Zn/air cells. The successful development of bifunctional air electrodes depends on selecting electrochemically stable support materials and electrocatalysts for O₂ reduction and evolution, and the fabrication of suitable porous structures that are

capable of extended operation. In this program, the properties of corrosion-resistant substrates such as semi-graphitic carbon, graphite or non-carbon materials were investigated. For the electrocatalyst, stability in a strongly alkaline environment and over the range of potentials from -300 to +700 mV *vs* Hg/HgO was considered. The structure must provide the

three-phase boundary necessary for the electroreduction of oxygen and yet be suitably hydrophobic to prevent flooding of the electrode by the electrolyte.

The major effort has focused on developing a viable electrocatalyst and support consisting of a graphitized form of either Shawinigan Black or Cabot Monarch 120 in the active layer. The first phase explored the use of "monocatalysts": *a*) nickel cobaltite (NiCo_2O_4), *b*) cobalt oxide (Co_3O_4), and *c*) pyrochlores ($\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$ and $\text{Pb}_2\text{Ir}_2\text{O}_{7-y}$). The performance of several electrodes was determined in both half-cell studies and in single Zn/air cells, using a simple cycle to provide both charging and discharging conditions.

The higher loading used in some of the electrodes containing NiCo_2O_4 or Co_3O_4 as catalyst did not provide a significant performance advantage. Furthermore, no immediate advantages were evident using Cabot Monarch 120 as the substrate rather than Shawinigan Black. The pyrochlore catalysts consistently showed superior activity in the discharge cycle (oxygen reduction), leading to a better overall energy efficiency. No advantage was observed in using the ruthenate rather than iridate in terms of extended performance. The anodic polarization behavior for all of the electrodes was surprisingly similar, suggesting that the low surface areas of the pyrochlores may have limited their catalytic activity. The single Zn/air cell tests, completed in the facilities at MATSI Inc. (Atlanta, GA) established promising performance with the electrode incorporating NiCo_2O_4 into the active layer and using Cabot Monarch 120 as the substrate.

The scope of the program was broadened to include the use of two electrocatalysts (a "bicatalyst" approach), *i.e.*, to incorporate two catalysts into the active layer of the electrode. Again a series of electrodes was fabricated, using either the graphitized Shawinigan Black or graphitized Cabot Monarch 120 as the substrate. The list of electrocatalysts was expanded to include two additional catalysts, the

perovskites—lanthanum nickelate and lanthanum calcium cobalt oxide. The composition of the active layers for the eight electrodes are tabulated.

No.	Carbon	Catalyst(s)
1	SB	LaNiO_3
2	SB	$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$
3	SR	LaNiO_3
4	SR	$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$
5	SB	$\text{NiCo}_2\text{O}_4 + \text{CoTMPP}$
6	SR	$\text{NiCo}_2\text{O}_4 + \text{CoTMPP}$
7	SB	$\text{NiCo}_2\text{O}_4 + \text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$
8	SR	$\text{NiCo}_2\text{O}_4 + \text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$
SB	Shawinigan Black	
SR	Cabot Monarch 120	

The synthesis of the two perovskites proved more difficult than anticipated, the thermal decomposition of the amorphous citrate complex resulted in "detonation". It was therefore necessary to use conventional approaches, thermally decomposing a mixture of the nitrates to give catalyst powders, which yielded fairly low surface areas.

After fabrication of the electrodes, four single Zn/air cell tests were initiated (R. Putt, MATSI Inc.) using the electrodes number 1-4, operating in 35 wt% KOH at room temperature under cyclic conditions: *i*) cathodically polarized at 10 mA/cm² for 4 h; *ii*) anodically polarized at 5 mA/cm² for 8 h.

Half-cell tests were completed with the electrodes number 5-8, again in 35 wt% KOH at room temperature and under the same cyclic conditions. The electrodes using graphitized Cabot Monarch 120 as the substrate in the active layer both failed quickly, completing only 25 cycles. In contrast electrodes 5 and 7, with graphitized Shawinigan Black as the substrate in the active layer, realized over 100 cycles, accumulating over 1200 h of operation.

B. 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.

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 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

- LANL was awarded U.S. Patents describing the developments in membrane catalyst layers for fuel cells (No. 5,211,984, issued May 18, 1993; No. 5,234,777, issued Aug 10, 1993) and the use of the thermoplastic (TBA⁺) form of the ionomer (No. 5,234,777, issued Aug. 10, 1993).
- Freeze-thaw cycle tests of PEM fuel cells demonstrated no deleterious effect on performance. These results suggest that the direct application of a thin-film catalyst to the membrane generates a very good bond between catalyst and membrane to effectively prevent delamination under the demanding freeze-thaw cycling conditions.
- A new flow-field design was designed for PEM fuel cells which contains a macroporous flow field for the reactant gases. Higher limiting currents were obtained than in cells with ribbed flow fields.
- The removal of the gas diffusion anode backing layer was found to dramatically improved the performance of a DMFC at 80°C, with both liquid and vapor feeds.

Future Directions

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

The primary focus of this program is to develop efficient and cost-effective polymer electrolyte fuel cells (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.

Pt/C Electrode Optimization

LANL Membrane Electrode Assemblies. Two important developments have occurred during this year related to ultra-low loading, high-performance membrane electrode assemblies for PEFCs.

(1) A U.S. Patent (No. 5,211,984, issued May 18, 1993) entitled "Membrane Catalyst Layer for Fuel Cells" which covers this work has been issued to Mahlon Wilson of LANL as Inventor and assigned to the University of California. A second U.S. Patent, (No. 5,234,777, issued Aug. 10, 1993) describing the latest developments in this technique based on the use of the thermoplastic (TBA⁺) form of the ionomer has been subsequently granted to the same Inventor/Assignee.

(2) The first licensing agreement has been signed with a U.S. industrial company to utilize LANL technology for membrane/electrode assemblies in PEFCs.

The licensing agreement originated from a Commerce Business Daily announcement early in 1992, to which several companies responded. There are strong indications that the thin-film membrane/electrode technology developed as part of this program at LANL will soon be implemented in proton-exchange membrane (PEM) fuel cell stacks being developed for high performance and reliability at very low Pt catalyst cost. This catalyst layer technology has been developed at LANL during the last three years, and provides effective methods for applying robust thin-film catalysts onto ionomeric membranes. Such films contain extremely low Pt loadings (about 0.1 mg Pt/cm²). Industrial interest in the process has been substantial. For example, DuPont has clearly stated that their business decisions regarding PEM fuel cells have changed as a result of the development of this catalyzed-membrane technology. During the year, significant interest in this catalyst technology was expressed by representatives of several U.S. industries contemplating the development of effective, low-cost PEM fuel cell stacks for transportation applications.

CO₂ Tolerant Pt-Ru Anodes. The deleterious effects of CO₂ observed with a Pt-based PEFC anode catalyst were reported in 1992. With a simulated reformate anode feed stream of 75% H₂, 25% CO₂ (containing less than 2 ppm CO), a loss of about 250 mA/cm² at 0.50 V was observed. This loss was much greater than expected from dilution effects alone, and it was suggested that either electrochemical reduction of the CO₂ or the reverse water-gas shift process taking place at the Pt anode catalyst was responsible for the *in-situ* formation of CO. As an extension of this study, Pt-Ru anode catalysts were tested in fuel cells because of their ability to catalyze the oxidation of CO. A Johnson-Matthey FCA-6X catalyst (8% Pt, 12% Ru/C) was used with different catalyst loadings. The effect of 25% CO₂ on the polarization curves for all the loadings employed was minor. In Fig. 16, it is demonstrated that the current loss at 0.5 V is only about 80 mA/cm². As also shown in Fig. 16, oxygen injection into the Pt-Ru anode roughly halved the current loss at 0.5 V. If CO is added intentionally to the H₂/CO₂ feed at the level of 5 ppm or above, its deleterious effect is significant even with a Pt-Ru anode. Thus, the Pt-Ru catalyst does not seem to be able to accommodate significant levels of CO present in the feed stream. It appears, therefore, that the advantage of the Pt-Ru is not to enhance oxidation of CO, but rather to minimize the extent of the CO₂ reduction process(es).

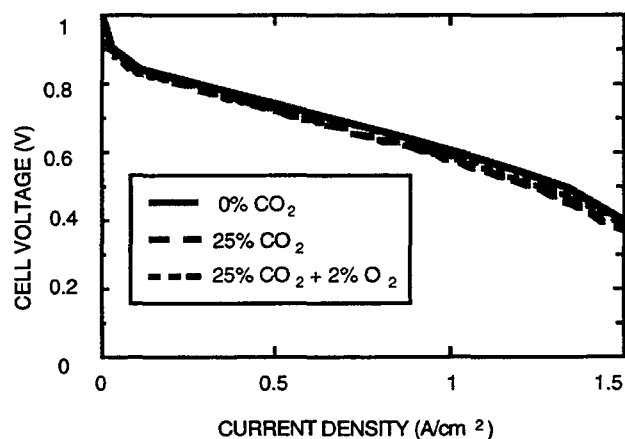


Figure 16. Polarization curves depicting the relatively small effect of CO₂ and the further remediation by O₂ bleed measured for a PEFC with a thin film Pt-Ru anode catalyst.

Single-Cell Testing

Freeze/Thaw Tolerance of LANL PEFCs. One of the concerns frequently raised about using PEM fuel cells for transportation applications is their vulnerability to freezing. Single cells were examined after freeze-thaw cycles to see if any damage or performance loss resulted. The typical cell was assembled and brought up early in the week and allowed to stabilize. Polarization curves were run and the cell hardware was disconnected from the station and placed in a freezer at -10°C over the weekend. On Monday, the cell hardware was reconnected and thawed out using integral cartridge heaters. Polarization curves were again run and the freeze cycle was repeated the following weekend. Because the hardware itself may be damaged by freezing, as the carbon blocks are porous and filled to a certain extent with water, old hardware blocks with a poor flow field design were used (As it turned out, no damage to the hardware was evident.). As a result, the baseline performance of the cells was somewhat below what is usually attained (with Membrane "C").

Figure 17 shows the results for one such cell during three freeze-thaw cycles. After the first freeze, the performance increased slightly. The performance then decreased slightly over the next two freezes, although this could reflect a small performance loss that is observed in the first several weeks from the accumulation of water in the cathode backing layer. These results suggest that the direct application of a thin-film catalyst to the membrane generates a very good bond between catalyst and membrane to effectively prevent delamination under the demanding freeze-thaw cycling conditions.

New Flow Field Design. A new, high-performance, macroporous flow field that has significant advantages

over the conventional machined graphite flow fields in PEM fuel cells was developed. This new flow field should be significantly less expensive than conventional flow fields machined in graphite plates, and it enables easy and effective sealing to provide better performance for cells of larger areas. The macroporous flow field typically consists of pyrolyzed PAN fiber pressed into a sheet of the desired thickness. The resulting product possesses high electronic conductivity and mechanical strength, with a porosity of about 60% and an average pore size of about 30 μm . One of the expected advantages of the porous flow field is that it will compress to provide a more uniform force and electronic contact over the active area of the fuel cell than a machined, ribbed structure.

A radial flow configuration that does not require any sealing on the flow field was designed. As shown in Fig. 18, this flow geometry utilizes an outer ring and an inner ring machined into the carbon separator plate. The reactant gases are introduced into the outer ring, pass through the macroporous flow field, and exit through the inner ring. The gases are prohibited from escaping by gasketing placed around the periphery of the flow field.

Hardware for radial flow cells with 5-cm^2 and 25-cm^2 active areas were fabricated. The 25-cm^2 cell was used for hydrogen/air or reformat/air cell testing, employing membrane/electrode assemblies based on both Dow membranes and Membrane "C". The performance of the 25-cm^2 cells with the new flow field was retained at a level practically equal to that obtained with 5-cm^2 H_2/air cells up to a current density of 1 A/cm^2 , as shown in Fig. 19. (The catalyst loading for each

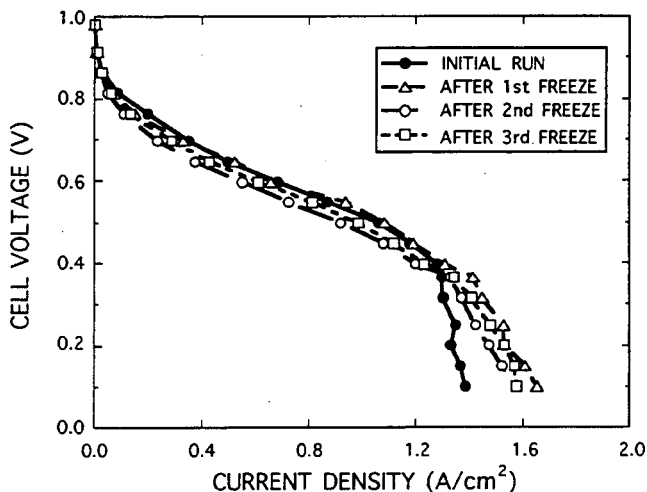


Figure 17. Freeze-thaw test results.

RADIAL FLOW HARDWARE

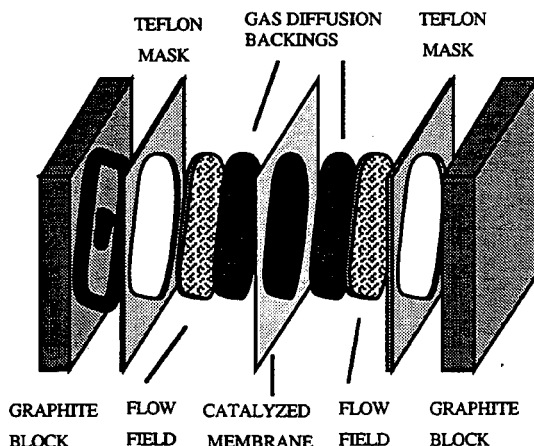


Figure 18. Schematic of the macroporous flow field PEM fuel cell assembly.

electrode was 0.14 mg Pt/cm^2). The limiting current on air in Fig. 19 is significantly higher than typically observed in 25-cm^2 cells with ribbed flow fields. A cell with the new flow field has been life-tested for 100 days, with the current measured at 0.5 V maintaining 90% of its initial level at the end of the test.

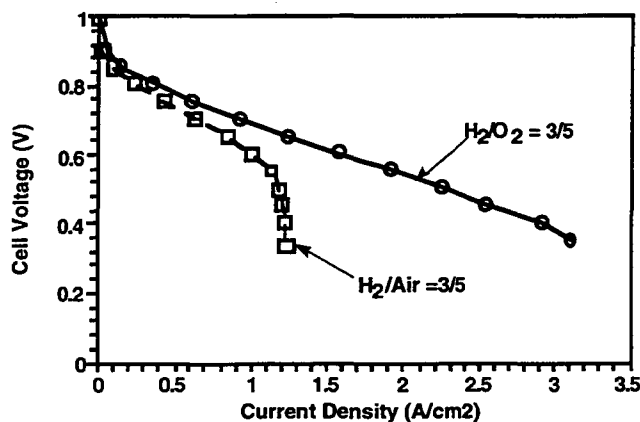


Figure 19. Performance of a 25 cm^2 PEM fuel cell using a macroporous flow field

Membrane Characterization

Measurement of electroosmotic drag coefficients in various protonic membranes continued. The water drag measurement is carried out by using the membrane as a separator between two compartments of different water vapor activity and measuring the EMF that develops as a result of this water chemical potential gradient. The magnitude of the EMF depends on the number of water molecules dragged per unit protonic charge. Figure 20 shows a plot of measured normalized EMF vs. log of water vapor activity ratio across such a cell. The slope of this line is proportional to the electroosmotic drag coefficient, n , which implies a dragged complex of average formula $\text{H}^+(\text{H}_2\text{O})_n$. It is evident that all membranes examined this year, Nafion 117, Dow Experimental Membrane, and Membrane C (Chlorine Engineers) exhibited a similar constant drag over this wide range of water vapor activities (0.1-1.0). The drag value computed from the slope, as specified for each membrane in the figure legend, is very close to $1.0 \text{ H}_2\text{O}/\text{H}^+$ over the complete range of membrane water contents, $2 < l < 14$, ($l = \text{H}_2\text{O}/\text{SO}_3\text{H}$). The similarity and uniformity of these electroosmotic drag coefficients mean that this parameter does not vary significantly among perfluorosulfonic acid membranes, in spite of their different equivalent weights and/or different molecular structures. The apparent low sensitivity of the electroosmotic drag to specific membrane properties lowers the likelihood that better control of water distribution in the

Comparison of Electroosmotic Drag Data for Three Membranes

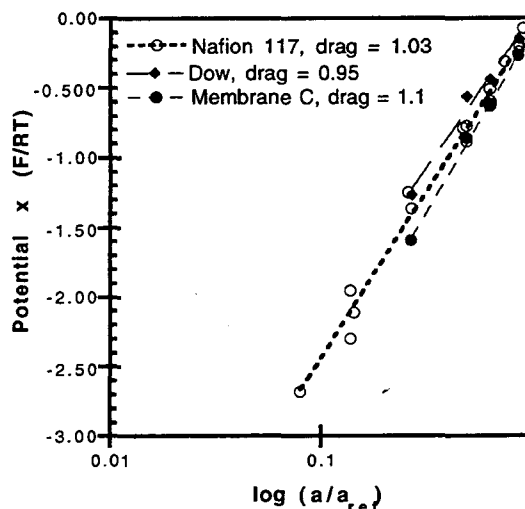


Figure 20. Comparison of electroosmotic drag in proton-exchange membranes.

PEFC can be achieved by membrane modifications aimed specifically at the minimization of the electroosmotic drag. Based on additional results reported earlier, thinner polyfluorosulfonic acid membranes of sufficient integrity seem to be the most promising approach to improved water management in PEFCs, although improved water permeability could also contribute significantly.

Direct Methanol Oxidation

A significant increase in the performance of a direct methanol PEFC was obtained by employing anode liquid feeds in direct contact with the anode catalyst and by increasing the cell temperature to $100\text{--}110^\circ\text{C}$. A current density of 0.1 A/cm^2 at cell voltage of 0.5 V and a maximum cell current density of close to 1 A/cm^2 were obtained with modest catalyst loadings.

The use of liquid concentrations up to 5 M MeOH failed to improve the performance compared to that obtained with a vapor feed. This performance was attributed to the relatively thick gas diffusion backing which served as a barrier to liquid methanol access and as a trap for the CO_2 product. Thus it was concluded that a new, more open structure with a hydrophilic backing on the anode side was needed when liquid methanol feeds are employed. A schematic representation of the new cell structure is presented in Fig. 21. It consists of a macroporous, hydrophilic flow field that replaces the machined ribs employed before, through which the liquid anode reactants can effectively flow. This flow field is in direct contact

with the anode catalyst layer, without an intervening barrier of any kind. The quality of the flow field/catalyst layer contact is good, as judged by the measured high-frequency cell resistance which is very similar to that of PEM fuel cells of the usual construction employing the same (Nafion 117) membrane. This good contact is facilitated by the substantial thickness of the anode catalyst layer in the DMFC ($> 50 \mu\text{m}$), which provides an electronically conducting continuous structure that effectively bridges the gaps (ca. $30 \mu\text{m}$) in the macroporous flow field.

Polarization curves obtained with this cell using a 2 M MeOH liquid feed are shown in Fig. 22 for three cell temperatures. The performance of the cell at 80°C on vapor feed ($P_{\text{MeOH}} = 0.75 \text{ atm}$, $P_{\text{H}_2\text{O}} = 1.0 \text{ atm}$) and on 2 M MeOH liquid feed are very similar, with the liquid feed showing a slight edge. (In the case of vapor anode feed, some condensation of water vapor takes place at a cell temperature of 80°C , enabling membrane cooling/hydration). With both types of reactant streams, the performance at this temperature improved significantly by removing the gas diffusion anode backing layer. Introduction of a liquid feed while eliminating the diffusion barrier at the anode permitted a substantial increase in the cell temperature without adversely impacting the membrane. (The elevated temperatures did not adversely affect the membrane because it was in direct contact with liquid water on the anode side.). As the cell temperature is increased, the anode kinetics improve and the performance increases accordingly. The best performance ($100 \text{ mA}/\text{cm}^2$ at 0.5 V) was obtained with the liquid feed at 110°C .

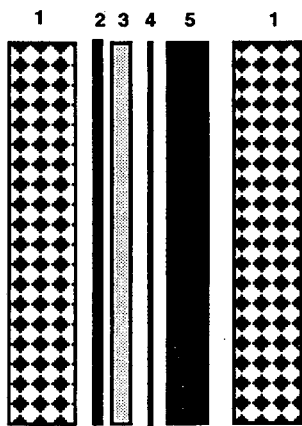


Figure 21. Exploded cross section of the DMFC with liquid fuel feed.

1. Macroporous hydrophilic flow fields, 0.5-mm thick.
2. Pt-Ru/C/Nafion anode, 50-mm thick.
3. Nafion 117 membrane, 175-mm thick.
4. Pt/C/Nafion thin film cathode, 5-mm thick.
5. E-TEK gas diffusion backing, 300-mm thick.

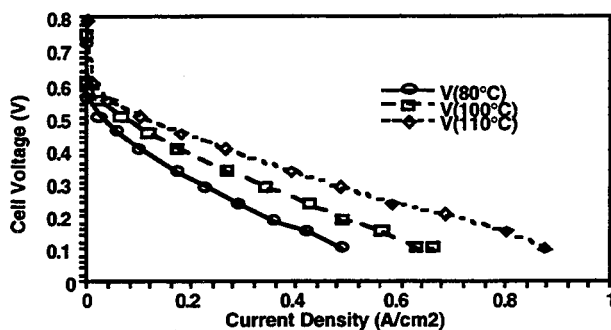


Figure 22. Performance of DMFC with liquid fuel feed as a function of operating temperature.

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Electrocatalysis of Fuel Cell Reactions

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Objectives

- Investigate oxygen reduction in new acidic electrolytes.
- Evaluate new fuel cell electrocatalysts.

Approach

- Use XAS to study the chemical/electrochemical properties of fuel cells electrocatalysts.

Accomplishments

- XAS of adsorbed Pb on Pt catalysts suggests that the electrocatalysis of small organic molecules on Pb-modified Pt cannot be attributed to adsorption of oxygen species on Pb, rather it must be because of the disordered nature of the Pb adlayer.

Future Direction

- Project has been completed.
-

The purpose of this project is to increase the understanding of electrocatalysis on a molecular level and to apply this knowledge to improve the performance of fuel cells for transportation applications. The goals are to reduce the Pt requirements for solid PEFCs, to develop non-Pt catalysts for oxygen reduction, and to identify catalysts for the direct oxidation of methanol. Work in 1993 included extended X-ray absorption (XAS) studies of Pt alloy catalysts supported on carbon and UPD-modified Pt electrocatalysts.

EXAFS Studies of Pt Alloy Catalysts. During the year *in situ* XAS measurements were completed on Pt/Cr, Pt/Fe, Pt/Co and Pt/Ni alloy catalysts supported on carbon that were obtained from two suppliers (ETEK Corp. and Johnson Matthey). Results were also obtained on a Pt/Mn catalyst from Johnson Matthey. *In situ* XAS data were recorded in 1 M HClO₄ at several potentials at both the Pt L₃ and L₂ edges and at the K edge of the respective first-row transition metal alloying elements. The effect of the alloying element on the Pt *d*-band occupancy was determined from analysis of the XANES data at the Pt L₃ and L₂ edges. The values for the *d*-band vacancies were calculated from the differences in area under the absorption spectra in the XANES region with respect to that found for a Pt foil. The calculated *d*-band vacancies for bulk Pt is 0.3 per Pt atom. The effect of the

alloying element on the Pt-Pt bond length was determined from the EXAFS at the Pt L₃ edge.

Table 1 summarizes the analysis of the EXAFS data for the Johnson Matthey catalysts in 1 M HClO₄ at 0.3 V *vs.* SCE, where there are no complications from either hydrogen or oxide adsorption. Table 2 shows the effect of alloying on the Pt *d*-band vacancies at 0.3 V *vs.* SCE (the double layer region) and 0.6 V *vs.* SCE (the oxygen reduction region). Comparison of the data in Tables 1 and 2 show that there is a direct correlation between the number of *d*-band vacancies and the Pt-Pt bond distance in the alloys. Figure 23 shows that there is a "volcano" relationship between these parameters and the electrocatalysis of oxygen reduction by the alloys in PEM fuel cells. The results in Table 2 indicate that there is a significant increase in the *d*-band vacancies for the unalloyed Pt/C catalyst in going from 0.3 to 0.6 V. This is attributed to incipient oxidation of Pt on the surface of the Pt particles and the formation of Pt(OH)_x species. No such increase in *d*-band vacancies was observed for the alloyed catalysts at 0.6 V. This indicates that on the Pt alloy catalysts there is inhibition of Pt(OH)_x formation by adsorption of oxygenated species from the electrolyte. Thus there are more bare Pt sites available for adsorption of molecular oxygen. This can account for the enhanced catalysis.

Table 1. Two Shell Fits for Pt EXAFS of Alloy Catalysts, 0.3 V *vs.* SCE

Shell Data		Alloying Element (M)				
		Mn	Cr	Fe	Co	Ni
Pt-Pt	N	7.8	11.1	6.5	6.9	9.1
	R (Å)	2.76	2.71	2.70	2.68	2.68
	Δs^2 (Å ²)	0.006	0.006	0.004	0.006	0.007
	ΔE	1.2	4.8	2.1	5.7	7.5
Pt-M	N	2.75	2.07	3.3	2.48	2.72
	R (Å)	2.68	2.70	2.64	2.63	2.61
	Δs^2 (Å ²)	0.002	0.004	0.005	0.006	0.011
	ΔE_o	-8.0	-7.4	-5.6	-8.4	-9.1

M = Alloying element

N = Coordination number

R = Bond length

Δs^2 = Debye-Waller factor

ΔE_o = Energy shift (eV)

EXAFS Studies of Adsorbed Pb on Pt Catalysts.

In situ XAS was used to study the structure of adsorbed Pb on Pt supported on carbon in 1 M HClO₄ + 5 × 10⁻³ M Pb²⁺, in the potential range of -0.24 to 1.15 V *vs.* SCE. XANES measurements indicated that, in the UPD region, the Pb species are essentially neutral Pb atoms. At all potentials positive to the main UPD peak in the cyclic voltammogram, the Pb is in the Pb(II) state. Analysis of the EXAFS data for potentials more negative to 0.0 V required a two-shell fit involving Pb-Pb and Pb-Pt interactions. At more positive potentials, in the UPD region, the data could be fitted to a single Pb-Pt shell, indicating a high degree of

lateral disorder in the layer. There is no evidence of Pb interaction with oxygenated species in the UPD region. On stripping the UPD layer, the Pb was present as hydrated Pb²⁺ ions. At more positive potentials there was clear evidence of incorporation of

Table 2. Effect of Alloying Element on Pt *d* Band Vacancies, Johnson Matthey Catalysts

Electrocatalyst	<i>d</i> -Band Vacancies per Pt Atom	
	(0.3 V <i>vs.</i> SCE)	(0.6 V <i>vs.</i> SCE)
Pt/C	0.329	0.370
Pt/Mn	0.331	0.344
Pt/Cr	0.360	0.358
Pt/Fe	0.368	0.370
Pt/Co	0.401	0.390
Pt/Ni	0.409	0.404

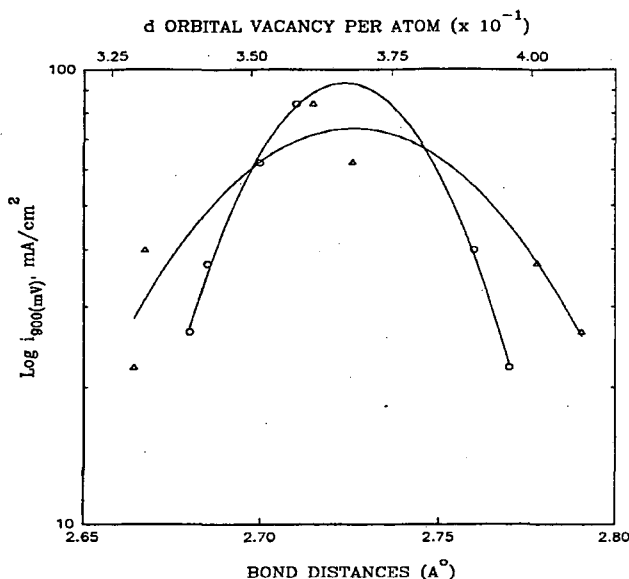


Figure 23. Correlation of oxygen electrode kinetics ($i_{900\text{mV}}$, mA/cm²) on Pt and Pt alloy electrocatalysts in a PEM fuel cell. (o) Pt-Pt bond distance, (Δ) *d*-band vacancies.

Pb into the platinum oxide layer. The electrocatalysis of oxidation of small organic molecules that occurs on Pb-modified Pt is not due to adsorption of oxygen species on Pb, rather it must be because of the disordered nature of the Pb adlayer. This permits access to the Pt so the catalyst can function as a bifunctional catalyst.

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