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ANNUAL REPORT FOR 1987

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APPLIED SCIENCE DIVISION

**Technology Base Research Project
for Electrochemical Energy Storage:
Annual Report for 1987**

July 1988

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**TECHNOLOGY BASE RESEARCH PROJECT
FOR
ELECTROCHEMICAL ENERGY STORAGE**

**ANNUAL REPORT
FOR 1987**

Applied Science Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

Edited by Kim Kinoshita, Technical Manager

July 1988

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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EXECUTIVE SUMMARY

The U.S. Department of Energy's Office of Energy Storage and Distribution provides continuing support for an Energy Storage Program, which includes R&D on advanced electrochemical energy storage and conversion systems. A major goal of this program is to develop electrochemical power sources suitable for application in electric vehicles and/or electric load-leveling devices. The program centers on advanced secondary batteries and fuel cells 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 Exploratory Technology Development and Testing (ETD) Project and the Technology Base Research (TBR) Project. ETD Project management responsibility has been assigned to Sandia National Laboratory (SNL), and the Lawrence Berkeley Laboratory* (LBL) is responsible for management of the TBR Project. The ETD and TBR Projects include an integrated matrix of research and development efforts designed to advance progress on several candidate electrochemical systems. The role of the TBR Project is to perform supporting research for the advanced battery systems under development by the ETD Project, and to evaluate new systems with potentially superior performance, durability and/or cost characteristics. The specific goal of the TBR Project is to identify the most promising electrochemical technologies and transfer them to industry and/or the ETD Project for further development and scale-up. This report summarizes the research, financial and management activities relevant to the TBR Project in CY 1987. This is a continuing project, and reports for prior years have been published; they are listed at the end of the Executive Summary.

* Participants in the TBR Project include the following LBL scientists: E. Cairns, K. Kinoshita and F. McLarnon of the Applied Science Division; and L. DeJonghe, J. Evans, R. Muller, J. Newman, P. Ross and C. Tobias of the Materials and Chemical Sciences Division.

General problem areas addressed by the project 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 TBR Project is divided into three major project elements: Exploratory Research, Applied Science Research, and Air Systems Research. Highlights of each project element are summarized according to the appropriate battery system or electrochemical research area.

EXPLORATORY RESEARCH

The objectives of this project 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 projects were conducted on **molten-salt cells** based on Li alloy negative electrodes and metal disulfide positive electrodes. These cells exhibit very high performance, ease of manufacture, and freeze-thaw capability. Two organizations are pursuing techniques to stabilize the performance of FeS_2 electrodes in these cells.

- ANL has achieved 1000 cycles (discharge at 50 mA/cm^2 for 4 h, charge at 25 mA/cm^2 to a cut-off voltage of 2.05 V) and 7000-h operation at 397°C with a small prismatic upper-plateau Li-Al/ FeS_2 cell with 25 mol% LiCl-42 mol% LiBr-37 mol% KBr electrolyte. No capacity loss was observed during the first 500 cycles, at which time equipment malfunction occurred. Then a $\leq 20\%$ capacity loss was observed to 1000 cycles. Overdischarge protection was demonstrated in an upper-plateau Li-Al/ FeS_2 cell that is Li-limited. A cell operated with discharge cutoff voltages of 1.0 to 1.3 V maintained a coulombic efficiency of 99% for over 900 cycles.

- Gould, Inc. has observed that starved-electrolyte Li-alloy/FeS₂ cells containing LiCl-LiBr-KBr electrolyte exhibited almost zero loss in upper-plateau capacity after 300 cycles (5000 h) at 400°C. The capacity utilization for these cells was 65%, which is considerably less than the 80-85% observed at ANL with flooded-electrolyte cells.

APPLIED SCIENCE RESEARCH

The objectives of this project 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.

Alkaline Cells often use Zn as the negative electrode, and it is this electrode that typically limits the lifetime of these cells. Efforts are underway to identify electrode and electrolyte compositions that will improve the cycle-life performance of the Zn electrode.

- LBL has observed that an electrode of pure CaZn(OH)₄ cycled at constant current in 31 wt% KOH showed a distribution of active material, after 50 cycles, that was much more uniform than that observed with Zn electrodes containing an additive of 25-33 mol% Ca(OH)₂.
- LBL has successfully employed Zn and Cd micro-electrodes in porous Zn electrodes to study the chemical and transport processes that occur in secondary porous Zn electrodes in KOH electrolytes. The measurements indicate that during cycling, material redistribution occurs and the electrode becomes limited by transport of Zn(OH)₄²⁻, dissolution of ZnO, or precipitation of Zn(OH)₄²⁻ as ZnO.

Zinc/Halogen Cells use flowing electrolytes to promote the transport of Zn ions across the cell and to remove halogen as the cell is charged. The cell performance is limited by the tendency of the electrodeposited Zn to assume unwanted shapes, and efforts are aimed at understanding the complex phenomena that control the Zn electrode morphology.

- Mathematical modeling at LBL on the effect of inhibitors on electrodeposition indicates that recirculation flow can explain the decrease in leveling action in notches (below a critical angle) compared to the leveling action in stagnant electrolyte.
- Illinois Institute of Technology (IIT) has observed that the formation of Zn dendrites is completely suppressed when Br₂ is present in the ZnBr₂ solution during electrodeposition at ~20 mA/cm², up to a net Zn loading of 160 mAh/cm².
- EXAFS (extended X-ray absorption fine structure) was used by Brookhaven National Laboratory (BNL) to study Zn complexes in acidic and basic electrolytes. In 1 M ZnBr₂ the data could be fitted to a ZnBr⁺·3H₂O model and in 3 M ZnBr₂ to a ZnBr₂·2H₂O model.

Improved Components for Alkali/Sulfur Cells, such as superior alternatives to the β"-Al₂O₃ ceramic electrolyte and the high-temperature sulfur-polysulfide electrode used in Na/S cells, stable Li-ion conductors for Li/S cells, and a class of organosulfur electrodes for low-temperature β"-Al₂O₃ cells are under investigation.

- Investigations of novel, low-temperature (120-150°C) secondary cell which contains a liquid sodium negative, β"-Al₂O₃ electrolyte, and a class of organosulfur (RSSR, R = aliphatic, aromatic, ethereal or fluorinated organic moiety) positives continue at LBL. Experiments indicate that the performance of these cells is enhanced by use of a CoPc electrocatalyst in the positive electrode and by varying the organic moiety attached to the S-S bond.

- Experiments are underway at LBL to confirm an advanced mathematical model of the sulfur electrode in Na/S cells. Because of the difficulties of performing wetting and wicking measurements on the sulfur/polysulfide/graphite system directly, an analogous system (water/bromobenzene/glass fiber) was investigated. This study led to the conclusion that beyond a sulfur volume fraction of 0.75, the polysulfide phase is no longer interconnected, and it does not move.
- ANL has found that the fabrication of small electrolyte tubes from ANL Glass (composition in mol%: 42 Na₂O, 8 Al₂O₃, 5 ZrO₂ and 45 SiO₂) requires careful control of the environment. Because ANL Glass is hygroscopic, moisture must be absent to fabricate a useful glass electrolyte for testing in Na/S cells. Small-scale cells (22 mAh) were successfully cycled at 400 μ A for 0.5 h (discharge) and 200 μ A for 1 h (charge) for 100 cycles (2-3% DOD).
- Massachusetts Institute of Technology (MIT) has observed that the addition of chlorine has little effect on K⁺-ion conduction in potassium chloroborate glasses, in contrast to the results obtained earlier for Li⁺-ion and Na⁺-ion conduction in the corresponding Li and Na glasses.
- Stanford University is exploring the development of alternative electrodes and electrolytes for the cell

Work on the following cell has been initiated to investigate alternatives to the negative electrode/ β -Al₂O₃ assembly

The NaAlEt₄ electrolyte, which can be used at about 120°C, was found to be stable at high Na activities.

Corrosion Processes in High-Temperature, High-Sulfur Activity Molten Salts are under investigation, and the aim is to develop low-cost container and current-collector materials for use in alkali/sulfur and other molten-salt cells.

- IIT observed that the cyclic voltammograms of Mo₂C- and TiN- coated samples in Na₂S_x melts were similar to that of Mo, and suggest that Mo₂C appears to resist sulfur attack.

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 detected four major peaks at 400° (I), 500-600° (II), 770° (III) and 840°K (IV) in the thermal desorption spectra of CO₂ adsorbed on potassium-covered Ag (111) surfaces. The peaks observed at the higher temperatures may involve interactions between the adsorbed CO₂ molecules to yield oxalate-type or even larger CO₂-coupled polymeric aggregates that are formed by a radical-coupling mechanism.
- Jackson State University has observed by *in situ* Raman spectroscopy that an enhanced Raman spectrum can be obtained from 1000-Å thick layers of Li on Ag. *In situ* Raman measurements of Li in LiAsF₆/PC were not successful because of the strong Raman scattering from species in solution.
- The University of Minnesota has observed that the high-frequency charge-injection process in poly(vinylferrocene) (PVF) is the same for PVF prepared by spin coating and by solvent casting. However, charge transport is higher in the spin-coated film than that in the solvent-cast film (i.e., 10⁻⁷ cm²/s vs 10⁻⁹ cm²/s).
- Studies as the University of Pennsylvania suggest that a correlation exists between the type of complex a cation forms in poly(ethylene oxide) and its ionic mobility.

- Experiments at LBL demonstrated that Mg can be anodically dissolved with 100% current efficiency with a valence of two in PC electrolytes. However, to date, none of the attempts to electrodeposit metallic Mg from its compounds in nonaqueous electrolytes of PC, tetrahydrofuran or dimethylsulfoxide have been successful.
- Johns Hopkins University has observed that both Fe and Ni show spontaneous passivation with a wide passive range and low passive current densities in highly purified 0.5 M LiClO₄/PC. Preliminary measurements indicate that Fe undergoes passive breakdown in 0.5 M LiClO₄/PC containing both water and propylene glycol at the 500-ppm level.

Cross-Cutting Research is carried out to address fundamental problems in electrocatalysis and current density distribution, solutions of which will lead to improved electrode structures and performance in batteries and fuel cells.

- A mathematical model developed at LBL predicts that KCl precipitation can limit the utilization of the FeS₂ electrode, usually on the lower voltage plateau, of Li(Si)/FeS₂ cells.
- LBL is developing a spectroscopic ellipsometry technique for *in situ* studies of electrode/electrolyte interfaces. The formation of anodic oxide films on Cu and Ag was investigated to assess the utility of this technique. The measurements with a 20-μm probe beam have revealed local variation of anodic film thickness and composition on a scale much smaller than the grain size.
- A mathematical model is being developed by LBL to account for the role of the morphology of the substrate on bubble size, which profoundly affects the dynamics of gas evolution on electrode surfaces. An equation was derived which relates the maximum bubble size that can form to the radius of surface protrusions.

AIR SYSTEMS RESEARCH

The objectives of this project 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, which are needed for electrically rechargeable metal/air (Zn/air, Fe/air) cells; and novel alkaline Zn electrode structures, which could be used in either electrically recharged or mechanically recharged cell configurations.

- LBL has discovered one particular type of furnace black (SRF N774) that appears to be an especially good precursor for forming a highly graphitized and very corrosion-resistant carbon black for use in bifunctional air electrodes.
- CWRU has concluded from extensive studies of heat-treated macrocycles that a transition metal is essential to obtain very active O_2 reduction catalysts. Their studies further indicate that the transition metal is adsorbed principally by interaction with the residual N_2 in the heat-treated macrocyclic catalyst.
- Experiments at LBL demonstrated that a moving bed of Zn particles exhibit low ohmic resistance (i.e., minimizing parasitic voltage drop across the electrode itself) and it can be discharged at a superficial current density of 100 mA/cm^2 .
- Pinnacle Research Institute (PRI) has observed that less electrical energy is required to electrodeposit (recharge at $\sim 280 \text{ mA/cm}^2$ in alkaline solution containing 51 g/l Zn) Zn on a Mg substrate (0.52 Wh/g) than on a glassy carbon substrate (0.98 Wh/g). The Zn dendrites were easily removed from the Mg substrate, thus simplifying the production of a Zn slurry for use in a slurry Zn/air cell.

Aluminum/Air Battery R&D is directed at improving the performance of air electrodes and developing Al anodes with lower corrosion rates and higher open-circuit potential in alkaline electrolytes.

- Experimental and theoretical studies are underway at SRI International to elucidate the corrosion mechanism of Al alloys. The corrosion of various Al-Li-In (Group I), Al-Li-In-Bi (Group II), and Al-Mg-Mn-In (Group III) alloys in 4 M KOH at 50°C was investigated. The results indicate that none of the alloys studied appear to offer any advantages over Alloy BDW (Al-1 Mg-0.1 In-0.2 Mn) as a fuel for alkaline Al/air batteries.

Fuel Cell Research, managed by 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 include:

- LANL has achieved a significant improvement in the performance of low-Pt-loading electrodes (0.4 mg/cm^2) by sputtering a thin layer of Pt (0.05 mg/cm^2) on the side of the electrode in contact with the Nafion membrane. The H_2 overpotential was reduced from 170 mV to 70 mV at 1 A/cm^2 with anodes containing the sputtered Pt.
- The Dow perfluorinated polymer evaluated by LANL produced a higher performance than that achieved with Nafion. A fuel cell operating on H_2/air (3/5 atm) attained 0.8 W/cm^2 at 71°C with the Dow membrane (125- μm thickness) while Nafion (175- μm thickness) tested under comparable conditions yielded only 0.4 W/cm^2 . The enhanced performance obtained with the Dow membrane is attributed to the lower molecular weight and the reduced thickness.
- LANL has demonstrated in long-term tests at 300 mA/cm^2 that fuel cells containing Nafion membranes with external humidification showed steady performance with no apparent dehydration problems for 1000 hours.

- EXAFS studies of pyrolyzed transition metal (Fe and Co) macrocycles (phthalocyanine and tetramethoxyphenylporphyrin) at BNL indicate that monodispersed, N_2 -coordinated, Fe and Co atoms are the electrocatalyst sites for O_2 reduction.
- LBL is developing photothermal deflection spectroscopy (PDS) for investigation of electrochemical interfaces. Preliminary experiments on the oxidation of methanol on Pt and an under-potential deposition process by which ad-atom catalysts are formed have shown that PDS is a very sensitive *in situ* method to study surface phenomena at electrode/electrolyte interfaces.
- Porous gas-diffusion electrodes containing high-area Pt supported on carbon were used by LBL to investigate the reduction of O_2 in KOH and K_2CO_3 . Poorer performance was observed in K_2CO_3 , which is attributed to the lower wetted areas and slow OH^- transport. The reduction current in KOH is kinetically limited, whereas in K_2CO_3 local pH changes occur in the pores of the electrode during reduction which result in lower performance than in KOH. This performance may be improved by modifications to the electrode structure. Models were developed for the porous electrodes which accounted for the diffusion and reaction of O_2 and ionic transport in KOH and K_2CO_3 . Good agreement was obtained between the model and performance data.

Management Activities

During 1987, LBL managed 25 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 TBR projects. LBL staff members also participated in the following reviews, meetings, and workshops:

- 2nd International Battery Conference on Applications and Advances, California State University, Long Beach, CA, January 13-15, 1987.
- Gordon Research Conference on Electrochemistry, Santa Barbara, Ca, January 19-23, 1987.
- EPRI Molten Salt Battery Program Meeting, EPRI, Palo Alto, CA, January 23, 1987.
- DOE/EPRI Fuel Cell Workshop, Clearwater, FL, February 16-17, 1987.
- Energy and Resources Group Colloquium, University of California, Berkeley, CA, February 18, 1987.
- DOE/SNL Zn/Br₂ Battery Program Review, Danbury, CT, March 5, 1987.
- DOE/OESD Strategic Planning Meeting, Washington, DC, March 10-11, 1987.
- Aluminum/Air Battery Review Meeting, Washington, DC, March 12, 1987.
- National Association of Corrosion Engineers, CORROSION '87, San Francisco, CA, March 9-13, 1987.
- Industrial Research Meeting, LBL, Berkeley, CA, March 23-25, 1987.
- Fuel Cell Planning Meeting, EPRI, Palo Alto, CA, April 1-2, 1987
- International Conference on Localized Corrosion, Orlando, FL, June 1-5, 1987
- DOE/SNL Zn/Br₂ Battery Program Review, SNL, Albuquerque, NM, June 23, 1987
- Lithium/Iron Sulfide Battery Review and Planning Meeting, EPRI, Palo Alto, CA, June 25, 1987
- DOE/SNL Na/S Battery Program Review, SNL, Albuquerque, NM, July 21-22, 1987
- Fuel Cell Program Meeting, LANL, Los Alamos, NM, July 23, 1987
- Na/S Battery Review Meeting, EPRI, Palo Alto, CA, August 4, 1987
- 22nd IECEC, Philadelphia, PA, August 10-14, 1987

- DOE/OTS Battery Assessment Meeting, INEL, Idaho Falls, ID, September 9-10, 1987
- Zn/Air Battery Program Meeting, Washington, D.C., September 15, 1987
- DOE Electrochemical Energy Storage Program Lead Center Coordination Meeting, Washington, D.C., September 16-17, 1987
- Fall Meeting of the Electrochemical Society, Honolulu, HI, October 18-23, 1987
- DOE/EPRI Fuel Cell Workshop, Morgantown, WV, October 27-29, 1987
- 8th Battery and Electrochemical Contractors' Conference, Tysons Corner, VA, November 16-19, 1987
- Annual Meeting of the American Institute of Chemical Engineers, New York, NY, November 16-21, 1987
- DOE/SNL Na/S Battery Review, Tysons Corner, VA, November, 20, 1987
- DOE/SNL Zn/Br₂ Battery Review, Danbury, CT, December 9-10, 1987

MILESTONES FOR THE TECHNOLOGY BASE RESEARCH PROJECT

Milestones accomplished in Fiscal Year 1987 by the TBR Project include:

- *Initiate new R&D projects on electrocatalysis and novel electrolytes for fuel cells.*

Because of funding limitations, no new contract on electrocatalysis was placed by LANL in 1987. However, a renewal contract was placed with the University of Virginia to investigate binary and ternary Pt alloys for O₂ electrocatalysts. In addition, LANL is seeking cooperative agreements with industry to develop improved O₂ reduction electrocatalysts. Air electrodes obtained from ELTECH Systems, Inc. under a confidentiality agreement are being evaluated at LANL. Ion-conducting polymers obtained from Dow Chemical under a similar agreement are also being evaluated by LANL for use as electrolytes in fuel cells.

- *Initiate new R&D project on molten-salt batteries.*

On the basis of an RFP ("Applied Research on Novel Concepts for Advanced Batteries") issued by LBL in FY 1986, Gould, Inc. was awarded a contract on "Development of Low Melting Molten Salt Electrolyte to Eliminate Iron Disulfide Electrode Capacity Loss." After the award, Gould, Inc. transferred their personnel and equipment devoted to the molten-salt battery project from their facilities in Rolling Meadows, Illinois to Cleveland, Ohio. This move resulted in a considerable delay in the project, and consequently new R&D on molten-salt batteries was not initiated in 1987.

- *Establish an initial set of parameters for optimum membrane structures in fuel cells.*

On the basis of in-house experiments at LANL and discussions with fuel-cell researchers, the following physicochemical properties were specified for membrane structures in polymer-electrolyte fuel cells:

Thickness (mils)	2 to 7
H ⁺ resistance (ohm-cm ²)	0.1
Tensile strength (psi) at break	2500
Elongation (%) at break	100 to 150
Mullen burst strength (psi)	100 to 150
H ₂ permeability (cm ³ -mil/ft ² -h-atm)	260
O ₂ permeability (cm ³ -mil/ft ² -h-atm)	140
Minimum temperature (°C) of thermal/hydrolytic stability	150
Crease/crack (ability to withstand 5 folds in hydrated or dry)	Pass
Tear strength (ability to withstand tearing in hydrated or dry)	Pass
Minimum operational life (h) in an electrochemical cell	5000

- *Go/no-go decision to continue development of the chemical-vapor-deposition process to protect low carbon steel or Al from corrosion in sulfide/polysulfide melts.*

The Institute of Gas Technology (IGT) was under subcontract to the IIT to prepare chemical-vapor-deposition (CVD) coatings for corrosion testing in Na/S and Li-alloy/FeS₂ cells. Because of the difficulties encountered, IGT decided to withdraw from the project. After consultation with LBL, and an assessment of the various CVD methods, a decision was reached to continue the effort on the preparation of CVD coatings at IIT. IIT has constructed laboratory space where a plasma-enhanced CVD process to prepare corrosion-resistant coatings is being evaluated.

- *Demonstrate reproducible performance and greater than 50% utilization of sulfur electrode in sealed cells with the new ANL glass electrolyte.*

A glass composition (mol%) of 42 Na₂O, 8 Al₂O₃, 5 ZrO₂ and 45 SiO₂ was identified as a potential solid electrolyte for Na/S cells. A new fabrication facility was built to produce glass tubes for cell tests. Using this facility, glass tubes of 30-cm length and 2- to 6-mm o.d. were successfully produced and tested in Na/S cells. A small cell containing 22 mAh of sulfur at 326°C achieved 100 cycles (2-3% DOD) at 0.4 mA/cm². This cell was able to discharge the sulfur electrode at 50-53% utilization, but the cell capacity declined after the 12th cycle at these deeper DODs. Cracks in the glass electrolyte in the vicinity of the metal-to-glass seal is a probable cause for the capacity decline. Further work is underway

to improve the thermomechanical compatibility of the glass electrolyte and the header material used in the cell and to reproduce cells that demonstrate high utilization of sulfur.

- *Achieve stable capacity (<10% decline in 500 cycles) and reproducible high performance in Li/FeS₂ cells.*

A 12-Ah Li-Al/LiCl-LiBr-KBr (310°C mp)/FeS₂-CoS₂ (85:15 mol%) cell (sealed prismatic bicell with 100-cm² separator of BN felt, cell KHP-4) has achieved greater than 500 cycles at a 2-h discharge rate and a 4-h charge rate at 400°C. The capacity decline remains at <3%, the coulombic efficiency is 98.5%, and the utilization is about 80% of the theoretical FeS₂ electrode (upper plateau) capacity.

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2. "Technology Base Research Project for Electrochemical Energy Storage — Annual Report for 1985," LBL-21342 (July 1986).
3. "Technology Base Research Project for Electrochemical Energy Storage — Annual Report for 1984," LBL-19545 (May 1985).
4. "Annual Report for 1983 — Technology Base Research Project for Electrochemical Energy Storage," LBL-17742 (May 1984).
5. "Technology Base Research Project for Electrochemical Energy Storage, — Report for 1982" LBL-15992 (May 1983).
6. "Technology Base Research Project for Electrochemical Energy Storage — Report for 1981," LBL-14305 (June 1982).
7. "Applied Battery and Electrochemical Research Program Report for 1981," LBL-14304 (June 1982).
8. "Applied Battery and Electrochemical Research Program Report for Fiscal Year 1980," LBL-12514 (April 1981).

SUBCONTRACTOR FINANCIAL DATA - CY 1987

Subcontractor	Principal Investigator	Project	Contract Value (K\$)	Term (months)	Expiration Date	Status in CY 1987*
<u>EXPLORATORY RESEARCH</u>						
Molten-Salt Cells						
Argonne National Laboratory	P. Nelson	Molten-Salt Cells	545	12	9-87	C
Gould, Incorporated	G. Barlow	Molten-Salt Electrolytes	113	12	7-87	R
Stanford University	R. Huggins	New Battery Materials	300	12	11-87	C
Ambient-Temperature Lithium Cells						
Duracell, Inc.	A. Dey	Li/SO ₂	1500	48	12-85	T
University of Pennsylvania	G. Farrington	Polymeric Electrolytes	85	12	2-88	C
University of Minnesota	W. Smyrl	Solid State Cells	169	12	6-88	R
EIC Laboratories, Inc.	K. Abraham	Secondary Li Batteries	150	12	6-87	T
<u>APPLIED SCIENCE RESEARCH</u>						
Lawrence Berkeley Laboratory	E. Cairns, L. DeJonghe, J. Evans, R. Muller, J. Newman, P. Ross, and C. Tobias	Electrochemical Energy Storage	1500	12	9-87	C
Zinc/Halogen Cells						
Illinois Institute of Technology	R. Selman	Zn Deposition	70	12	9-87	C
Brookhaven National Laboratory	J. McBreen	Zn Morphology	80	12	9-87	C
Lawrence Livermore National Laboratory	D. Miller	Transport Properties	0	12	9-87	T
Components for Alkali/Sulfur Cells						
Argonne National Laboratory	P. Nelson	Solid Electrolytes	330	12	9-87	C
Massachusetts Institute of Technology	H. Tuller	Li Conducting Glasses	100	12	6-87	C

Subcontractor	Principal Investigator	Project	Contract Value (K\$)	Term (months)	Expiration Date	Status in CY 1987*
<u>APPLIED SCIENCE RESEARCH - cont.</u>						
Corrosion Processes in High-Temperature, High-Sulfur-Activity Molten Salt						
Illinois Institute of Technology	R. Selman	Corrosion Resistant Coatings	162	12	11-87	C
Components for Ambient-Temperature Lithium Cells						
Case Western Reserve University	D. Scherson	Spectroscopic Studies	67	12	11-87	C
Jackson State University	H. Tachikawa	Raman Spectroscopy	53	12	6-87	C
Johns Hopkins University	J. Kruger	Corrosion/Passivity Studies	88	12	7-87	C
<u>AIR SYSTEMS RESEARCH</u>						
Metal/Air Cell Research						
Case Western Reserve University	E. Yeager	Air Electrodes	213	12	5-88	C
Pinnacle Research Institute	L. Morris	Zn/Air Battery	195	12	1-88	C
Aluminum/Air Battery R&D						
Lawrence Livermore National Laboratory	A. Maimoni	Al/Air Power Cell R&D	0	12	9-87	T
Fuel Cell R&D						
Los Alamos National Laboratory	J. Huff	Fuel Cell R&D	800	12	9-87	C
Brookhaven National Laboratory	J. McBreen	Fuel Cell Research	150	12	9-87	C

* C = continuing, T = terminating, R = subject included in a request for proposals (RFP) issued by LBL in FY 1986.

LIST OF ACRONYMS

AES	Auger electron spectroscopy
AIAA	American Institute of Aeronautics and Astronautics
AIChE	American Institute of Chemical Engineers
ANL	Argonne National Laboratory
BNL	Brookhaven National Laboratory
CVD	chemical vapor deposition
CWRU	Case Western Reserve University
DHE	dynamic hydrogen electrode
DMDS	dimethyl disulfide
DOD	depth of discharge
DOE	Department of Energy
ECD	electrochemical deposition
EMF	electromotive force
EPRI	Electric Power Research Institute
ESCA	electron spectroscopy for chemical analysis
ETD	Exploratory Technology Development and Testing
EV	electric vehicle
EXAFS	extended X-ray absorption fine structure
FIC	fast ion conducting
FT	Fourier transform
FTIR	Fourier transform infrared spectroscopy
GC	glassy carbon
GDE	gas diffusion electrode
HOPG	highly oriented pyrolytic graphite
HPM	hot-pressing method
IAD	implicit alternating direction
IECEC	Intersociety Energy Conversion and Engineering Conference
IGT	Institute of Gas Technology
IIT	Illinois Institute of Technology
IRS	infrared reflectance spectroscopy
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LLNL	Lawrence Livermore National Laboratory
LUMO	lowest unoccupied molecular orbital
MEA	membrane-electrode assemblies
MIT	Massachusetts Institute of Technology
NMR	nuclear magnetic resonance
OCV	open-circuit voltage
OEP	octaethyl porphyrin
OESD	Office of Energy Storage and Distribution
OPG	ordinary pyrolytic graphite
OR	oxygen reduction
OTS	Office of Transportation Systems
PAA	polyacrylamide
PAN	polyacrylonitrile
PC	propylene carbonate
Pc	phthalocyanine

PDE	partial differential equation
PDS	photothermal deflection spectroscopy
PE-CVD	plasma-enhanced chemical-vapor deposition
PEM	proton-exchange membrane
PEO	poly(ethylene oxide)
PG	propylene glycol
PRI	Pinnacle Research Institute
PTFE	polytetrafluoroethylene
PVF	poly(vinylferrocene)
RCCE	rotating concentric cylinder electrode
RHE	rotating hemispherical electrode
RDE	rotating disk electrode
RRDE	rotating ring-disk electrode
SASB	steam-activated Shawinigan acetylene black
SEM	scanning electron microscopy
SERS	surface-enhanced Raman spectroscopy
SIMS	secondary ion mass spectroscopy
SNL	Sandia National Laboratories
TAA	tetraazaannulene
TBR	Technology Base Research
TDMS	thermal desorption mass spectroscopy
TEM	transmission electron microscopy
TETD	tetraethyl thiuram disulfide
THF	tetrahydrofuran
TMPP	tetramethoxylphenyl porphyrin
T.P.	two voltage plateaus
TSPc	tetrasulfonated phthalocyanine
U.P.	upper plateau
UPD	underpotential deposition
UV	ultraviolet
VLSI	very large-scale integration
XANES	X-ray near edge absorption spectroscopy
XPS	X-ray photoelectron spectroscopy

I. INTRODUCTION

This report summarizes the progress made by the Technology Base Research (TBR) Project for Electrochemical Energy Storage during calendar year 1987. The primary objective of the TBR Project, which is sponsored by the Department of Energy (DOE) and managed by Lawrence Berkeley Laboratory (LBL), is to identify electrochemical technologies that can satisfy stringent performance and economic requirements for electric vehicles and stationary energy storage applications. The ultimate goal is to transfer the most promising electrochemical technologies to the private sector or to another DOE project (e.g., Sandia National Laboratories' Exploratory Technology Development and Testing Project) for further development and scale-up.

Besides LBL, which has overall responsibility for the TBR Project, Los Alamos National Laboratory (LANL), Brookhaven National Laboratory (BNL) and

Argonne National Laboratory (ANL) participate in the TBR Project by providing key research support in several of the project elements.

The TBR Project consists of three major project elements:

- Exploratory Research
- Applied Science Research
- Air Systems Research

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

II. EXPLORATORY RESEARCH

The major thrust of this project element is to evaluate promising electrochemical couples for advanced batteries for electric vehicles. Approaches to stabilize the performance of rechargeable high-temperature molten-salt cells were investigated.

MOLTEN SALT CELLS

Molten-Salt Cells based on Li alloy negative electrodes and metal disulfide positive electrodes exhibit very high performance, ease of manufacture, and freeze-thaw capability. Two organizations are pursuing techniques to stabilize the performance of FeS₂ electrodes in these cells.

Molten-Electrolyte Cell Research

L.A. Redey and T.D. Kaun
(Argonne National Laboratory)

Research is being conducted to achieve major improvements in the performance and reliability of secondary batteries based on molten-salt electrolyte, Li-alloy negative electrodes, and FeS₂ positive electrodes. The research program included effort on: 1) the development and testing of small-scale, upper-plateau FeS₂ prismatic and rod-cell designs; 2) studies of molten-salt electrochemistry in LiCl-LiBr-KBr (310°C m.p.); and 3) development of overcharge and over-discharge protection for cell operation in a battery configuration. The objective of these tasks is to achieve advances in the current technology that will yield a

specific energy of 200 Wh/kg at a 4-h discharge rate, a specific power of 200 W/kg, and a cycle life of 1000 cycles. An improved Li-alloy/FeS₂ cell has demonstrated promise of achieving these performance and cycle-life goals.

The improved Li/FeS₂ cell developed at ANL has two major changes: (i) a novel electrolyte, 25 mol% LiCl-37 mol% LiBr-38 mol% KBr (m.p. 310°C), rather than 58 mol% LiCl-42 mol% KCl (m.p. 352°C), and (ii) a higher loading density (2.4 vs 1.5 Ah/cm²) for the FeS₂-15 mol% CoS₂ electrode, which is then operated only on its upper voltage plateau (U.P.) (1.75 V vs Li-Al) rather than its two voltage plateaus (T.P.). This U.P.-FeS₂ cell (100 cm² BN-felt separator) at 400°C has demonstrated a 100% increase in specific power and a 50% improvement in specific energy and capacity utilization, as compared to that of the earlier T.P.-FeS₂ cell at 427°C. The results obtained with a group of five upper-plateau FeS₂ cells (see Table 1) show that the capacity utilization is 80 to 90%, depending upon discharge rate. The disulfide electrodes remained at 90% of their initial values of capacity utilization, and the coulombic efficiency was 96 to 99% throughout the tests. The high utilization of the U.P.-FeS₂ capacity provided a quite good accounting of the sulfur capacity throughout the cycle-life tests. Excellent cycle-life stability has also been demonstrated with the 1000-cycle (7000 h) operation of cell KHP-4. No cell capacity loss was exhibited in the first 500 cycles (see Fig. 1), and thereafter, problems with the equipment in the test facility (e.g., glovebox failures) resulted in a 20% decline in capacity for the full 1000 cycles. A reference electrode indicated that the cell capacity became limited by the Li-alloy electrode. The high specific-power capability

Table 1. Cycle-Life Tests of Upper-Plateau Disulfide Electrode Cells^a

Cell No., KHP-	Composition of Limiting Electrode	U.P. Utilization /Rate, h	Capacity Change % /Cycles
1	FeS ₂ :CoS ₂ (85:15 mol%)	89/4	1/400
3	FeS ₂ :CoS ₂ (85:15 mol%)	88/4	4/260
4	FeS ₂ :CoS ₂ (85:15 mol%)	80/2	18/1020
5 ^b	Li-Al, Carbon	55/1.3	10/900
6 ^c	FeS ₂ :NiS ₂ :Li ₂ S (50:50:5 mol%)	93/4	5/250

a. Prismatic bicells: LiCl-LiBr-KBr (310°C m.p.) with BN-felt separator (100 cm²), 400°C operation.

b. Furnace malfunction, 3 days at 565°C.

c. Overcharge tolerance attempted at 450°C.

Figure 1. Cycle life of Cell KHP-4, U.P. FeS_2 electrode stability test. Cell capacity became limited by the Li-Al electrolyte after cycle 500.

of the cell was not degraded during the 1000-cycle operation (i.e., cell resistance vs DOD was unchanged). Apparently, both time- and cycle-related capacity-loss mechanisms of the earlier T.P.- FeS_2 cells have been overcome.

An increased understanding of the reasons behind the improved stability and high performance of the U.P.- FeS_2 cell was obtained through an investigation of its molten-salt electrochemistry. The physical characteristics of the LiCl-LiBr-KBr molten salt allow the U.P.- FeS_2 cell to operate at a substantially lower temperature (400 vs 450°C) and a higher Li^+ -ion activity (62 vs 58 mol% Li^+) than is possible with LiCl-KCl. Additionally, its broad liquidus at 400°C supports high-current-density (100 to 150 mA/cm^2) operation at high utilization (~80% of the U.P.- FeS_2 capacity). The electrochemistry of U.P. FeS_2 in LiCl-LiBr-KBr exhibits increased reversibility, as indicated by the reduced peak separation of the high-voltage reaction peaks in the cyclic voltammograms. The capacity stability of the dense U.P. FeS_2 is aided by improved electrode kinetics at the lower operating temperature of 400°C (similar to the kinetics of FeS_2 in LiCl-KCl at 450°C). Thermal decomposition and solubility of FeS_2 are minimal at this temperature. Also, generation of soluble polysulfides at 1.95 to 2.1 V was not indicated in the cyclic voltammograms for this electrode/electrolyte system.

Overdischarge protection for the U.P.- FeS_2 electrode was demonstrated in a cell with a capacity that was limited by the negative electrode (i.e., Li-limited). At a high loading density of the FeS_2 electrode, discharge must be restricted to the upper-plateau capacity to avoid excessive electrode expansion. This has been achieved by limiting the discharge cutoff voltage to ≤ 1.25 V, but for battery operation, this requirement is unacceptable. A Li-limited U.P.- FeS_2 cell has been

operated with discharge cutoff voltages ranging from 1.0 to 1.3 V and a coulombic efficiency of 99% for over 900 cycles.

The experimental results suggest that two mechanisms can be used to provide chemical overcharge tolerance for Li-alloy/metal sulfide cells. Such mechanisms would allow safe capacity equalization in batteries without the need for complex chargers or charging techniques. Overcharge tolerance by a Li shuttle mechanism has been demonstrated in a prismatic cell. This mechanism involves Li dissolution at the negative electrode, chemical diffusion of dissolved Li to the positive electrode, and release of electrons and Li^+ ions at the positive electrode. Self-discharge rates of a polarized Li-alloy electrode indicated the general feasibility of this overcharge protection technique. A modified FeS_2 cell has been operated which verified the ability to design overcharge tolerance by creating a bimodal self-discharge rate characteristic. The modified cell contains a Li-alloy electrode of Li-Al with an additive. A substantial increase in self-discharge rate during charging of the modified Li-alloy electrode enables an ~0% charge acceptance at trickle-charge current densities without polarization of the FeS_2 electrode.

A polysulfide/sulfur shuttle mechanism utilizes the Li polysulfide that is generated on the positive electrode from Li_2S during the overcharge period. The anodic formation of polysulfide prevents the harmful electrochemical dissolution of the positive active material by limiting the potential rise of the positive electrode. The effectiveness of this method is being studied.

Development of cell hardware was pursued to improve the specific energy and specific power by reducing the non-active material weight while still maintaining the electrode performance and cycle life. In FeS_2 cells having rod-shaped electrodes, a lower-cost Mo wire formed from a powder could be substituted for sheet current collectors. A computer model is being developed to determine the performance characteristics of a rod-electrode cell design for the Li-Al/dense U.P.- FeS_2 couple. The effect of reducing the current-collector weight can be modeled with a good degree of confidence, but a change to a radial current distribution requires more analysis. A few test cells were operated that simulate a section of a rod-electrode cell and also duplicate details of flat-plate test cells. High capacity utilization of 85-90% was obtained at 25 to 50 mA/cm^2 (based on separator area). This indicates good prospects for attaining comparable specific energy. At this time, the resistivity of the rod-electrode cell is 1.1 $\text{ohm}\cdot\text{cm}^2$, or about 50% higher than that of the flat-plate cell. Its reduced capacity utilization at high discharge current density (Fig. 2) can also be improved by further increases in the conductivity of the FeS_2 electrode-bed. A multi-rod cell has been projected to achieve a specific energy of 190 Wh/kg and specific power of 200 W/kg at 80% DOD.

Figure 2. Effect of radial current distribution (for rod electrode) upon capacity utilization of U.P. FeS_2 electrode.

A new class of Li-alloy/metal disulfide secondary cells of thin, bipolar construction, and very high specific power and high power-to-energy ratio are being developed and studied. Several versions of these cells (varied in their chemistry and geometry) were operated with 0.1- to 1000-ms, high-current-density pulses (3-50 A/cm^2). A 25- W/cm^2 peak power, 200- kW/dm^3 power density, and 350- Wh/dm^3 energy density have been achieved with repetitive 1- to 10-ms pulses for several cycles in Li-Al/ FeS_2 cells. It was found that 1) the power of well-designed cells is limited by the ohmic resistance of the cell components when the current-pulse durations are less than 10 ms, and 2) the relationship of voltage loss vs current density at any specified state of discharge is nearly linear for identical pulse times. On this basis, it is relatively simple to measure, characterize, and compare the performance of bipolar battery cells.

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Development of Stable Upper-Plateau Capacity in Iron Disulfide Electrodes

G. Barlow (Gould Inc.)

The Li-alloy/ FeS_2 disulfide couple is currently being investigated in high-temperature molten-salt batteries because of its high theoretical specific energy and specific power. The successful implementation of the Li-alloy/ FeS_2 couple has not been possible to date primarily because of an unacceptable decay in the capacity of the upper-plateau discharge reaction. The goal of the present research is to attain a better understanding of the mechanisms which lead to the decline of the upper-plateau capacity and to define a solution to the problem.

Iron pyrite thermally decomposes at a relatively high rate at typical cell operating temperatures of $\geq 450^\circ\text{C}$. However, thermogravimetric studies have shown that at a temperature of $\sim 300^\circ\text{C}$ the rate of decomposition is negligible. This implies that lowering the cell operating temperature in the range of 300 to 400°C , by utilizing lower-melting-point electrolytes, would significantly reduce the rate of sulfur loss and hence the loss of upper-plateau capacity.

In-cell tests of iron disulfide electrodes incorporating various lower-melting-point electrolytes, which were cycled over both the upper and lower voltage plateaus, exhibited some decrease in the rate of loss in the upper-plateau capacity to $\sim 0.14\%$ per cycle in the

operating temperature range of 350 to 400°C. However, this rate of capacity decline is still much too high for a long-cycle-life battery for electric vehicles.

In recent tests, hermetically sealed cells of a starved-electrolyte design containing a MgO separator and a LiCl-LiBr-KBr electrolyte at 400°C were cycled over the upper voltage plateau transition region. The rate of upper-plateau capacity loss in these cells was found to decrease dramatically. The cells, which are still on test, have exhibited almost zero loss in upper-plateau capacity after 300 charge/discharge cycles and ~5,000 hours at 400°C. During cycling, the cells were charged at 10 mA/cm² and discharged at current densities ranging from 10 to 100 mA/cm². The average discharge voltage of the cells was found to decline almost linearly with increasing current density over this range, as did the capacity at current densities >30 mA/cm². In these starved-electrolyte cells, a maximum

utilization of 65% was observed for the upper-plateau capacity, which is considerably less than the 80 to 85% observed by Kaun¹ at ANL in his work on flooded-electrolyte cells. Further work is required to determine the reasons for this difference in the upper-plateau utilization, since much smaller variations in the positive electrode utilization are observed between starved and flooded cells containing FeS positive electrodes. The incorporation of a 15 wt% CoS₂ additive to the iron disulfide electrode did not improve the cell performance over that of positive electrodes consisting of FeS₂ and electrolyte.

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III. APPLIED SCIENCE RESEARCH

The objectives of this project 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 cross-cutting research on improving the understanding of electrochemical engineering principles, corrosion of battery components, surface analysis of electrodes, and electrocatalysis.

A. ALKALINE CELLS

Zinc is often used as the negative electrode in alkaline cells, and it is this electrode that typically limits the lifetime of these cells. Efforts are underway to identify electrode and electrolyte compositions that will improve the cycle-life performance of the Zn electrode.

Zinc Electrode Studies

E.J. Cairns and F.R. McLarnon (Lawrence Berkeley Laboratory)

The purpose of this research is to study the behavior of electrodes used in secondary batteries and metal/air cells, and to investigate practical means for improving their performance and lifetime. Systems of current interest include ambient-temperature rechargeable cells with Zn electrodes (Zn/air, Zn/NiOOH, Zn/AgO, Zn/Cl₂, Zn/Br₂, and Zn/Fe(CN)₆³⁻). The approach used in this investigation is to study life- and performance-limiting phenomena under realistic cell operating conditions.

Micro-Electrode Studies: Zn and Cd micro-electrodes (μ -electrodes) are being used to investigate processes in cycling porous Zn electrodes, which were cycled for 30 to 60 cycles in 17 and 30% KOH electrolytes. The active material tended to redistribute towards the center of the electrode in cells with 17% KOH electrolyte, and toward the edges of the electrode in 30% KOH electrolyte.

During the first 20 to 30 cycles the Zn and the Cd μ -electrode potentials changed very little as the porous Zn electrode was charged and discharged. The potential differences between the various μ -electrodes were usually only about 2 to 4 mV at any particular time, although the μ -electrode potentials varied by about 10 to

20 mV during a cycle. Surprisingly, a potential minimum was frequently observed near the beginning of a charge. Small potential gradients were observed at the edge of the electrode in the 17% KOH cell, which correlated well with the position of the Zn active-material boundary. It was not apparent whether the potential gradients were due to secondary current distribution effects or to a decrease in the porosity near the electrode edge as material moved toward the center of the electrode.

As cycling continued "structure" developed in the Zn μ -electrode data, as seen in Fig. 3. The Cd μ -electrodes also showed an increase in polarization but to a much smaller extent, and later during the cycling than the Zn μ -electrodes. Calculated molalities showed that the increase in μ -electrode polarization was almost entirely due to changes in the Zn(OH)_4^{2-} concentration, which often decreased to 10% of the nominal concentration during charge and increased to 300% of the nominal concentration during discharge. X-ray photographs of the electrodes indicated that the largest changes in the μ -electrode potentials and concentrations occurred in areas which may have experienced an increase in current density due to material redistribution.

The μ -electrode potentials and calculated molalities indicate that the electrode is not limited by transport of reactants and products in early cycles. However, as cycling continues and material redistribution occurs, the electrode becomes limited by transport of Zn(OH)_4^{2-} ,

Figure 3. Zn μ -electrode potentials during charge cycle 32 in 30% KOH electrolyte. (XBL 882-577)

dissolution of ZnO, or precipitation of Zn(OH)_4^{2-} . This limitation is probably due to an increase in the current density and a decrease in the electrode porosity in areas where the μ -electrode polarization is increasing.

Mathematical Modeling: A one-dimensional, time-dependent model was implemented to elucidate the cause of active material redistribution in the Zn electrode. This model takes into account the transport of electrolyte species, heterogeneous reactions, kinetics, and current density variations.

A simplified version of this model, where the concentration terms are omitted from the equations for Ohm's Law in the electrolyte phase and the electrolyte velocity is assumed to be zero, provides insight into the transient electrolyte changes over the course of one cycle. The results for the changes in the concentrations of zincate ion (Zn(OH)_4^{2-}) and hydroxide ion (OH^-) are shown for both Zn and NiOOH electrode compartments for one cycle (5.0-h charge, 15 minute open-circuit period, 2.5-h discharge) in Fig. 4. The concentrations represent a particular location in the center of the cell. The results were found to be very sensitive to the value of the precipitation/dissolution rate constants (both were 2.5×10^{-5} cm/sec for Fig. 4). The following trends have been found from the model:

- (1) By the end of the charge cycle, the concentration of OH^- increases only about 15% whereas the concentration of Zn(OH)_4^{2-} decreases by about a factor of 50% from their initial values.

Figure 4. Calculated concentrations from Zn/NiOOH cell model for one cycle (5.0-h charge, 15-min. open-circuit, 2.5-h discharge). The precipitation/dissolution rate is 2.5×10^{-5} cm/sec. These concentrations are at a particular location in the middle of the cell. Symbols represent concentrations as follows: ■, OH^- in the Zn compartment; □, OH^- in the Ni compartment; ●, Zn(OH)_4^{2-} in the Zn compartment; ○, Zn(OH)_4^{2-} in the Ni compartment. (XBL 882-578)

- (2) The differences in concentrations of both Zn(OH)_4^{2-} and OH^- in the Zn and NiOOH electrode compartments are relatively small, which shows there is rapid transport from one side of the microporous separator to the other.
- (3) During discharge, the concentrations of both Zn(OH)_4^{2-} and OH^- change more rapidly than during the charge cycle. After precipitation of zincate (as ZnO) occurs (at 6 h, Fig. 4) the concentrations remain relatively unchanged. Also, the concentration differences between the Zn and NiOOH electrode compartments are much greater after the onset of precipitation, during discharge. This could be explained by the observation that the precipitation of zincate (as ZnO) was faster in the Zn compartment due to the higher concentrations of Zn(OH)_4^{2-} in the Zn compartment than in the NiOOH compartment.

In addition, the model equations were solved using different rate constants of precipitation/dissolution to determine what effect this parameter had on the results. During charge, if the value was set at 5.0×10^{-5} cm/sec, there was very little change in the concentrations of both Zn(OH)_4^{2-} and OH^- from their initial values. However, if the rate was set at 1.5×10^{-5} cm/sec, the concentration of Zn(OH)_4^{2-} dropped nearly to zero by the end of charge. This demonstrates that there is only a narrow range of values of this parameter that gives meaningful results.

Cycling of Zinc/Nickel Oxide Cells: Three factors under investigation for improving Zn/NiOOH cell cycle-life performance are: 1) electrolyte composition, 2) electrode composition, and 3) charging method. Zn/NiOOH cells using 25-33 mol% Ca(OH)_2 -additive in the Zn electrodes, 31 wt% KOH or 15 wt% KOH-15 wt% KF electrolytes, and a 30-ms on/90-ms off pulse-charging regimen were investigated. Although one of these cells lasted for over 500 cycles, they generally failed from dendritic shorting within 20 to 60 cycles. The Ca(OH)_2 -additive electrodes cycled in 31 wt% KOH exhibited diamond-shaped crystals characteristic of CaZn(OH)_4 . No such crystals were observed in Ca(OH)_2 -additive electrodes cycled in KOH-KF electrolyte because CaF_2 formation is thermodynamically favored over CaZn(OH)_4 . An electrode of pure CaZn(OH)_4 cycled at constant current in 31 wt% KOH was well-behaved and showed a very uniform distribution of material after 50 cycles, much better than observed with the Ca(OH)_2 -additive electrodes. Cells containing negative electrodes of ZnS and ZnSe, having very low solubilities in 31 wt% KOH, produced very high overpotentials on formation, along with low charging efficiencies. Several new separator materials were evaluated, but none of them provided a superior barrier to dendrite penetration, as compared to three layers of microporous polypropylene (Celgard).

The cells described above transferred Zn to the NiOOH electrode at the same rate as standard Zn-electrode cells. An average of 45% of the weight gained by the NiOOH electrode during cycling was present as Zn, consistent with the interpretation that Zn ions displaced Ni ions in the α -nickel hydroxy-hydrate of the NiOOH electrode. Impregnating the NiOOH electrode with ZnO prior to cycling might slow the rapid transfer of Zn to the NiOOH electrode in the early cycling of the cell, and allow the Zn electrode to be reduced in weight, thereby maintaining satisfactory cell specific energy. Mechanical deposition of ZnO from an aqueous slurry into the NiOOH electrode on a vacuum table loaded only about one-fourth the amount required, so this may need to be carried out by an electrochemical process.

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B. ZINC/HALOGEN CELLS

Flowing electrolytes are used in Zn/halogen cells to promote the transport of Zn^{++} across the cell and to remove halogen as the cell is charged. The cell performance is limited by the tendency of the electrodeposited Zn to assume unwanted shapes, and efforts are aimed at understanding the complex phenomena that control the Zn electrode morphology.

Surface Morphology of Metals in Electrodeposition

C.W. Tobias (Lawrence Berkeley Laboratory)

The objective of this project is to develop a pragmatic understanding of the detail processes and their interactions in the macrocrystallization of metals, necessary for the design and optimization of rechargeable galvanic cells. Studies undertaken in this project include observation of the formation of groove patterns from electrodeposition of metals in flow cells and at rotating disk electrodes. Deposit roughness is measured by a

Clevite instrument, while more detailed images of surface structure are obtained by SEM. Electrolyte properties, including transport coefficients, are obtained by classical methods. Observations on nucleation frequency as a function of electrode overpotential are performed on rotating disk electrodes, using steady state and transient techniques. A special flow cell, equipped with capability to take time-lapse photographs and real time video recordings, is used to observe and record macroscopic crystal growth and the development of characteristic patterns in the electrodeposition of Zn. Microprofiled Pt electrodes, on which predetermined surface roughness elements are grafted by VLSI process technology, serve as reproducible substrates for the study of propagation of patterns in macromorphology. Growth of surface profiles is modeled using finite difference—finite element or boundary element—techniques for solution of the Laplace equation.

According to the adsorption theory of leveling and brightening, the lower rate of diffusion of inhibitors into recesses, relative to transport to the more accessible areas on the surface, results in accelerated smoothing and evening of the electrodeposits. Simulation of advancing profiles based on the simultaneous solution of the Laplace equation for the electric fields, however, predicts a more rapid leveling action than is generally found by measuring actual deposit profile thicknesses. In our view this discrepancy is caused by a neglect of microscopic flows into recesses (notches, V-grooves) in computer implemented simulations.

Enhanced transport of inhibitors into recesses would tend to decrease the leveling action by interference with the deposition process in the more remote areas. As a first approach to the elucidation of this problem, the flow field in Couette and Poiseuille flows past angular notches over a range of Reynolds numbers and notch angles were solved. The Polyflow program was used for the finite element routine. Results indicate that there is a recirculation pattern in notches below a critical angle. As the Reynolds number is increased, the recirculation region grows in strength and eventually becomes asymmetrical. The solution of the convective diffusion equation based on the results of the hydrodynamic analysis indicates that these recirculation flows can indeed explain the decrease in leveling action when compared to a condition of stagnant electrolyte. Thus, while effective convective transport is essential for the transport of the reacting metal ion, the same condition has an adverse effect on leveling.

To accommodate the improved video-microscope system, in which the resolution was advanced from 1.1 to 0.5 μm , an existing flow cell was reconstructed to allow *in situ* microscopy. The new cell features improved current distribution on the main electrode and a reference port through which potentials may be measured. For chronoamperometric measurements, as well as for other purposes in which optical observation is not

necessary, a rotating disk assembly has been modified. A computer-control scheme directly interfaced with Lotus 1-2-3 has been developed for controlling various experiments. The system writes macros for Lotus 1-2-3, turns all electrical circuits on/off, performs chronopotentiometry or chronoamperometry, and will also run interrupt measurements. For *ex situ* studies of microstructures, a method has been developed for preparing ultrathin samples of Zn deposits suitable for transmission electron microscopy.

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Dendritic Zinc Deposition in Flow Batteries

J.R. Selman (Illinois Institute of Technology)

The objective of this research is to study the growth of Zn dendrites and the morphology of Zn deposits from acidic ZnBr₂ solutions under well-defined convection conditions. In addition, the propagation of a two-dimensional wavy surface is analyzed by mathematical modeling, and the effects of corrosion caused by the presence of Br₂ are investigated experimentally and analytically.

The dendritic growth history of Zn deposited from acidic ZnBr₂ solutions was investigated experimentally using a rotating concentric cylinder electrode (RCCE) cell. The deposition of Zn from ZnBr₂ solution is mainly resistance-controlled (primary current distribution). Therefore, the rotation rate has no strong effect on the growth rate of dendrites. Addition of Br₂, KCl, or an organic additive reduces the linear growth rate and retards the onset of dendrite formation. However, of the various additives, Br₂ is the most effective for suppressing dendrite formation at low current density (~20 mA/cm²). The formation of dendrites is completely suppressed up to a net loading of 160 mAh/cm². This result again indicates the importance of Zn corrosion by Br₂ in the functioning of the Zn/Br₂ battery.

The AC-impedance response of the working and counter electrodes of the RCCE cell was measured. A good correlation was observed between the measured ohmic resistance and electrode deposit quality. Therefore, AC-impedance measurements are a promising

technique for *in situ* monitoring of the Zn deposit in an operating battery.

The morphology of Zn deposits was studied using both the rotating hemispherical electrode (RHE) and the RCCE. In the pH range of 1.7 to 5.0, no change of the morphology of the Zn deposited from ZnBr₂ solutions is apparent. Typically, three-dimensional nodules that show no alignment are obtained. However, when concentration polarization is significant, evidence of secondary flow in the form of spiral markings that are characteristic for the RHE become visible. Porous (mossy) Zn deposits are formed only at low current density (< 1 mA/cm²). This may be the case when a low overall charging current (or overpotential) is applied. Also, regions of low current densities can occur, caused by (1) the "potential shadowing" effect of the protruding part of a dendrite profile, (2) an extended current path (e.g., to a recessed area), or (3) non-uniform corrosion rate distribution. The presence of Br₂ causes extensive damage to the crystal structure of the Zn dendrites. The degree of damage increases with decreasing charge current density and increasing rotation rate. The corroded appearance of the Zn crystals is believed to be the result of chemical attack by Br₂.

The general behavior of the secondary current distribution and the propagation of the profile of a parallel-plate electrode was analyzed by using a two-dimensional model. It is found that the shape of the electrode profile strongly affects the current distribution. For example, when a profile has an extended flat region away from the protruding part, prolonged deposition results in the appearance of a secondary peak. The apparent tip radius of the profile increases with time because of the lateral deposition near the peak of a propagating profile.

The presence of corrosion significantly affects the propagation rate of an electrode profile. At low convection rates, where the phase shift of the mass transfer rate is less than 90°, a smoothing effect results. However, when convection is increased, the phase shift becomes greater than 90°, and a destabilizing effect results.

Zinc Electrode Morphology in Acid Electrolytes

J. McBreen (Brookhaven National Laboratory)

The purpose of this work is to elucidate the factors affecting the morphology of Zn electrocrystallization in battery electrolytes, with the emphasis is on the physical and atomistic aspects of the process. The following research areas were investigated in 1987: (i) structure determination of zinc bromide complexes by extended X-ray absorption fine structure (EXAFS), (ii) *in situ* EXAFS studies of the formation of Zn complexes in

alkaline electrolyte, and (iii) the development of EXAFS techniques for *in situ* studies of battery electrodes.

EXAFS Studies of Zinc Bromide Electrolytes. Extensive analysis of EXAFS data helped to understand the influence of the bromide to Zn ion ratio in the electrolyte on the kinetics and morphology of Zn deposits. The predominant zinc bromide complex depends on the electrolyte concentration and the bromide to Zn ion ratio. In 0.1 M ZnBr_2 the Zn ions are mostly hydrated ions. In 1 M ZnBr_2 the data could be fitted to a $\text{ZnBr}^+ \cdot 3 \text{H}_2\text{O}$ model and in 3 M ZnBr_2 to a $\text{ZnBr}_2 \cdot 2 \text{H}_2\text{O}$ model. The data for an electrolyte of 1 M ZnBr_2 + 3 M KBr could be fitted to a $\text{ZnBr}_3^- \cdot \text{H}_2\text{O}$ model. These analyses are for two-shell fits with a Zn-O distance of 1.87 Å and a Zn-Br distance of 2.38 Å. In 3 M ZnBr_2 + 3 M AlBr_3 the data could be fitted to a simple single-shell ZnBr_4^- model with a Zn-Br distance of 2.4 Å.

EXAFS Studies of Zincate Formation. Cells were designed to investigate the formation of Zn complexes in the vicinity of discharging Zn electrodes. The cells were zinc/silver oxide cells with a thin (0.375 mm) electrolyte film between the electrodes. The X-ray beam was passed through the electrolyte film. Dispersive EXAFS measurements of electrodes discharged over an 8-h period were made at LURE-CNRS in Orsay, France. The cell contained an electrolyte of 12 M KOH with various additions of silicate and sorbitol. In some experiments, up to four times the equilibrium solubility of Zn was observed. Preliminary data analysis has not revealed the formation of complexes other than those found in zincate solutions.

EXAFS Studies of Battery Electrodes. Transmission EXAFS was used to study the structural changes that occurred during the $\text{Ni(OH)}_2/\text{NiOOH}$ reaction on non-sintered nickel oxide electrodes in 8.4 M KOH. The Ni atoms in Ni(OH)_2 are octahedrally coordinated to six oxygen atoms with a Ni-O distance of 2.05 Å. On charge the octahedral coordination becomes distorted, to yield an arrangement of four oxygen atoms with a Ni-O distance of 1.88 Å and two oxygen atoms with a Ni-O distance of 2.07 Å. This distortion has not been previously reported, presumably because of the poor quality of the X-ray diffraction patterns for NiOOH.

The cells used in this study were further modified to conduct cyclic voltammetry of Ni electrodes. The cyclic voltammetry studies were performed simultaneously with the dispersive EXAFS measurements at LURE-CNRS. One interesting observation was an anomalous decrease in the X-ray absorption white line on oxidation of Ni(OH)_2 . This is consistent with the distorted Ni-O coordination in NiOOH.

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C. COMPONENTS FOR ALKALI/SULFUR CELLS

Superior alternatives to the β "- Al_2O_3 ceramic electrolyte and high-temperature sulfur-polysulfide electrode used in Na/S cells, and stable components for Li/S cells, are under investigation.

Low-Temperature Beta"-Alumina Cell

L.C. DeJonghe (Lawrence Berkeley Laboratory)

The focus of this program is to investigate the properties of organosulfur electrodes in sodium/organosulfur cells, which operate between ambient and intermediate temperatures (25-150°C). These organosulfur electrodes are based on the general redox reaction for organic disulfide, $\text{RSSR} + 2\text{e}^- \rightarrow 2\text{RS}^-$, where R is an organic moiety such as CH_3 , C_6H_5 , $\text{CH}_3\text{OCH}_2\text{CH}_2$, etc. Among the advantages of such a generic redox couple for energy storage include the ability to control the physical, chemical, and electrochemical properties of the organosulfur species by appropriate choice of the organic moiety. Many organic disulfides are available commercially, and although they share some chemical and electrochemical similarities due to the disulfide linkage, their physical properties are as different as the organic moieties attached to the sulfur-sulfur bond.

Sodium/organosulfur cells were tested in cases having epoxy and elastomeric O-ring seals, allowing access to the positive organosulfur electrode compartment for injection of solvents or other additives, and/or allowing the positive electrode to be renewed when desired. Sodium/tetraethyl thiuram disulfide (Na/TETD) cells operating at 120 to 150°C were cycled galvanostatically under computer control with continuous monitoring of internal cell resistance, open-circuit voltage, cell temperature, and positive electrode pressure, as a function of current density and state of charge. Laboratory-scale Na/TETD cells were assembled with maximum practical specific energies of over 110 Wh/kg. At 130°C, Na/TETD cells were cycled at a specific power of 6 W/kg between 10 and 90% of available capacity at an overall energy efficiency of 75% and a realized specific

energy of 80 Wh/kg. Carefully assembled cells are capable of delivering peak current densities of 100 to 150 mA/cm² for a period of a minute or more, corresponding to a peak power of 40 to 60 W/kg. The TETD electrode is unable to sustain the peak rates of discharge for an appreciable fraction of available capacity, most likely due to slow mass transport in the positive electrode melt, as confirmed by viscosity measurements.

Na/RSSR cells (R = aliphatic, aromatic, ethereal, or fluorinated organic moiety) with typical theoretical specific energies ranging from 360 Wh/kg when R = (C₂H₅)₂NCSS to 770 Wh/kg when R = CH₃ were investigated. The open-circuit voltage (OCV) of Na/RSSR cells can be varied by the choice of the R group. For example, OCV of a sodium/diphenyl disulfide cell is 2.0 V, whereas the incorporation of a highly electronegative fluorine atom in the para position on the phenyl ring increases OCV of the sodium/difluorodiphenyl disulfide cell to 2.4 V. Many of the simple aliphatic and aromatic disulfides are quite non-polar and are incapable of dissolving the sodium thiolate salts generated on cell discharge, therefore requiring the use of solvents in the positive electrode. Accordingly, CH₃SSCH₃ (DMDS) electrodes were assembled using a range of 30 to 80% solvent to facilitate cell discharge. A further increase in cell performance is achieved by use of an electrocatalyst in the positive electrode such as cobalt phthalocyanine (CoPc) to lower the charge-transfer resistance for the RSSR/RS⁻ couple. At an operating temperature of 105°C, Na/DMDS cells having 1 wt% CoPc in the positive electrode maintained discharge rates of 50 mA/cm² at 1.2 V to 50% of available capacity and 15 mA/cm² at 1.3 V to 100% of capacity, and they can be recharged at 20 mA/cm² at a nominal voltage of 2.2 V.

The synthesis of fluorinated and/or perfluorinated organic disulfides and the use of electrocatalysts to minimize charge-transfer polarization in organosulfur electrodes are currently being investigated. The use of highly oxidizing, low-viscosity organosulfur compounds, combined with electrocatalysts, should lead to cells of both high specific energy and power. The majority of the organosulfur electrodes being investigated for intermediate-temperature cells are also being tested in Li cells at room temperature, particularly those disulfides which are liquid at room temperature. A key issue for all organosulfur cells at this time is to demonstrate long cycle life at reasonable specific power, and with high peak specific power. For Li/RSSR cells, studies are also underway to determine the reversibility of the Li electrode.

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Mathematical Modeling of the Sodium/Sulfur Cell

E.J. Cairns and F.R. McLarnon (Lawrence Berkeley Laboratory)

The objective of this study is to develop and confirm an advanced mathematical model of the sulfur electrode in Na/S cells. The cell being modeled is of the

tubular central-Na type, and includes a thin layer of α - Al_2O_3 felt around the β - Al_2O_3 solid electrolyte in order to prevent deposition of sulfur on the solid electrolyte during cell charge. The model consists of a set of non-linear partial differential equations (PDE's) which describes the processes of diffusion, migration, and convection taking place during the operation of such a cell. Solution of the linearized equations is effected on a digital computer via implementation of the Newman-IAD method, a finite-difference technique for the solution of second-order linear PDE's.

Fluid flow through the sulfur electrode, which is essentially a porous graphite felt, is accounted for by use of the differential form of Darcy's law, $v = kVP$, for flow-through porous media. This requires the use of capillary pressure and relative permeability, both of which are functions of the fluid-matrix system. Due to the difficulty of directly performing measurements on the sulfur/polysulfide/graphite system, an analogous system (water/bromobenzene/glass fiber) was used. Established theory was then applied in order to estimate the capillary pressure and relative permeability values for the system of interest, using the experimental data. Figure 5 shows the relative permeability of the sulfur (wetting) and polysulfide (non-wetting) phases as functions

Figure 5. Computed values of relative permeability of sulfur and sodium polysulfide in graphite felt. Values are shown for both the imbibition (displacement of polysulfide by sulfur), and the drainage (replacement of sulfur by polysulfide) cycles. Beyond a sulfur volume fraction of 0.78, the polysulfide phase is discontinuous and no longer moves. (XBL 882-579)

of the saturation (volume fraction). Beyond a value of saturation of 0.75, the polysulfide phase is no longer interconnected, and it does not move. The relative permeabilities of the sulfur and polysulfide phases are 1 and 0 respectively in this region. The only other physical property remaining to be measured is the graphite felt conductivity. All other physical properties are available in the literature.

The results of this modeling will be compared with data from an operating cell which has been designed to allow measurement of ionic potentials throughout the sulfur electrode. An attempt will be made to predict the effect of various charge-discharge regimens upon cell operation.

Glass Electrolytes and Advanced Cell Concepts

I.D. Bloom and C.C. Christianson (Argonne National Laboratory)

Glass electrolytes for Na/S cells are potential alternatives to ceramic electrolytes, such as $\text{Na}\beta$ - Al_2O_3 , that are currently being used. The objective of this research is to develop a glass that is highly conductive for Na^+ ions, is chemically stable in the hostile Na/S cell environment, and can be easily fabricated at low cost. Based on the conductivity experiments and chemical stability tests, a glass with the composition (in mol%) 42 Na_2O , 8 Al_2O_3 , 5 ZrO_2 and 45 SiO_2 was chosen. This composition, hereafter called ANL Glass, met the initial acceptance criteria, i.e., high Na^+ -ion conductivity (221 ohm-cm at 300°C) and acceptable chemical stability (comparable to that of $\text{Na}\beta$ - Al_2O_3 and Dow borate glass).

To make electrolyte structures, such as tubes, from ANL Glass requires close attention to physical and chemical properties. Because of the hygroscopic nature of ANL Glass, all of the fabrication experiments are performed in the absence of moisture. Under Ar, for example, ANL Glass cannot be extruded easily through a graphite die. It was found to react with and stick to the extrusion die. Under a dry O_2/N_2 (synthetic air) or a dry O_2/Ar atmosphere, straight tubes of ANL Glass have been drawn using a mechanically guided, Swagelok-connector-tipped, stainless-steel blowpipe. By minimizing all contact with moisture and CO_2 , tubes of sufficient quality have been produced to allow small-scale cell construction and testing.

Sealed Na/S cells were constructed using the above glass tubing. A typical cell was filled with a sulfur-graphite mixture (22 mAh) and was sealed using the Swagelok connector left from the blowpipe. After conditioning at 310°C , cycling was initiated with small currents (400 μA discharge for 0.5 h and 200 μA charge for 1 h). Cycling was continued until 100 cycles had

been achieved at 2 to 3% depth-of-discharge (DOD). The temperature and current were increased to 326°C and 1 mA/cm²; (C/22 rate; voltage cutoffs: 1.92 and 2.4 V), respectively. Under these conditions, greater than 50% utilization of the sulfur electrode was achieved. A total of 30 additional cycles were achieved before cell breakage.

Sealing tubes of ANL Glass to a header will require careful matching of the thermal expansion coefficients of the materials involved. In addition, there are requirements that the header be an insulator (ionic and electronic), be chemically stable with respect to the Na/S cell system, be as pore-free as possible, and be chemically compatible with ANL Glass (so they will chemically bond). High-MgO ceramics would seem to be ideal candidates for this application.

Candidate ceramics in the MgO-Al₂O₃-BaO-B₂O₃ system have been prepared and characterized by metallography, dilatometry, and differential thermal analysis. Candidate ceramics have been sintered at five different temperatures, 1045, 1145, 1245, 1345, and 1445°C. Metallographic examination of MgO E (composition in mol%: 89 MgO, 1 Al₂O₃, 5 BaO and 9 B₂O₃; 1445°C sinter) shows it to consist of primary crystals of a MgO-rich phase surrounded by a BaO-rich eutectic. Among the materials characterized, two materials, MgO G and MgO J (composition in mol%: 89 MgO, 1 BaO, 1 CaO, 1 Al₂O₃ and 8 B₂O₃ and 90 MgO, 1 Al₂O₃ and 9 B₂O₃, respectively; 1245°C sinter), seem to have the closest match of thermal expansion to that of ANL Glass.

The ANL glass-membrane sensor/reference has been used in a variety of cell systems to demonstrate its versatility. For example, in systems such as (Mo)Na₂S_x | ANL Glass | Na₂S_y(Mo) (x, y = 3, 4, 5)⁵ at 309°C, after thermal equilibration the EMF measurements varied with Na activity and were reproducible to ±1 mV. The readings were stable for at least 18 h.

In NaCl/AlCl₃ melts (60 mol% AlCl₃) at 123°C, stable potentials were not obtained with ANL Glass. However, stable potentials were obtained in the system Al | Na₂S₄, NaCl, AlCl₃ | T Glass | NaCl, AlCl₃ Al (T Glass composition, in mol%: 40.7 Na₂O, 10.8 Al₂O₃, 8.3 ZrO₂ and 40.2 SiO₂; resistivity 215 ohm-cm at 300°C). The much-higher ZrO₂ + Al₂O₃ concentration (19.1 vs 13 mol% in ANL Glass) gives T glass a much higher chemical stability towards the melt, probably by slowing the kinetics of the reaction of NaAlCl₄ with Na₂SiO₃.

Coulometric titrations of polysulfide and transition-metal-chloride electrodes (~2 mAh capacity in 16.7-μAh steps) were performed using the reference electrode. The titration curve of sulfur, for example, shows a broad plateau down to 71 mol% S, as expected. Immediately following the plateau is a linear region from 71 to 60 mol% S (2.06-1.77 V). This titration shows very precisely the transformation from two-phase material to single-phase material.

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Electrical Conduction and Corrosion Processes in Fast-Ion Conducting Glasses

H.L. Tuller (Massachusetts Institute of Technology)

Glasses with high alkali ion conductivity have been demonstrated previously, but MIT has found that some of the most conductive glasses are often among the least

stable in Li.¹ MIT has pursued a number of approaches over the past year to combat this problem, including the addition of stabilizing ions to the bulk glasses, the formation of chemically passive layers on highly conductive glass substrates, and the development of an improved understanding of the transport properties of fast-ion-conducting (FIC) glasses with the objective of formulating highly conductive glasses with improved stability.

Stabilization Studies

Earlier studies by MIT² on CaO additions (up to 10 mol%) to bulk lithium borate glasses demonstrated: (i) ionic conductivities drop somewhat, and (ii) thermal stability is improved. In addition to the bulk studies, MIT has initiated the following work on passivation layers.

Ion Exchange: Lithium metaborate glasses were placed in molten-salt baths of $\text{LiNO}_3\text{-Ca(NO}_3)_2$ at 365°C for ~100 h. The Ca ion-exchanged glasses were then investigated by X-ray, XPS, and SIMS. ESCA profiles confirmed that Ca exchange at least to the depth of 1 μm . Complex impedance measurements are now proceeding to establish the resistivity of the exchanged layer and subsequent studies of the stability will be performed in MIT's electrochemical titration apparatus.

Ion Implantation: Ion implantation is also being investigated as a means of surface modification. Preliminary work has begun with Ca as the implant. Samples are being prepared for study.

Evaporation of Lithium Metaborate Thin Films: Films of $\text{Li}_2\text{O-B}_2\text{O}_3$ glasses, earlier found by MIT to be among the most stable glasses at high a_{Li} ,³ were evaporated at a rate of 120 Å/min at 150°C to a thickness of ~1 μm . Preliminary ESCA analysis suggests that the film is boron deficient. Subsequent evaporations will be performed from B_2O_3 -enriched sources.

Transport Studies

An extensive series of measurements, including electrical conductivity, glass transition temperature, and density, was completed this year on the alkali chloroborate glass system, with a recent focus on K^+ -ion conductors. Figure 6 shows that chlorine has surprisingly little effect on K^+ -ion conduction, in contrast to the behavior observed earlier for the Li and Na glasses. Although the K^+ -ion glasses are dilated by chlorine, the chlorine has anomalous effects on T_g (see Fig. 7), in contrast to the other systems, which translates into increased network stiffness and coherency. Data obtained on the three types of alkali-ion conductors have enabled us to isolate the role of electrostatic and strain contributions to ionic conduction and thereby provide insight for identifying stable, highly conductive glasses. Raman spectroscopy measurements on lithium-calcium and potassium borate glasses are now being performed by Professor Balkanski's group in Paris.

Figure 6. Log σ vs chloride substitution for Li, Na and K diborate glasses. (XBL 887-2387)

Figure 7. Dependence of T_g on alkali halide content for alkali diborate glasses. (XBL 887-2387)

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New Battery Materials

R.A. Huggins (Stanford University)

The objective of this program is develop materials for high-performance secondary batteries. The emphasis of the research is to understand the important structural, thermodynamic and kinetic properties of these materials which influence their behavior as cell components. An important aspect of this program is to understand the relationship between fundamental thermodynamic and kinetic parameters (e.g., phase equilibria, Gibbs' free energy values and chemical diffusion within solid phases, and the microscopic and macroscopic electrochemical phenomena) which influence the behavior of battery materials.

Sodium-Based Electrode and Electrolyte Systems. A program was initiated to investigate Na-based electrode systems that employ electrolytes containing organic solvents or low-temperature molten organometallic salts. The molten-salt cell

investigated previously by other workers was studied. Our results are in agreement with those obtained previously. At 230° C, the cell operates reversibly at ~2.2 V using a current density of 20 mA/cm². An alternative negative electrode/electrolyte combination, in which the negative electrode material does not react with the electrolyte, should confer significant advantages to the design and operation of these cells since the use of the relatively high-impedance Na β ''-Al₂O₃ tubes may be avoided. Further, the use of an electrolyte that operates at a lower temperature than that employed in the cell is desirable. Consequently, work has been initiated to investigate alternatives to the negative electrode/

β ''-Al₂O₃ assembly. In particular, the reactivity of Na to a number of metals, M, is being studied in cells of the type,

The NaAlEt₄ electrolyte, which can be used at about 120°C, is stable at high Na activities.

To date, several Na alloy systems have been tested. The behavior of these alloy systems as positive electrodes can be divided into different classes, based on the nature of the alloying element.

- (1) Alloys containing "heavy" metal elements (i.e., Cd, Bi, Sn, Pb). These metals show, in general, fast reactions with Na, leading to several hetero-phase reaction plateaus on discharge. Typically, current densities of 1 to 2 mA/cm² can be employed without excessive electrode polarization.
- (2) Alloys containing "light" metal elements (i.e., Zn, Si, Mg). These metals show little or no tendency for reaction with Na under the conditions employed here.
- (3) Alloys containing transition metal elements (i.e., Fe, Mn, Ni, Cu). In general, these alloys corrode, resulting in discoloration of the electrolyte.

Based on these results, work is now continuing along two lines. First, it is intended to characterize more fully some of the systems which show fast reactions with Na. In particular, the coulometric titration curves for these systems will be determined and the chemical diffusion coefficient of Na in the alloys will be measured. Second, the screening procedure will be extended to binary alloys that contain, as one component, an element which reacts well with Na (e.g., Cu-Sn bronzes). This approach has recently been used successfully in this laboratory in intermediate-temperature Li-based cells with the use of Mg₂Si as a alternative negative electrode material for 44% Li-Si alloy.

Preparation of Thin-Film Electrode and Electrolyte Materials Using Atmospheric-Pressure Chemical Vapor Deposition. The atmospheric-pressure, chemical-vapor-deposition technique is being used to deposit thin films of FeS₂ using Fe(CO)₅ as a source of Fe. The use of H₂S as the source of sulfur results in the preparation of films with the approximate composition FeS_{1.5} in the temperature range 200 to 350°C. Powder X-ray diffraction studies have shown that these films contain predominantly a mixture of marcasite (the rutile form of FeS₂) with Fe₃S₄ (which has the spinel structure). It has been found that treatment of these films at 500°C in air for 12 h results in the formation of a tightly-adhering film of pyrite with a grain size of typically < 1 μ . This observation is in agreement with that found previously by heat treating bulk samples of marcasite. Further, it has been demonstrated that films containing substantial amounts of pyrite may be deposited directly at temperatures $\geq$ 300°C.

The electrochemical reactions of low-temperature marcasite/spinel films (deposited on Mo foil) with Li have been investigated at room temperature in cells of the form

The results of preliminary experiments indicate that such films can be discharged at current densities up to 0.1 mA/cm^2 with minimal electrode polarization. Further, a constant-voltage plateau is observed at $\sim 1.7 \text{ V}$ vs Li with a capacity in excess of 1 Li per FeS_x .

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D. CORROSION PROCESSES IN HIGH-TEMPERATURE, HIGH-SULFUR-ACTIVITY MOLTEN SALTS

The aim of these projects is to develop low-cost containers and current-collector materials for use in alkali sulfur and other molten-salt cells.

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

J.R. Selman (Illinois Institute of Technology)

Electrochemical deposition (ECD) from molten alkali metal fluoride baths and plasma-enhanced chemical-vapor deposition (PE-CVD) are used to prepare coherent coatings of Mo, Mo_2C and TiN. The promising corrosion resistance observed with these coatings in short-term tests in molten polysulfides suggests that they may be useful in coatings for current collector and containment materials in high-sulfur-activity applications such as in Na/S and Li-alloy/ FeS_2 secondary batteries.

The objective of this research is to optimize the processes to obtain coatings with reproducible thicknesses and smooth surface morphologies by ECD and to deposit protective coatings at relatively low temperatures by PE-CVD. In addition, the corrosion resistance of Mo, Mo_2C and TiN coatings in Na_2S_x and LiCl-KCl (saturated with Li_2S or FeS_2) melts will be characterized.

To control deposition from fused electrolytes, nucleation pulses and relatively low-growth current densities will be applied. Increasing the number of nucleation centers and maintaining a constant low rate of growth results in a good Mo coating. The plating of Mo_2C is a complex electrode process (i.e., co-deposition of Mo and C), which involves the insertion of C atoms into the interstices of the Mo lattice and the subsequent growth of a dense layer. These processes are therefore more difficult to control. During the nucleation and growth stages, temperature apparently plays a prominent part in determining the surface morphology. The effect of contamination of the electrolyte by water was also investigated. Water levels up to 250 ppm in inert-gas atmospheres showed little effect on the electrochemistry of deposition.

Testing the corrosion resistance of Mo, Mo_2C and TiN coatings in a high-sulfur-activity environment requires an elaborate procedure involving cyclic voltam-

metry and SEM examination. A 100-h test at 300° C in Na_2S_x was adopted. During this period the coated Ni substrates are subjected to a continuously varying polarization between -0.18 V and +0.12 V, corresponding to the limits of the melt compositions — Na_2S_2 and Na_2S_5 . Any cracks or pinholes in the coating produce a cathodic voltammogram with peaks characteristic of the Ni substrate (reduction of NiS and Ni_3S_2).

The above testing procedures are aimed at a relatively rapid characterization of the quality of the coatings, which are expected to have a very low rates of corrosion. They are substitutes for a much-longer static corrosion test. However, such long-term tests are being planned in cooperation with developers of Na/S batteries.

Mo-, Mo_2C - and TiN-coated samples were found to behave similarly in Na_2S_x melts. The cyclic voltammograms were typical of those for Mo, which has the highest corrosion stability. A cathodic peak corresponding to the formation of a Na_2S_2 blocking layer, and a steep increase in the anodic current due to kinetically unrestricted sulfide oxidation to Na_2S_5 , were observed.

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E. COMPONENTS FOR AMBIENT-TEMPERATURE NONAQUEOUS CELLS

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

Spectroscopic Studies of the Passive Film on Alkali and Alkaline Earth Metals in Nonaqueous Solvents

D.A. Scherson (Case Western Reserve University)

This research project has as its major focus a detailed examination of the reactivity of common organic solvents toward alkali metals. The approach being utilized involves the investigation of vapor-deposited alkali metals on well-characterized single cry-

stal metal surface in ultra-high vacuum, followed by the exposure of such surfaces to nonaqueous solvents. The nature of the reaction products is investigated by low-energy electron diffraction, Auger electron spectroscopy (AES), thermal spectroscopy, and complemented by work-function measurements. It is expected that a careful analysis of these results will provide the much-needed information on the nature of the passive layer that forms at the nonaqueous solvent/alkali metal interface that is relevant to secondary Li-based battery applications.

The results obtained during 1987 may be summarized as follows:

- (i) Carbon dioxide does not adsorb on clean Ag(111) surfaces even at temperatures as low as -186°C. This conclusion is based on *in situ* measurements of work function and AES analyses for which no changes were observed in the values of $\Delta\phi$, and no carbon or oxygen could be detected on Ag after long exposure to CO_2 .
- (ii) No extra diffraction spots were observed upon depositing Pt at submonolayer coverages on the Ag(111) surface even after annealing up to temperatures of 400°C.
- (iii) About a monolayer of K deposited on Ag(111) gives rise to a change in work function of about -2.5 eV. This corresponds to a surface composition of 18% as determined from the relative intensities of the AES peaks.
- (iv) The maximum work function change induced by the adsorption of CO_2 to saturation coverages on a K-covered Ag(111) surface was approximately +0.8 V. This is consistent with a partial charge transfer from the K to the lowest unoccupied molecular orbital (LUMO) of CO_2 , an effect that is expected to be accompanied by a bending of the otherwise linear $\text{O}=\text{C}=\text{O}$ molecule.
- (v) Four major peaks at temperatures of 400 (I), 500-600 (II), 770 (III) and 840°K (IV) were detected in the thermal desorption spectra of CO_2 adsorbed on K-covered Ag(111) surfaces. The relative heights of peaks III and IV were found to depend on the ratio of K to CO_2 coverage. In particular, peak III was more prominent when excess K was present, whereas peak IV predominates when the ratio was inverted. It seems conceivable that peaks I and II are associated with single CO_2 molecules coordinated to K atoms on the surface in two different configurations, whereas the peaks observed at the higher temperatures may involve interactions between the adsorbed CO_2 molecules to yield oxalate-type or even larger CO_2 -coupled polymeric aggregates that are formed by a radical-coupling mechanism. Similar species have been proposed in the case of codeposition of Li or Na and CO_2 in Ar matrices at low temperatures, based on infrared spectroscopy analysis.

***In Situ* Raman Spectroscopy of Lithium Electrode Surface in Ambient-Temperature Lithium Secondary Battery**

H. Tachikawa (Jackson State University)

The objectives of this project are (i) to adapt the *in situ* Raman spectroscopic technique for the identification of substances in surface layers on Li electrodes in nonaqueous-electrolyte systems, and (ii) to apply this technique to other electrodes (e.g., Zn) in aqueous electrolytes which are used in the secondary batteries. *In situ* Raman spectroscopic investigations of Li electrode surfaces are expected to provide information for preventing or minimizing the formation of surface layers which are responsible for the poor rechargeability of Li electrodes in nonaqueous electrolytes such as LiAsF_6/PC , LiClO_4/PC , $\text{LiClO}_4/\text{THF}$, $\text{LiAsF}_6/\text{THF}$, $\text{LiClO}_4/2\text{-Me-THF}$, and $\text{LiAsF}_6/2\text{-Me-THF}$. Investigations are being conducted on surface layers present on Li foil and Li electrodeposited onto thin-film metals (i.e., Au, Ni, Ag).

Surface-enhanced Raman spectroscopy (SERS) was used to study the surface layers on Li in several solvent-solute systems. Thin Li films ranging from 20 to 1000 Å were electrodeposited on an anodized thin-film Ag electrode in LiClO_4/PC . Three spectroscopic measurement techniques were tried:

- (1) *In situ* Raman spectroscopy data of the electrode surface in solution were recorded.
- (2) The spectrum of the electrode was recorded in an Ar atmosphere after transferring the solution into the reservoir portion of the cell. (A very small amount of solution may have been present on the electrode surface).
- (3) The spectrum of the electrode was recorded *in vacuo* after extensive pumping of the cell to remove traces of the solution from the electrode surface.

Measurement technique (1) did not yield satisfactory results because of strong Raman scatterings from solution species, consequently measurement techniques (2) and (3) were used for most experiments. The Raman intensity reached the highest level with Li deposits of ~100 Å. Many Raman bands were observed in the spectrum between 130 and 1700 cm^{-1} , with most of the bands arising from the vibration modes associated with the solvent (PC) and two strong bands at 137 and 940 cm^{-1} from LiClO_4 . The intensity of the bands from both the solvent and the supporting electrolyte remained high, even after depositing 1000 Å of Li. Raman bands originating from Li_2CO_3 were observed at 1089 cm^{-1} and at low frequency. The intensity of these bands are much weaker than those of the solvent or the electrolyte.

The intense Raman scattering signals from a 1000-Å deposit of Li on anodized Ag support the theoretical calculations by Zeman and Schatz that indicate an anodized Li surface provides a higher Raman enhancement than other metal surfaces exposed to a wide range of excitation energies.

PUBLICATION

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Polymeric Electrolytes for Ambient-Temperature Lithium Batteries

G.C. Farrington (University of Pennsylvania)

The objective of this program is to investigate the chemical and electrochemical characteristics of polymeric electrodes for use in high-specific-energy batteries. The principal goal of the research program in 1987 has been to explore the possibility that poly(ethylene oxide) (PEO) solutions of transition metal salts may exhibit both ionic and electronic conductivity, and therefore be of interest as homogeneous cathode materials in high-specific-energy batteries. Another goal of the research was to investigate the mechanisms that control the conductivity and transport properties of transition metal complexes with PEO.

To explore the ionic conductivity and electrochemical activity of PEO solutions of transition metal salts, electrolyte compositions of $(\text{PEO})_n\text{MnBr}_2$, in which n is 8 and 16, were prepared. These materials are particularly interesting because it should be possible to electrochemically oxidize and reduce the Mn(II) species within the electrolyte. The electrochemistry of the Mn(II)-containing electrolytes was studied using DC polarization and complex AC impedance analysis. As anticipated, the materials are reasonably good electronic conductors, and the Mn(II) species appear to be electrochemically active. Further studies to characterize the electrochemical reactivity and ionic conductivity of the Mn(II) complexes are underway, as is the preparation of other solutions of electroactive transition metal cations in PEO.

Earlier work showed that the ionic conductivity of $\text{PEO}_8\text{NiBr}_2$ is strongly influenced by whether or not the electrolyte was hydrated at some time during its preparation. An electrolyte film prepared under very dry conditions was shown to have a somewhat low ionic conductivity and a near-zero transport number for Ni(II). However, if the dry film is allowed to hydrate and then it is dehydrated, its conductivity is much higher

than before, and the Ni(II) transport number is nearly 0.6 at 140°C.

During the past year, the study of solvation of cations dissolved in PEO was extended to complexes of PEO and CoBr_2 , specifically, $\text{PEO}_{8-16}\text{CoBr}_2$. Although the conductivity of $\text{PEO}_{8-16}\text{NiBr}_2$ is greatly affected by hydration/dehydration, the conductivity of $\text{PEO}_{8-16}\text{CoBr}_2$ complexes is not. In addition, hydration/dehydration has no effect on the transport number of Co(II) in PEO, which is nearly zero. Spectroscopic measurements have provided some clues as to the origin of this unexpected behavior. It appears that the differences in the properties of these two polymer materials are intimately linked to the difference between the coordination chemistry of Ni(II) and Co(II). Ni(II) forms four-fold coordinated, square-planar complexes in freshly prepared PEO electrolytes. When water is introduced into the system, the formation of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is highly favored, and its presence is revealed by well-defined optical absorption peaks in the red (710, 760 nm) and blue (400 nm) wavelength regions of the visible spectrum. The samples change in color from brown to green.

Co(II) forms a stable tetrahedral complex in $\text{PEO}_{8-16}\text{CoBr}_2$ which is deep blue in color and has a group of peaks between 600 and 750 nm, typical of Co(II) in a tetrahedral environment. When $\text{PEO}_{8-16}\text{CoBr}_2$ is hydrated, its color changes to pink; an intense peak in the red region decreases while the new, much-less-intense peaks centered near 500 nm grow. These new peaks are typical of Co(II) in the octahedral environments. These results suggest a correlation between the type of complex a cation forms in PEO and mobility. Further study of this behavior is underway.

PUBLICATION

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Exploratory Cell Research and Fundamental Processes Study in Solid State Electrochemical Cells

W.H. Smyrl (University of Minnesota)

The objectives of this program are to perform research to support the development of high-performance rechargeable batteries that are desired for the development of viable electric vehicles or utility load-leveling systems. The program has two specific thrusts that are carried out concurrently in a coordinated study: (i) exploratory cell research, and (ii) the study of

fundamental processes of solid-polymer-electrolyte systems. The technology developed in this laboratory for Li polymer batteries continues to be the basis for the research reported here. The present work seeks to broaden the metal systems to include metals that have lower cost and may offer other advantages over Li. The alternative metals under consideration are Na, Mg, Ca, Pb, and Al for negative electrodes. Most of the effort on positive electrodes is focused on V_6O_{13} because of its successful demonstration in Li batteries. In addition, the research addresses fundamental measurements of transport in the polymer electrolyte by novel techniques with microstructured electrodes. The use of ultra-smooth electrode interfaces will facilitate the development of very-thin-film polymer batteries.

Single crystals of V_6O_{13} were prepared for the intercalation studies with the metal systems listed above. The single crystals were grown by subliming polycrystals at 550 to 600°C. Coulometric titration of Li into the single-crystal material in propylene carbonate solutions of Li salts confirmed the earlier literature results. The thermodynamic properties (intercalation composition vs voltage) and the reversibility of the systems were determined for each metal.

Platinum micro-band electrodes were fabricated and used in the voltammetry studies on Li salts in poly(ethyleneoxide) (PEO). The measurements were made to ascertain the diffusivity of Li^+ ions in PEO (molecular weight of 3×10^5). The diffusivity was determined from the limiting currents for Li deposition as a function of concentration. The maximum diffusivity occurred at a mole ratio of about 8 M of PEO to 1 M of LiClO_4 . On the microelectrodes, the current in the diffusion-controlled region is independent of scan rate. These studies demonstrate the usefulness of this technique as for the determination of transport properties in polymer electrolytes of high resistivity.

Ultra-flat and smooth electrodes were prepared with an electroactive polymer, poly(vinylferrocene) (PVF), on Au-coated silicon wafers. Polymer films of thicknesses from 20 to 800 nm were prepared by spin coating from methylene chloride. Impedance investigations have shown that the high-frequency charge injection process is basically the same as that for solvent-cast films. At lower frequencies, however, the spin-coated films have a higher charge diffusivity, i.e., D_{ct} is $\sim 10^{-7} \text{ cm}^2/\text{s}$ for spin-coated films and $10^{-9} \text{ cm}^2/\text{s}$ for solvent-cast films. The faster transport in the spin-coated films will enable faster charge and discharge of the redox films when used as battery electrodes.

Preliminary results were obtained in four studies to improve ionic transport in the electrolyte.

- (1) The divalent salts, MgCl_2 , CaCl_2 , $\text{Cu}(\text{ClO}_4)_2$, CuCl_2 , $\text{Zn}(\text{ClO}_4)_2$, $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, and $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, have been prepared in PEO.
- (2) Composite electrolytes of $\text{PEO-NaI-Na}(\beta\text{-Al}_2\text{O}_3)$ were prepared with varying vol% Na^+ -conducting

oxide. Enhanced conductivities at room temperature were obtained with 55 vol% compositions.

- (3) A new room-temperature polymer, which consists of a polymer containing vinylene carbonate in the backbone, was prepared that duplicates a recent study reported in the literature. When polymerized with 12-crown-4-ether complexes of a Li salt, a solid is formed with high conductivity. Solvent casting of the product, or copolymerization, would enable thin films to be fabricated.
- (4) Equipment has been assembled to carry out the fabrication of thin-film electrolytes by a hot-pressing method (HPM), which requires less time for electrolyte preparation and with a wider variety of salts.

Electrochemical cells containing negative electrodes of Mg thin film and positive electrodes of V_6O_{13} have been prepared with the salts listed above, and cycling of the cells at 100°C has begun.

Metals Couples in Nonaqueous Electrolytes

C.W. Tobias (Lawrence Berkeley Laboratory)

The objective of this project is to explore practical alternatives to aqueous or high-temperature molten-salt systems for the efficient electrochemical reduction and oxidation of reactive metals. A variety of experimental techniques are employed in this project. Gas chromatography, Fourier analysis infrared spectroscopy, mass-spectrographic analysis, adsorption spectrophotometry, and NMR are being utilized to study the stability of solvents. Current efficiency of metal deposition is measured by coulometry. Metal quality is analyzed by wet methods, emission spectra, and X-ray diffraction. Solvent and salt preparation is done in-house. Solubility and conductivity measurements are performed prior to investigations of electrode behavior. All experimental procedures are carried out in recirculated-helium glove boxes. Electrode overpotential measurements are performed using galvanostatic or potentiostatic transient techniques. Semi-quantitative information on electrode behavior is obtained by cyclic voltammetry.

Magnesium has been anodically dissolved with 100% current efficiency with a valence of two in propylene carbonate (PC) solutions of $AlCl_3$ and $Mg(BF_4)_2$. In $AlCl_3$ solutions the anodically-stripped surface is clean but roughened. In $Mg(BF_4)_2$ solutions a bright Mg surface is formed beneath a yellow surface layer. In both solutions the rate of Mg dissolution is limited by the cathodic reaction. NMR studies of the plating baths have proved unable to detect water at less than 100 ppm levels. However, preliminary studies indicate that the anion present in the Mg salt has a strong influence on the association of water in the plating bath.

To date none of the attempts to deposit Mg at ambient temperature from its compounds have produced metallic Mg deposits. In addition to propylene carbonate, tetrahydrofuran and dimethylsulfoxide have also failed to yield any Mg deposits. Variations of current density, salt preparation, and the use of electroplated alloys of Mg and Na as pre-strikes have not resulted in noticeable improvements.

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Corrosion, Passivity and Breakdown of Alloys Used in High Energy Density Batteries

(J. Kruger, The Johns Hopkins University)

The objective of this program is to investigate the phenomena of passivation and its breakdown on metals and alloys in non-aqueous solvents for rechargeable Li batteries. A great effort has been expended over the last 100 years at elucidating the mechanism of passivity of Fe-based alloys in aqueous solutions, however, very little attention has been focused on the corresponding phenomena in non-aqueous solutions. In this project, the corrosion of Fe and Ni in purified PC containing 0.5 M $LiClO_4$ as the solvent was investigated. Small amounts (0-500 ppm) of water, propylene glycol (PG) and LiCl were added to determine the effect of these common impurities on the passivation and breakdown processes. All of the solution were handled in vacuum lines which allowed highly purified baseline PC solutions to be prepared.

Slow potentiodynamic scans were made on Fe and Ni to determine the range of passivity and the effect of the impurities. Additional scans were obtained on Pt to determine the fraction of the measured current that could be attributed to Fe (or Ni) oxidation and the fraction of the current from reaction of the solution. In addition, a potentiodynamic scan with Pt was used to determine the potentials at which the impurities were oxidized. Scanning electron microscopy of the samples

after the electrochemical measurements helped to characterize the pitting morphology.

The behavior of Fe and Ni in highly purified PC solutions is shown in Fig. 8. Both materials showed spontaneous passivation in this solution, with a wide passive range and low passive current densities. Identical scans were obtained on Pt, which indicates that the currents measured are due solely to oxidation of Fe (or Ni). At increasing polarization, Ni undergoes a localized breakdown of its passive film and pitting commences (see Fig. 9). These pits appear to nucleate at surface imperfections, such as polishing scratches.

Iron suffers breakdown in the presence of both water and PG at the 500 ppm level. (Tests in LiCl-containing solutions are being conducted at the present time). On the other hand, Ni seems relatively unaffected by these impurities over the concentration range studied to date, despite the fact that breakdown occurs in impurity-free solution. Some increase in the activity of the surface occurs, but appears to do so uniformly, with no increased predisposition towards localized attack.

Future effort is aimed at determining the mechanism of passivation and breakdown observed with Fe and Ni, and on preliminary work with 304 SS to investigate the effects of impurities on its passivation. Ellipsometry will be utilized to obtain a more in-depth understanding of the mechanism of passive film formation and break-

Figure 8. Polarization curves of Fe and Ni in highly purified 0.5 M LiClO₄/PC solutions. Scan rate: 0.5 mV/sec. Voltage referred to aqueous saturated calomel. (XBL 887-2388)

Figure 9. Secondary electron image of Ni surface after polarization scan in highly purified solution. The marker in the upper left-hand corner represents 10μ. (XBB 887-6813)

down. Surface analysis of the films grown in PC solutions will be examined by X-ray photoelectron spectroscopy to relate the nature of the film to the passivation and breakdown mechanisms.

F. 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

J.S. Newman (Lawrence Berkeley Laboratory)

This program involves fundamental investigations of the transport and interfacial phenomena important in electrochemical systems. Results of this work are used to analyze experimental data, to identify important system parameters, and to aid in the design and scale-up of electrochemical systems. Specific projects include analysis of the thin-gap flow cell for electrochemical synthesis and energy storage, mathematical modeling of the Li-Al/FeS battery and the Li-Si/FeS₂ battery, investigation of porous electrodes with applications to molten-salt systems, and AC impedance analysis of both Zn and Fe corrosion.

A model for predicting the current, concentration, and potential distributions in a thin-gap channel flow

cell was developed. The model does not invoke the thin-diffusion-layer assumption or the assumption of straight current lines, and it allows for multiple reactions. The model, however, does not include the effect of migration; thus, it is only valid for systems with excess supporting electrolyte. This model can be used for the design and scale-up of channel-flow electrochemical reactors, and also to show the effects of interacting diffusion boundary layers and of the axial component of current.

A one-dimensional mathematical model describing sustained current oscillations observed in the iron-sulfuric acid system, under potentiostatic conditions, was developed. This model assumes that the sustained oscillations are due to a continuous cycling of a portion of the electrode between the active and the passive states. The electrode surface is covered by a porous ferrous sulfate film. Transient changes in the potential and concentration profiles in the pores of the salt film and in the diffusion layer are responsible for the continuous cycling. Results from this model are compared to the experimental current-time curves. The calculated current-time curve shows oscillatory behavior, but their characteristics differ from the experimental results. The calculated thickness of the ferrous sulfate film is substantially thinner than expected from a steady-state analysis and from the previously reported work of others.

Due to lack of quantitative agreement between experimental and calculated results, two modifications to the present model are proposed in a qualitative manner. These modifications suggest that one may wish to: (i) remove the requirement of passivation, and assume that the current oscillations are caused by continuous cycling in the fraction of the electrode surface area that is covered by ferrous sulfate; (ii) assume that the current oscillations are caused by continuous cycling in the porosity of the salt film in combination with changes in the amount of active area. Both proposed modifications would include kinetics of salt-film precipitation and dissolution. It is anticipated that finite precipitation and dissolution kinetics will increase the calculated salt-film thickness. Further work would be required to incorporate either modification into the model in a quantitative way.

The behavior of the thermodynamic, open-circuit potential of the $\text{LiAl/LiCl}_2\text{KCl/FeS}$ cell was investigated, and nonequilibrium results obtained from a computer model of the cell are presented. The nonequilibrium computer model predicts the cell voltage, temperature, and heat-generation rate during cell operation. Position-dependent behavior such as reaction rates and concentrations within the cell were also calculated. The effects of state-of-charge, electrolyte composition, porosity, KCl precipitation, and temperature on cell behavior were investigated. The results of the model predict that KCl precipitation can limit the utilization of

the FeS_2 electrode, usually on the lower voltage plateau. This finding compares favorably with available experimental data.

At current densities large in magnitude and also large compared to the exchange current density, a conducting disk in an insulating plane has a very nonuniform current distribution across the surface. The current distribution near the center is governed predominantly by ohmic effects, but near the edge, electrode kinetics become important. The current and potential distributions on the electrode, especially near the edge of the electrode where the nonuniformity is most extreme, were examined for electrode kinetics in the Tafel region. The results are valid for any and all large values of current density and provide a definitive description of the way in which the current and potential distributions approach the purely ohmically controlled (primary) distributions as the current is increased. The current density at the edge of the disk is found to increase with the square of the average current density. These results for the edge region of a disk at high currents can be applied to electrodes of more general geometry.

A model which uses Duhamel's theorem to simulate cyclic voltammetry experiments at stationary and rotating disk electrodes is being improved. The model can account for mass transfer effects, faradaic reactions, and adsorption phenomena, which will permit the quantitative interpretation of data. In particular, it is being used to study linear sweep voltammograms of the reduction of nitrate in acidic, Ni-containing solutions.

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Engineering Analysis of Gas Evolution

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The objective of this project is to establish the influence of electrode geometry, surface morphology, and electrolyte composition on bubble size and residence time, and to elucidate the role of free and forced convection as it affects overpotential behavior and ohmic resistance in electrode gas evolution processes. Gas coverage and detachment from electrode surfaces, as well as

behavior in suspension, is being investigated by normal- and high-speed cinematography. The channel flow cell constructed for this purpose incorporates an easily changeable, coplanar square 1 x 1 cm electrode surface, which is illuminated by fiber optics to achieve sufficiently high intensity of illumination. The counter-electrode is situated in the walls normal to the electrode that is observed. Electrode overpotential is continuously monitored.

Coalescence phenomena between identical (H_2-H_2) or different (H_2-O_2) gas bubbles are observed on precisely aligned microelectrodes facing each other. Spherical bubbles may be evolved at suitably low rates, until they touch and the actual coalescence event occurs. Supersaturation at hydrogen- or oxygen-evolving electrodes is measured by electrochemical techniques and correlated to surface coverage and bubble frequency.

Ten by ten quadratic planar matrices of square Pt surface elements with 100- μ m edge length, electrically isolated from each other, serve as models to simulate polycrystalline surfaces. Matrices were manufactured on silicon wafers by Hewlett-Packard Company and by Bell Laboratories. These unique devices facilitate the nucleation, growth, and coalescence of bubbles at predetermined locations, and the simultaneous monitoring of electrode potentials. A data acquisition system, designed and built, and a program developed in-house, monitors current to each of 100 segments and controls the growth of bubbles.

The equation of Bashforth and Adams has been used to calculate the configurations of axisymmetric bubbles formed on a curved surface, such as on a hemispherical solid. The volume of the largest stable equilibrium bubble that can adhere to a flat horizontal surface is a function of the characteristic length of the system,

$$L_c \equiv \left[\frac{\gamma}{\rho g} \right]^{1/2}$$

(γ : surface tension, ρ : density, g : acceleration of gravity), and the equilibrium contact angle τ and is given by

$$\frac{V_{\max, \text{flat}}}{\pi L_c^3} = 0.285 \theta^{2.96} \quad (\theta \text{ in radians})$$

The bubble configurations of maximum volume for contact angles greater than 60° have re-entrant contact angles. A stability analysis that accounts for axisymmetric disturbances in bubble shape extending over the entire surface of the bubble shows that although re-entrant contact angles usually indicate instability, the profiles with re-entrant contact angles at the point of maximum volume are stable.

The determination of maximum bubble volume has been extended to account for the destabilizing effect of the solid support curving away from the bubble. The situation described applies exactly to a bubble growing on a hemispherical protrusion on the surface, and by

extension, to a bubble growing on a wire or screen. The reduction in the maximum stable bubble volume ($V_{\max, r_w}$) for such a case can be described by the simple function

$$\frac{V_{\max, r_w}}{V_{\max, \text{flat}}} = \left[\frac{r_w}{r_w + L_c} \right]^{0.95 \theta}$$

where r_w is the radius of the protrusion.

This result is the first step in accounting for the role of the morphology of the substrate on bubble size, which profoundly affects the dynamics of gas evolution on electrode surfaces. In practice, gas is often evolved on more complex electrode geometries and on orientations other than horizontal, and further extensions of the classical theory to describe these cases will prove valuable to understanding the factors affecting gas evolution.

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Surface Layers on Battery Materials

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The objective of this work is to apply *in situ* surface techniques to provide direct experimental information on the formation and properties of surface layers on battery-electrode materials and to find new means for controlling properties that enhanced cell performance. The formation of anodic oxide films on two common metals (i.e., Ag, Cu) was investigated to assess the utility of spectroscopic ellipsometry and Raman spectroscopy for *in situ* surface studies.

A new mechanism for the anodic formation of silver oxide on Ag has been derived from spectroscopic ellipsometer measurements. The mechanism involves the rapid formation of an oxide monolayer followed by the slower growth of a thin primary layer and simultaneous film dissolution; the latter process accounts for most of the oxidized material generated at low potentials. At sufficiently high potentials, the primary layer reaches a critical thickness (100-200 Å) at which secondary crystals are nucleated. These crystals initially grow by the transfer of oxide materials from the primary layer, resulting in a sharp decrease in its thickness (Fig. 10). After the crystals have grown to a point where their solubility no longer depends on size, the thickness of the primary layer before nucleation is re-established.

A study of the anodic oxidation of Cu in alkaline media by spectroscopic ellipsometry and SEM has been found to result in the initial growth of a compact Cu_2O layer, followed at higher potential, by the formation of a highly porous $\text{Cu}(\text{OH})_2$ layer. The compositions of these films have been identified by the use of newly developed Raman spectroscopy equipment for *in situ* measurements and by *ex situ* X-ray diffraction. Predictions of optical models agree well with measurements (Fig. 11). Angularly-resolved elastic light scattering is also being developed to investigate the nucleation of anodic oxides.

Ellipsometer measurements of anodic oxides with a 20- μm probe beam have revealed local variations of film thickness and composition on a scale much smaller than the grain size (Fig. 12). For the further investigation of spatially varying surface layers, an analysis of different principles for the operation of an imaging ellipsometer with high spatial resolution has resulted in a preferred design which employs an array detector for photometric measurement.

Figure 10. Thickness of primary or underlayer (A) and secondary or crystal layer (B) of silver oxide on silver derived from ellipsometer measurements for a film formed by a potential step at time zero to 200 mV vs Ag/AgCl, 4M KCl. Note the decrease of primary layer thickness at onset of secondary layer growth. (XBL 876-3024)

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Figure 11. Spectroscopic ellipsometer measurements (Δ , $\bullet$, $\blacksquare$) and corresponding model predictions ($\times$, $\circ$, $\square$) for the anodic oxidation of Cu in 1M KOH at 22 $\mu\text{A}/\text{cm}^2$ for 150 sec ($\blacksquare$, $\square$), 320 sec ($\bullet$, $\circ$) and 493 sec (Δ , $\times$). (XBL 884-1339)

Figure 12. Ellipsometric profilometry of Ni(OH)₂ with a 20- μm probe beam. Locally varying refractive index and thickness on polycrystalline Ni of 200- to 300- μm grain size. Reduced form of 102-Å film after 5 potential cycles between -0.2 and +0.4 V vs Hg/HgO in 1 M KOH at 50 mV/s. (XBL 884-1340)

Application of PDS to Electrochemical Interfaces

E.J. Cairns and F.R. McLarnon (Lawrence Berkeley Laboratory)

Photothermal deflection spectroscopy (PDS) is being developed as a sensitive *in-situ* method for investigation of electrochemical interfaces. This method is a novel application of PDS, and should prove to be an

exceptional addition to the few *in-situ* techniques currently in use. An advantage of this technique is that the electrode surface is not required to be optically smooth. The same system is also used to simultaneously measure concentration gradients adjacent to the electrode surface. This additional information is helpful in determining the surface chemistry. Various types of electrochemical interfaces can be studied by this method, e.g., corrosion, secondary electrodes, and electrocatalysts. The objective of this work is to study direct electro-oxidation of methanol on Pt ad-atom catalysts. Increased understanding of these catalysts will aid in the development of high-performance direct methanol/air fuel cell systems.

PDS is a comparatively simple system. Monochromatic light is directed through the electrolyte onto the electrode at a normal incidence. Absorption of light by the surface causes heating of the electrode, thereby forming a thermal gradient adjacent to the electrode, and an associated gradient in the index of refraction. A probe laser beam is directed parallel to the electrode through this gradient and is deflected. The magnitude of this deflection is proportional to the surface absorption. Modulation of the light source and lock-in detection are implemented to increase the signal-to-noise ratio.

Electrochemical reactions will create concentration and associated refractive-index gradients, which can be measured by the probe beam. Since this deflection is not modulated, it can be separated from the deflection due to the surface absorption by the lock-in instrumentation, yielding simultaneous measurement of surface absorption and concentration gradients.

The primary parameter measured by PDS is the absorption of light at a surface. Scanning of the wavelength of the source allows spectra of the interfacial species to be obtained. Confirmation experiments on systems with known spectra have been successful. Absorption can be measured at constant wavelength while the electrode potential is changed. Cyclic voltammetry of Pt in 0.1 M HClO₄ along with the corresponding absorption and concentration gradient is shown in Fig. 13. This experiment shows that PDS is sensitive to the formation of single layers of molecules at the surface; in this case, the formation of platinum oxide is clearly seen. The microscopic concentration gradients formed are also evident.

Preliminary experiments on the oxidation of methanol on Pt and an under-potential deposition (UPD) process by which ad-atom catalysts are formed have shown that PDS will be an effective tool to increase the understanding of these systems. Developmental effort is

Figure 13. Simultaneous cyclic voltammetry and PDS of Pt in 0.1 M HClO₄. The upper plot shows the electrode current response to a cyclic potential scan at 100 mV/s. The DC deflection plot represents the concentration gradients formed in the electrolyte. Deflections positive to the REST deflection indicate that the electrolyte concentration near the electrode is higher than in the bulk, and deflections negative to the REST deflection indicate lower electrolyte concentrations. The AC deflection plot indicates the amount of light absorption at the electrode surface. The excitation light wavelength was 550 nm. (XBL 882-580)

under way to extend the spectral range of the system into the infra-red. This would allow *in-situ* vibrational spectra to be obtained, which can help identify organic surface species.

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IV. AIR SYSTEMS RESEARCH

The objectives of this project 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

Projects on metal/air cell research address oxygen electrocatalysis; bifunctional air electrodes, which are needed for electrically rechargeable metal/air (Zn/air, Fe/air) cells; and novel alkaline Zn electrode structures which could be used in either electrically recharged or mechanically recharged cell configurations.

Electrocatalysts for Oxygen Electrodes

E.B. Yeager (Case Western Reserve University)

The overall objective of this project is to develop more effective electrocatalysts for O₂ reduction and generation which have high activity and long-term stability. The research emphasis is on achieving a fundamental understanding of O₂ electrocatalysis. During 1987 the following topics were addressed.

1. Transition Metal Macrocycles

Cobalt and iron phthalocyanine sheet polymers that possess peripheral carboxylic acid groups were synthesized,¹ purified using gel chromatography and characterized using FT infrared, UV-visible spectroscopy and XPS. Surface-enhanced Raman spectra of the iron phthalocyanine sheet polymer, which was adsorbed at monolayer coverage on a smooth Ag surface, provide evidence that the nature of the adsorption and orientation of the polymer molecules on the substrate is different from that of the monomer. Earlier studies of adsorbed monolayers of FeTsPc on single crystal and polycrystalline silver have indicated that the plane of the macrocycle ligand is perpendicular to the surface.^{2,3} Efforts are in progress to directly image the adsorbed phthalocyanines on highly oriented pyrolytic graphite (HOPG) using scanning tunneling microscopy.

The FTIR technique has been used to investigate the interaction of thin layers of cobalt tetramethoxyphenyl porphyrin (CoTMPP) on Ag, Ni and HOPG surfaces. Well-defined reflectance spectra were obtained using thin layers that were equivalent to five mono-

layers. The spectra were essentially the same as those for the crystalline solid. Efforts are in progress to examine the submonolayer films.

2. Heat-Treated Macrocycles and Nitrogen-Containing Polymers

A transition metal macrocycle that is widely used as an electrocatalyst for O₂ reduction is heat-treated cobalt dibenzotetraazaannulene (CoTAA).^{*} New insight has been obtained from XPS studies of H₂TAA, CoTAA and NiTAA before and after heat treatment, particularly as to the role played by the transition metal and the carbon support in stabilizing the nitrogen during the heat treatment.

To further ascertain the role of the transition metal in the O₂ electrocatalytic activity of the dibenzotetraazaannulenes, experiments were conducted with CoTAA and H₂TAA supported on high area carbons such as steam-activated Shawinigan acetylene black (SASB) and Black Pearls 2000. The results obtained using rotating disk electrodes with thin porous coatings and with gas-fed electrodes in both acid and alkaline electrolytes showed that the transition metal is definitely necessary for good catalytic activity, in contrast to the conclusion reached by Wiesener's group.⁴ The comparable performance that is obtained with heat-treated H₂TAA and CoTAA is attributed by the Dresden group to an interaction of the metal-free macrocycle with Fe-containing impurities in the activated carbon (P-33, 0.74% Fe), which probably become coordinated to the macrocycle during the heat-treatment step. Such coordinated bonding should be rather stable and could be responsible for the retention of nitrogen at high temperatures.

The conclusions of Wiesener and co-workers support the model proposed by CWRU to explain the catalytic activity of the heat-treated transition metal macrocycles. In our model, the transition metal ions are adsorbed to the carbon surface principally through interactions with residual nitrogen derived from the heat-treated macrocycle. This model further suggests that other electronically conductive surfaces containing nitrogen functionalities are capable of binding transition metal ions as catalysts for O₂ reduction. Such catalysts have been prepared at CWRU by heat-treating nitrogen-containing polymers such as polyacrylonitrile (PAN) or polyacrylamide (PAA) with molecularly dispersed cobalt acetate. The performance of these

^{*} Provided by Dr. D. Ohms of the research group of Prof. K. Wiesener at the Technical University of Dresden. Dr. Ohms spent six months at CWRU under the IREX Program.

materials in porous gas-fed electrodes in both acid and alkaline electrolytes is comparable to that of heat-treated CoTMPP. The mechanism for O_2 reduction appears to follow the peroxide pathway, as it does with heat-treated CoTMPP. Air cathodes made from heat-treated PAN with cobalt acetate and SASB have also shown good long-term stability in alkaline electrolyte. The lower cost of such polymer-based catalysts, as compared with macrocycles, is also attractive.

3. Transition Metal Oxide Systems

The catalytic activity of perovskites of the general formula $LaFe_xNi_{1-x}O_3$ for peroxide decomposition was found to correlate with their magnetic properties. As x increases, the rate constant for peroxide decomposition increases and reaches a maximum at $x = 0.25$. Mossbauer and magnetic susceptibility measurements suggest that the presence of unusually high oxidation states such as Fe(IV) and/or the existence of mixed oxidation states such as Fe(III/IV) and Ni(II/III) may be responsible for the catalytic activity for peroxide decomposition.

With a view to characterizing the redox processes, as well as to examine the overall stability of the perovskites, the electrochemical properties of $SrFeO_{2.91}$ in Teflon-bonded electrodes containing high-area carbon (for enhancing the electrode conductivity) have been investigated by cyclic voltammetry and *in-situ* Mossbauer spectroscopy in alkaline media. The results provide evidence that the fraction of Fe(IV) sites undergoes a gradual and irreversible decrease upon exposure of the material to the alkaline solution. This result is attributed to the reduction of such sites by water, most likely generating a hydroxylated ferric species.

The redox properties and O_2 reduction kinetics of the $Pb_2Ru_2O_{6.5}$ pyrochlore⁵ were investigated using cyclic voltammetry and the rotating ring-disk electrode. The cyclic voltammogram for thin porous coatings of $Pb_2Ru_2O_{6.5}$ on ordinary pyrolytic graphite (OPG) is very complex. The overall redox process, however, is assigned to the Ru(IV)/Ru(V) transition. This catalyst has shown good activity for O_2 reduction in alkaline solutions. The Tafel plots are linear with a slope of -0.063 V/decade. Kinetic analysis of the rotating ring-disk data for the thin porous layer indicates an overall 4-electron process, but additional experiments with non-porous electrodes are needed to substantiate this. The value of the Tafel slope suggests a non-charge-transfer step as the rate-determining step following a fast initial electron transfer.

4. Bifunctional Oxygen Electrodes

Perovskites and pyrochlores catalysts have recently been examined in bifunctional air electrodes. A series of $LaFe_xNi_{1-x}O_3$ perovskites were examined both for O_2 reduction and generation in 5.5 M KOH (25°C) in

porous gas-fed electrodes containing Shawinigan acetylene black (SB), which was used because of its ability to reduce O_2 to peroxide. The maximum catalytic activity for O_2 reduction was found with compounds having 15 to 25 mol% Fe, which is consistent with the trend for peroxide decomposition activity. Several pyrochlores yielded much better performance in the anodic mode than that obtained with perovskites. This is partially due to a large difference (~ 1 order of magnitude) in the surface area. In the cathodic mode, $Pb_2(Ru_{1.67}Pb_{0.33})O_{6.5}$ is initially more active than $Pb_2Ru_2O_{6.5}$, whereas the latter was found to be much more stable in the anodic mode. The Tafel slope for $Pb_2Ru_2O_{6.5}$ in the anodic mode was ~ 40 mV/decade, which may be explained by the same mechanism proposed by CWRU for O_2 generation on RuO_2 electrodes.⁶

Mixtures of transition-metal-containing perovskites with either heat-treated macrocycles or nitrogen-containing polymers, such as H_2TMPP , cobalt octaethyl porphyrin (CoOEP) and PAN have also been investigated as catalysts for bifunctional air electrodes. Cobalt-containing perovskites were found to greatly increase the rate of O_2 reduction on gas-fed electrodes made with either H_2TMPP or PAN that was heat-treated with SB not containing any added transition metal. The increased activity is probably due to small amounts of transition metal ions dissolved as the oxyanions which adsorbed at nitrogen-containing surface functional groups on the heat-treated macrocycle or polymer. Heat-treated (400°C) CoOEP on XC-72 mixed with $La_{0.8}Sr_{0.2}Co_{0.9}Ru_{0.1}O_3$ has shown excellent performance for O_2 reduction in 4 M NaOH at 60°C.

5. Ionically Conductive Polymers in Porous Gas-Fed Electrodes

Ionically conductive polymers are being considered both as a replacement for the liquid electrolyte in the porous layer of gas-fed electrodes and also as an outer ionically conductive layer to allow electrodes to operate with gas overpressure. The latter approach was tested in alkaline solution using a caustic-resistant anion exchange membrane (Ionics, Inc.) with an active layer made from heat-treated CoTMPP supported on SASB. The polarization curves were essentially the same up to ~ 200 mA/cm² with and without the membrane. Furthermore, the membrane permitted the gas-fed electrode to withstand substantial overpressure of about 7 kPa (1 psi) on the gas side without releasing bubbles into the electrolyte. When an intermediate coating of a water-soluble anion exchange polymer is applied, the overpressure tolerance can be increased to ~ 75 kPa (11 psi).⁷

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Electrode Research for Electrically Rechargeable Zinc/Air Alkaline Battery

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As part of continued studies of a new concept for an electrically rechargeable Zn/air alkaline battery, the use of carbon materials as the principal structural element of the bifunctional air electrode is being examined. The advantage of carbon materials over metals and/or other materials is the potential for substantial savings in both weight and cost. However a technical challenge that must be resolved for this material is to develop carbons

with sufficient corrosion resistance to meet the lifetime requirements for electric vehicle applications. The corrosion chemistry of acetylene black and the effect of oxygen evolution catalysts on the corrosion rate of acetylene black have been studied. These corrosion studies were extended to other families of carbons to develop structure-property relations for corrosion behavior.

A selection of furnace black carbons of varying surface area and industry type was heat-treated in purified helium at 2700°C and the corrosion resistance measured under conditions of oxygen evolution in 30% KOH at 55°C. The extent of graphitization was determined qualitatively by X-ray diffraction and by transmission electron microscopy (TEM). Separate linear correlations of the corrosion rate per unit mass with the BET surface area were observed for furnace blacks and for graphitized furnace blacks, with the rate for the graphitized blacks being a factor of ~2.5 lower on a unit area basis. The correlations had a relatively high standard deviation, however, indicating that BET area was probably not the only physical property affecting the corrosion rate. TEM analysis of the carbons after extended corrosion indicated a strong preferential attack of the ungraphitized regions, i.e., much greater selectivity than the factor of 2.5 indicated by the BET correlation. A unifying correlation was observed for both the furnace blacks and their graphitized forms using the corrosion rate per unit mass and the iodine adsorption number. It was concluded that there are specific sites on the carbon surface (titrated by iodide) that serve as the initiators for dissolution of carbon atoms from the bulk of the material. One particular type of furnace black, SRF (N774), appears to be an especially good precursor for forming a highly graphitized and very corrosion-resistant carbon black.

The experiments with graphitized furnace blacks indicated that corrosion resistance was more closely correlated to iodine adsorption number than to BET surface area. This may be indicative of site specificity for the corrosion reaction, but the types of sites on the carbon surface that are specific to iodine (or even that there are sites specific to iodine) are not known. To determine site specificity for iodine adsorption, iodine adsorption on single crystal graphite (HOPG) will be studied, comparing adsorption on the edge plane vs the basal plane. Iodine adsorption will be measured by a combination of techniques and compared to the chemistry of surface sites determined by X-ray photoelectron spectroscopy (XPS), thermal desorption mass spectroscopy (TDMS), and infrared reflectance spectroscopy (IRS).

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Electrical and Electrochemical Behavior of Particulate Electrodes

J.W. Evans (Lawrence Berkeley Laboratory)

The objective of this research is to provide the basic knowledge to enable particulate electrodes to be designed, evaluated and scaled up for use in electrochemical energy storage. Possible particulate electrodes are slurry electrodes (where the particles suspended in the electrolyte move into and out of the cell), fluidized-bed electrodes and moving-bed electrodes. The last two are under investigation at LBL, and investigations of the fundamental electrical and electrochemical behavior of fluidized-bed electrodes have been completed. The present focus of investigation is the moving-bed electrode which appears most suitable for use in discharging (electrodissolution) of Zn particles. These types of electrodes have low requirements for electrolyte pumping and thus are attractive for use in Zn/air batteries.

Experimental measurements indicate that a moving bed of Zn particles has little resistance (i.e., minimizing parasitic voltage drops across the electrode itself), and (superficial) current densities of several hundred mA/cm² can be maintained at these electrodes. Figure 14 shows the best performance to date for the cell discharged at two different currents (2.5 A corresponding to a superficial current density of 100 mA/cm², and 5 A). The horizontal line at 1.7 V and the vertical line at 35 Ah indicate the theoretically expected performance. The area of this rectangle is therefore the expected energy of the cell and the areas under the two curves

Figure 14. Results of constant current discharge experiments for a cell with moving bed Zn anode and a commercially available air cathode. (XBL 878-3618)

form a ratio to this area that is the energy efficiency on discharge. These energy efficiencies require improvement and this is possible with modification of the cell design.

A theoretical investigation of the response of an electrode to a non-ideal step change in potential has been completed. Stepping the potential (using a potentiostat) and observing the current transient is a widely used technique for studying the kinetics of electrochemical reactions or diffusion of electroactive species to (or from) the electrode. Commercial potentiostats are incapable of a true step changes; instead they typically "overshoot" the final potential and this overshoot is then followed by decaying oscillations leading to the final value. The investigation showed that these departures from an ideal step change can result in spurious currents that are comparable with those due to the step change itself.

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Technology Base Research on Zn/Air Battery Systems

H.B. Sierra Alcázar (Pinnacle Research Institute)

The overall goal of this project is to demonstrate, with models based on single-cell experimental data, the capability of the slurry Zn/air battery for application in electric vehicles (EVs). The characteristics of the slurry Zn/air battery at the single-cell level was investigated, with the main objectives of the second year effort: (i) to improve the discharge capacity and performance (specific energy and specific power) and (ii) to develop an efficient slurry recharge method. The recharge modes that were considered include hydraulic recharge, on-board electrical recharge (slow or fast), and a combination of hydraulic recharge with electric recharge at a central station.

Discharge Studies

The use of electrolyte additives to improve the discharge capacity was investigated. Additives were selected which would produce high oversaturation of zincate ion in KOH electrolyte. The maximum capacity extension obtained with the additives and additive combinations was determined from measurements of the critical current density at a Zn rotating disk electrode. The discharge capacity of 15 g/l sorbitol and 25 g/l silicate in 12 M KOH was found to be 276 Ah/l, and that of 25 g/l LiOH in 12 M KOH was found to be 306 Ah/l (at room temperature and 1000 RPM in both cases). The capacity extension increased with an increase in mass transfer rate (i.e., higher RPM) and temperature. The discharge capacities obtained with a 200 cm² bi-cell that

was discharged at constant 200 mA/cm² were 203 Ah/l and 229 Ah/l, respectively, for the sorbitol/silicate and LiOH additives at 55°C.

The major factor limiting the discharge capacity of the Zn slurry in the bi-cell was passivation of the air cathode, which is evident by (i) the continually decreasing cathode potential beginning at about 20% depth of discharge and (ii) the presence of a white powder (presumed to be ZnO) in the pores of passivated cathodes. The cathodes were reactivated and reused after treatment with fresh KOH. The end of discharge from cathode passivation occurred at 75% DOD (100% DOD defined as the inherent capacity) in experiments with LiOH as the additive.

The discharge performance of the slurry Zn/air bi-cell was evaluated under various conditions. As an example, Fig. 15 shows curves for the specific power vs current density obtained at various discharge capacities (Ah/l). Under equivalent operating conditions, the Zn powder slurries (particles 25% of 30 mesh and 75% of 100 mesh) provided a better discharge performance (cell voltage and peak power) than the Zn-coated polymeric beads (Sorapec beads) in 12 M KOH. The maximum peak power showed only a slight improvement with pure oxygen; e.g., 483 mW/cm² was obtained with pure oxygen and 444 mW/cm² was obtained with air in a cell containing a Zn powder slurry and an additive of 15 g/l sorbitol and 25 g/l silicate. The discharge performance deteriorated with DOD because of passivation of the air cathode. A peak power of 810 mW/cm² was obtained at 0% DOD, and then decreased sharply at about 20% DOD down to 243 mW/cm² at 60% DOD (with 25 g/l LiOH additive, O₂).

Figure 15. Specific power vs current density at various depths of discharge. Slurry Zn in 12 M KOH + 25 g/l LiOH. AE-100 air cathode depolarized with O₂, 55°C. (XBL-2389)

Recharge

Operating the slurry Zn-air system as a secondary battery requires a separate recharge cell. For Zn recharge, deposition of Zn on scraped planar electrodes (scraping was done manually at this stage) was found to be the most practical method to produce dendritic Zn powder (i.e., slurry Zn). A Zn substrate was not suitable for depositing Zn because of adhesion problems, but glassy carbon (GC) and Mg substrates allowed easy removal of the dendritic Zn deposits by scraping. A study of Zn recharge on these latter two substrates was undertaken. The parameters investigated included (i) current density, (ii) zincate concentration, (iii) mass transfer rate, (iv) temperature, (v) specific charge, and (vi) current waveform (constant current or ramps with one or several current variation rates). The main conclusions from this study follow.

- (1) Less energy is required to produce dendritic Zn on Mg than on GC substrates (e.g., 0.52 Wh/g for Mg and 0.98 Wh/g for GC), while charging at ~ 280 mA/cm² from zincate solution containing 51 g Zn/l at room temperature.
- (2) The coulombic efficiencies are about the same for both Mg and GC substrates: above 99% at high zincate concentrations and decreasing to about 88% at 51 g Zn/l. These results were observed at current densities of 100 to 750 mA/cm².
- (3) A lower zincate concentration, reduced mass transfer rate and higher temperature all favor the production of dendritic Zn, with less energy required for deposition.
- (4) The minimum average current density ($i_{\min}$) and the lowest energy required to produce an acceptable dendritic morphology were investigated. The results indicate that $i_{\min}$ decreases with decreasing zincate concentration and increases with increasing temperature. For example, at low zincate concentrations (51 g Zn/l), $i_{\min}$ is 97 mA/cm² at 30°C and about 266 mA/cm² at 70°C. The lowest energy required is nearly the same (0.22 Wh/g) for both temperatures.

More work is needed to determine the recharge conditions to obtain energy efficiencies over 50% for the secondary slurry Zn/air battery. In addition, data from a prototype recharge cell is required to project the overall performance of a battery system.

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B. ALUMINUM/AIR BATTERIES

Projects on Al/air battery R&D are directed at improving the performance of air electrodes and developing Al anodes with lower corrosion rates and higher open-circuit potential in alkaline electrolytes. A final report by Lawrence Livermore National Laboratory (LLNL) and its subcontractors on Al/air battery R&D has been published. Management responsibility for engineering development of the Al/air battery was transferred from LLNL to SNL in 1986, however, management of air cathode and Al anode research was retained by LBL. Research on air cathodes for Al/air battery is conducted at CWRU; this effort is described elsewhere in this report.

Development of Anode Alloys for Aluminum/Air Batteries

*D. Macdonald and M. Urquidi-Macdonald
(SRI International)*

The objectives of this project are: (i) to evaluate the corrosion resistance of various Al anode alloys of Al/air batteries, (ii) correlate their corrosion behavior with alloy composition, and (iii) to investigate the mechanisms by which minor alloying elements can have such a profound effect on the electrochemistry of the alloys in concentrated hydroxide media.

The electrochemistry of various Al-Li-In, Al-Li-In-Bi, and Al-Mg-Mn-In alloys in 4 M KOH at 50°C was investigated by delineating the partial anodic and cathodic processes as a function of potential from hydrogen evolution to alloy dissolution. The principal findings of this study are as follows:

- (1) The Al-Li-In (Group I) alloys exhibit very high corrosion rates under open-circuit conditions (e.g., Fig. 16 for Al-0.11 In), and are therefore not suitable as fuels for Al/air batteries. The alloys do not exhibit the desired activation phenomenon because they lack an alloying element that oxidizes to form a soluble product within the potential range of interest.
- (2) The Al-Li-In-Bi (Group II) alloys also exhibit high corrosion rates (see Fig. 17 for Al-0.003 Li-0.14 In-0.040 Bi) under open-circuit conditions and hence are also judged to be unsuitable as fuels for alkaline Al/air batteries. Bismuth does not give rise

Figure 16. The total current (i_T) and delineated anodic (i_A) and cathodic (i_H) current/voltage curves for Alloy 60511 in 4 M KOH at 50°C. Potential corrected for IR_s drop with $R_s = 0.6 \Omega$. (XBL-2390)

to an activation phenomenon and does not appear to yield any particularly advantageous characteristics over the simpler Al-Li-In system.

- (3) Group III alloys (Al-Mg-Mn-In) exhibit activation at potentials in the potential range -1.75 to -1.85 V (vs Hg/HgO, 4 M KOH) at 50°C, associated with the oxidation of Mn from the surface (e.g., Fig. 18 for Al-0.10Mn-0.48Mg-0.13In). However, all alloys in this group passivate at more positive potentials, followed by a region where the current varies nearly linearly with voltage. These same characteristics are exhibited by Alloy BDW (Al-1Mg-0.1 In-0.2 Mn), which has been proposed by Alcan as a fuel for alkaline Al/air batteries. None of the alloys studied in the present program appears to offer any advantages over Alloy BDW as a fuel for alkaline Al/air batteries.

Further efforts continue to analyze various mechanisms to account for the extensive impedance data for pure Al in 4 M KOH at 25°C. Six mechanisms were explored, including some that involve autocatalytic steps in the Al electrodisolution process. None of these mechanisms appears to be capable of accounting for the measured impedance any better than the simple irreversible coupled dissolution/hydrogen ion-atom evolution mechanism. Although these latter mechanisms can explain the inductive behavior at intermediate frequen-

Figure 17. Steady state polarization curves for Alloy 60518 in 4 M KOH, 50°C, showing the total current (i_T) and both anodic (i_A) and cathodic (i_H) partial currents. Potential corrected for IR_s drop with $R_s = 0.6 \Omega$. (XBL 887-2391)

cies, they do not seem to explain other features of the impedance as a function of frequency and applied potential, nor do they account for the steady-state partial anodic and cathodic current/voltage curves. Nevertheless, the impedance studies have established the following observations:

- (i) The anodic electrodisolution of Al proceeds via hydroxylated surface intermediates which form by the step-wise addition of OH^- to emerging Al ions.
- (ii) Autocatalysis (e.g., $\text{Al} + \text{Al}(\text{OH})_4^- \rightarrow \text{Al}(\text{OH}) + \text{Al}(\text{OH})_3 + e^-$) is detected in the impedance behavior, but it does not appear to exert a major influence over the interfacial electrochemistry.
- (iii) The anodic (Al dissolution) and cathodic (H_2 evolution) partial processes are coupled through competition for surface reaction sites.

Interestingly, the experimental data could only be simulated by assuming that the total number of reaction sites at the surface is potential dependent and that the transfer coefficients are very small (< 0.1). The potential-dependence of the number of reaction sites is attributed to the existence of a corrosion product film on the surface whose coverage is potential dependent, and the small transfer coefficients are attributed to the voltage drop that exists across this film.

Figure 18. The total current (iT) and delineated anodic (iA) and cathodic (iH) current/voltage curves for Alloy 60539 in 4 M KOH at 50°C. Potential corrected for IR_s drop with R_s = 0.6 Ω. (XBL 887-2392)

C. FUEL CELL RESEARCH

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

Fuel Cells for Transportation

S. Gottesfeld (Los Alamos National Laboratory)

The Fuel Cell program at Los Alamos National Laboratory (LANL) is currently focused on the development of proton-exchange-membrane (PEM) electrolyte for transportation applications. The main objectives of the program are to reduce the costs of the Pt catalyst and of the ionomeric membrane, to enhance the efficiency and the specific power of the fuel cell, and to achieve good performance with reformed methanol and air. The activities within the program have been devoted primarily to the development and characterization of electrodes based on low Pt loadings, evaluation of cell performance under various operating conditions, membrane testing, development and evaluation of methods to lower the CO level in the reformat, and to increase the CO tolerance at the anode.

Electrode Optimization in PEM Fuel Cells

A significant improvement in the performance of electrodes with low Pt loading (0.45 mg/cm^2) in PEM fuel cells was achieved by varying the Pt profile in the catalyst layer. In the first experimental approach, an ordinary Prototech electrode which contained 10 wt% Pt was replaced with similar electrodes (made by Prototech) with higher Pt concentrations. The overall Pt loading was held constant by employing thinner catalyst layers of the more concentrated Pt/C catalyst. The compositions tested were 10, 20, and 40% Pt/C, with the corresponding catalyst layer of 100-, 50-, and 25- μm thickness. The higher concentration of Pt provided significant improvements in cell performance. For example, the cell voltage at 1 A/cm^2 of a single cell employing a 7-mil Nafion membrane and operating on H_2 and air (3/5 atm) increased from 0.2 to 0.45 V when the Pt concentration in the catalyst layer was increased from 10 to 20%. The performance with higher concentrations of Pt (40%) was not significantly different, most probably because of the larger Pt particle sizes in the most concentrated catalyst sample. Further improvement in the performance of similar PEM cells were obtained by sputtering a thin layer of Pt onto the front surface of the Prototech electrode. The highest cell voltage in a fuel cell operating on H_2 and air (3/5 atm) was 0.55 V at 1 A/cm^2 , which was obtained at an electrode with the 20% Pt/C catalyst (50- μm -thick layer) and coated with an additional sputtered layer of Pt with nominal thickness of 500 Å. The additional sputtered layer adds only 0.05 mg/cm^2 of Pt to the overall loading, increasing it typically from 0.4 to 0.45 mg/cm^2 . The beneficial effects of concentrating the Pt catalyst near the membrane are due to a lowering of the overpotentials on both the H_2 and O_2 electrodes. For example, a H_2 anode made by sputtering a 1000-Å layer of Pt onto an uncatalyzed Prototech electrode exhibited an overpotential of only 70 mV at 1 A/cm^2 , whereas an overpotential of 170 mV was obtained under identical conditions with an ordinary (10% Pt/C Prototech) electrode. Apparently, penetration of the current into the Nafion-impregnated catalyst layer is very limited at current densities of the order of 1 A/cm^2 because of the limited proton conductivity deeper within the electrode structure. Catalyst utilization is thus more efficient when Pt is located as close as possible to the ionomeric membrane. Because the conductivity of the ionomeric additive in the catalyst layer improves with an increase in water content, local dehydration may further lower the access to sites located deep within the catalyst layer. This dehydration appears to be particularly severe at the anode at high current densities.

The total overpotential in Nafion-impregnated porous gas-diffusion electrodes was investigated by AC impedance measurements. The impedance results for the porous electrodes showed clearly that a distinction can be made between porous electrodes with deep or

shallow current penetration. An analysis, which is based on a one-dimensional transmission line model that considers gas diffusion through a thin electrolyte film, was conducted of two complete sets of impedance data for such electrodes. Satisfactory agreement between the experimental data and model were obtained at all electrode potentials, however, when the voltage dependence of the parameters was considered, the results were generally not consistent with the model. This result led to the development of a new model for the catalyst layer. The model considers the transport of a reacting gas within the agglomerates of carbon particles and the ionomeric material in which the catalyst particles are embedded. The expected steady-state and AC responses of a gas-diffusion electrode, which is attributed to this additional mass-transport limitation, have been carefully evaluated. Some important features in the experimental impedance spectra are accounted for by this model by considering both "agglomerate diffusion" and diffusion of the reacting gas through thin electrolyte films. Treatment of impedance results with this model is expected to answer important questions on mass-transport limitations within the catalyst layer which are crucial for the operation of PEM fuel cells at low air pressures.

An evaluation of pyrolyzed transition metal macrocyclics as potential substitutes for Pt catalysts in gas-diffusion cathodes in PEM fuel cells was undertaken. Four electrodes containing pyrolyzed macrocycles were tested in PEM fuel cells. Two electrodes were fabricated in-house from FeTMPP prepared from catalysts (43% Fe-TMPP supported on Black Pearls 2000) supplied by United Technologies Corporation. The two other electrodes contained a Co macrocyclic compound that was obtained from Electromedia Corporation. Each of the electrodes was sprayed with 10 layers of 1 or 2% Nafion solutions. Both the Co- and Fe-catalyzed electrodes showed good stability with time in three-week tests which is an encouraging result. The stability of these catalysts in contact with aqueous inorganic solutions was very poor, which seems to suggest that the PEM environment is much less aggressive, probably due to the absence of mobile anions. The performance of the FeTMPP or CoTMPP cathodes, however, was worse than that of Nafion-impregnated Prototech cathodes with 0.35 mg/cm² of Pt. This difference in performance is believed to be due to unoptimized fabrication of these electrodes.

Electrode Fabrication and Fuel Cell Evaluation

To obtain the maximum specific power with Nafion-impregnated electrodes of low (0.45 mg/cm²) Pt loadings requires optimization of the amount of Nafion used for impregnation and the Teflon content in the electrode. An optimum Nafion loading of ~3% Nafion in Prototech electrodes with a carbon cloth support was determined from experiments with electrodes impregnated with 2 to 10% Nafion. Lower loadings do not

allow protons to effectively access the catalyst, while higher loadings limit the mass-transport rate. Nafion-impregnated cathodes on carbon cloth prepared in-house showed a maximum performance with 40% Teflon. Other parameters that need to be optimized to obtain enhanced cell performance are the hot-pressing conditions and the humidification conditions. The optimum procedure is to heat the Nafion membrane and electrode assembly to 110°C for 5 minutes, and then hot-press them at 130°C (the glass transition temperature) for 30 sec at 50 atm. Determining the optimum humidification conditions is a key problem in the development of PEM fuel cells. Experiments with Nafion-impregnated electrodes containing low Pt loading has clearly demonstrated that cells at 80°C with pressurized reactant gases (3 atm H₂, 5 atm air) can be effectively humidified to operate at current densities of ≥ 1 A/cm². This was accomplished by passing the reactant gases through humidification bottles which were at temperatures 10 to 20°C higher than the temperature of the cell. Long-term testing of cells (active area 5 cm² and employing a Nafion membrane) at 300 mA/cm² under such humidification conditions showed steady performance with no apparent dehydration problems for 1000 hours. The test results of cells using an experimental Dow membrane with an external humidifier at 110 to 115°C showed even better results, which allowed an increase in the cell temperature to 100°C without a loss in performance. Tests with Nafion membranes in cells with internal humidification (cell and humidifier temperatures are identical) yielded performance at low current densities that was somewhat lower, but, at current densities of 1 A/cm², the performances became comparable because of the internal generation of water.

Membrane Testing and Evaluation

Dow Chemical supplied LANL with experimental membranes and membrane-electrode assemblies (MEA) for evaluation. The MEAs (50-cm² active area with 4 mg/cm² of Pt) were tested in cell hardware originally supplied by General Electric Company. These cells contain an internal humidification compartment. The best performance (power density of 0.8 W/cm² at 1.75 A/cm²) was obtained in a cell with a 125- μ m thick Dow membrane operating on pressurized H₂/O₂ (3/5 atm) at 71°C. A 75- μ m thick Dow membrane permitted the cell to achieve a power density of 1.0 W/cm² at 1.75 A/cm². For comparison, a cell with a 175- μ m thick Nafion membrane (EW = 1100) generated only 0.4 W/cm² (at 0.5 V). Two possible factors that contribute to the enhanced performance found with the Dow membranes are (i) the reduced membrane thickness and (ii) the lower molecular weight. The different slopes of the voltage-current relations for cells with the Dow membrane and the Nafion membrane suggest that the membrane thickness is the dominant factor determining the apparent overall cell resistance. However, the relative

importance of membrane thickness and of membrane "water retention" characteristics needs further evaluation. The performance of cells based on electrodes with low Pt loadings improved significantly with the Dow membranes. In these cells containing Nafion-impregnated electrodes with 0.45 mg/cm^2 Pt pressed against a Dow membrane, 0.62 V at 1 A/cm^2 and 0.5 V at 2 A/cm^2 were obtained with H_2/air (3/5 atm). Analysis of the current-voltage curves for these cell using the equation $E = E_0 - R_i - b \log i$ yields $E_0 = 1.02 \text{ V}$ (at 1 mA/cm^2), $b = 0.56 \text{ V/decade}$, and $R = 0.16 \text{ ohm-cm}^2$. The value of R shows the important improvement over that obtained with a cell employing a $175\text{-}\mu\text{m}$ thick Nafion membrane, for which $R = \sim 0.25 \text{ ohm-cm}^2$. The performance obtained in the cell with the Dow membrane approaches the goal of 0.7 V at 1 A/cm^2 in PEM fuel cells with low Pt loadings and operating on H_2 and air.

Reformer Kinetics and Mechanism: CO Preferential Oxidation

The effort in 1987 was focused on the optimization of the design and operation of the preferential oxidation step to reduce the CO content of the reformat while still minimizing the consumption of hydrogen. A series of experiments was conducted using a $2.1 \text{ mol}\%$ CO in a H_2 gas mixture, which clearly demonstrated that preferential oxidation of CO occurred. Experiments with reformat gas mixtures indicated no significant influence of the CO_2 concentration at the reactor inlet on the CO conversion. These experimental results have provided a data base for the design of a CO preferential oxidation unit for use with methanol reformers that will reduce the CO in the reformat to a level acceptable for PEM fuel cells.

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Advanced Chemistry and Materials for Fuel Cells

J. McBreen (Brookhaven National Laboratory)

The purpose of this work is to increase our understanding of electrocatalysis on a molecular level and to apply this knowledge to improve the performance of fuel cells. The goals of the project are to reduce the Pt requirements for solid polymer and phosphoric acid fuel cells and the development of new non-Pt electrocatalysts for O_2 reduction and the oxidation of C_1 compounds. In 1987, research was focused on EXAFS studies of pyrolyzed metal macrocyclics on carbon and *in situ* EXAFS studies of carbon-supported Pt in various electrolytes.

EXAFS Studies of Pyrolyzed Metal Macrocyclics

A systematic EXAFS study was made on the pyrolysis products of iron and cobalt tetramethoxyphenylporphyrin (TMPP) on Vulcan XC-72 carbon, which were obtained at several pyrolysis temperatures in the range from 460 to 1000°C . Analysis of the EXAFS data revealed the following. A mixture of several compounds (i.e., metals and metal oxides) are obtained when Fe-TMPP and Co-TMPP supported on carbon are pyrolyzed at the temperatures that yield maximum catalytic activity and stability. The metal oxides are presumably due to the oxidation of metal on exposure of the pyrolyzed sample to air. The presence of the metals and metal oxides makes interpretation of the spectroscopic data essentially impossible. However, chemical leaching of the pyrolyzed material removes the metals and metal oxides to reveal a material that is the electrocatalyst.

This catalyst has a structure that is similar to the core of the original TMPP macrocycle. With an increase in pyrolysis temperature there are two competing processes. One is the formation of the catalyst, and the other is decomposition of the macrocycle to the metal. In the case of Fe-TMPP there is some catalyst present even after pyrolysis to temperatures of 1000°C. At 900°C and above, the Co macrocyclics are reduced completely to the metal. For intermediate pyrolysis temperatures (450-800°C) there is evidence of three coordinating shells in the pyrolysis products. At 900°C and above the Fe catalyst has only one ordered coordinating shell. A decrease in the Debye-Waller factor indicates that in this case the nitrogens may also be bound to the carbon substrate. The pyrolysis products of Co-TMPP in the 600 to 800°C range impart strong hydrophobic properties to the Vulcan XC-72 carbon in KOH electrolytes. The EXAFS results indicate that monodispersed, nitrogen-coordinated Fe and Co atoms are the sites for electrocatalysis.

EXAFS Studies of Platinum on Carbon

Specially designed cells and electrodes were fabricated for transmission EXAFS and cyclic voltammetry studies of Pt supported on carbon. The cell consisted of a flooded working electrode, a dynamic hydrogen electrode (DHE), a separator and a Grafoil counter electrode. The cell had thin PTFE windows to permit transmission EXAFS studies. The electrode consisted of a rolled PTFE/Prototech catalyst mixture on a carbon-paper backing. The low PTFE loading (12%) permitted operation in the flooded mode. Cyclic voltammetry studies were done at 1 mV/S between 0.05 and 1.2 V (vs DHE) in 85% H₃PO₄, 0.1 N H₂SO₄ and 0.1 N CF₃SO₃H electrolytes. Sixty dispersive EXAFS spectra were recorded at 45-s intervals during the cyclic voltammogram. The dispersive EXAFS experiments were done at LURE-CNRS in Orsay, France.

The X-ray near edge absorption (XANES) results revealed several interesting effects. The results indicate that in CF₃SO₃H there is no anion or water absorption in the hydrogen region. In both H₃PO₄ and H₂SO₄, anion absorption was observed in the hydrogen region. In H₃PO₄, there was no evidence of oxide formation below 1.4 V (DHE), whereas oxide formation was observed in both H₂SO₄ and CF₃SO₃H at potentials as low as 1.0 V (DHE). The EXAFS data are currently being analyzed.

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Oxygen Reduction in Alkaline Fuel Cell Electrolytes

E.J. Cairns and F.R. McLarnon (Lawrence Berkeley Laboratory)

Voltage losses in the O₂ cathode represent the major inefficiency in aqueous fuel cells for transportation or stationary applications. Experimental and theoretical studies of oxygen reduction (OR) in aqueous alkaline electrolytes on smooth and supported Pt have been carried out.

The mechanism for OR on Pt in alkaline electrolytes is complicated by the concurrent oxidation and reduction of Pt. Rotating ring-disk electrode studies carried out with anodic and cathodic potential sweeps in 0.1 to 6.9 M KOH and 0.1 to 4.0 M K₂CO₃ revealed similar currents when corrected for O₂ solubility differences. In dilute electrolytes, OR proceeds primarily through the 4-electron pathway to water, independent of pH. In KOH, the mechanism for Pt oxidation changes and the fraction of current yielding a peroxide product increases at 2 to 3 M. These changes were not observed in K₂CO₃.

Porous gas diffusion electrodes (GDE) with supported Pt catalyst were studied in a special cell with low uncompensated solution resistance. Cyclic voltammograms yielded measurements of the wetted areas of carbon and Pt and the local electrolyte composition. GDE galvanostatic steady-state performance with 100% O₂ was measured in 2 to 11 M KOH and 2 to 5.5 M K₂CO₃. Comparisons with kinetic results suggest that OR on carbon contributes to the high currents in 6.9 M KOH at high overpotentials. In K₂CO₃, lower wetted areas and slow OH⁻ ion transport are responsible for the lower performance when compared with KOH.

Models for the steady-state operation of porous GDE's were developed. These models account for the diffusion and reaction of O₂ and ionic transport in KOH and K₂CO₃. Performance data showed good agreement with the model, using reasonable values for the electrode structural parameters. The non-kinetic Tafel slope and the half-order dependence on O₂ pressure, observed with K₂CO₃, were predicted without using adjustable parameters. Comparison between the model and experiment is shown in Fig. 19. The results suggest that modifications of the GDE structure will be necessary to obtain good performance with aqueous carbonate electrolytes.

PUBLICATION

1. K.A. Striebel, F.R. McLarnon, and E.J. Cairns (1987), "Platinum Fuel Cell Cathodes with Aqueous Carbonate Electrolytes," *38th Meeting of the International Society of Electrochemistry*, Maastricht, The Netherlands, Abstract No. 7.20.

Figure 19. Steady-state model fit to O₂ cathode data recorded in 2M K₂CO₃ electrolyte at 25°C with 1 atm O₂. (XBL-8711-4714A)

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