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Executive Summary Report for 1985

TECHNOLOGY BASE RESEARCH PROJECT FOR
ELECTROCHEMICAL ENERGY STORAGE

May 1986

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EXECUTIVE SUMMARY REPORT FOR 1985 TECHNOLOGY BASE RESEARCH PROJECT FOR ELECTROCHEMICAL ENERGY STORAGE

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Edited by Kim Kinoshita, Technical Manager

May 1, 1986

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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 1985. This is a continuing project, and reports for prior years have been published, and they are listed at the end of the Executive Summary.

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.

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* 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 Molecular Research Division.

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 ambient-temperature lithium cells, novel Na/S systems, and a thermally-regenerative system.

Ambient-Temperature Lithium Cells have the potential for high specific energy and specific power, but they typically exhibit short lifetimes when tested under deep-discharge regimens. An inorganic-electrolyte system, which offers improved lithium electrode rechargeability and the capability to withstand limited overcharge, is under investigation.

- Duracell, Inc. has observed that prototype cells (2/3A size with wound electrode design) of the $Li/LiAlCl_4$-SO_2/C system showed a gradual loss of capacity of about 1% per cycle on continuous cycling; cell capacity decreased to 50% after about 40 cycles on deep discharge to 2.0 V. However, cells discharged to 25 or 50% depth-of-discharge have demonstrated over 200 cycles without showing degradation.

Alternative Sodium/Sulfur Cell Designs, which represent significant departures from the Na/β''-Al_2O_3/S configuration under development in the ETD Project, were investigated during 1985. In the first design, an intermediate-temperature (180-250 °C) molten-salt mixture substitutes for the high-temperature (300-350 °C) sulfur-polysulfide melt typically used in the positive-electrode compartment, and in the second design a glass electrolyte is used instead of the β''-Al_2O_3 ceramic electrolyte. Each of these design variations could lead to a Na/S battery lower in cost than the present configuration.

- Experiments at the University of Tennessee on Na/β''-alumina/ SCl_3^+ in $AlCl_3$-NaCl cells indicate that the factor limiting the specific energy of this cell is the utilization

of the active material. A better cell design is needed to optimize the utilization of active materials for long cycle life.

- Dow Chemical Company has observed that the sulfur-corrosion resistance of a promising glass formulation is strongly dependent on the preparative procedure; the glass prepared at 1200 °C, after thorough mixing of the components, has a corrosion resistance that is two times greater than that of the glass obtained at 1000 °C after less mixing.

Thermally-Regenerative Systems convert heat directly into electricity, and their conversion efficiencies are therefore Carnot-cycle limited. The system under investigation uses sodium-ion-conducting β''-Al_2O_3 to separate two sodium reservoirs which are at different temperatures.

- Experiments are underway at Ford Motor Company to improve the performance and endurance of electrodes for their thermally regenerative electrochemical system (sodium heat engine). The studies indicate that sputtered titanium nitride electrodes appear to have the potential for long life at temperatures of 800-900 °C.

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, molten-salt, and non-aqueous. Other 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 zinc as the negative electrode, and it is this electrode that typically limits the lifetime of these cells. Efforts are underway to identify cell components that will improve the cycle-life performance of the zinc electrode.

- Evaluations at LBL indicate that the addition of 25 wt% $Ca(OH)_2$ to the zinc electrode can significantly slow the rate of zinc redistribution. Post-test analyses show

that an insoluble calcium-zinc compound forms and is uniformly distributed over the face of the electrode.

- SRI International has examined the photo-effect of passive zinc electrodes. The experiments show that these electrodes are n-type semiconductors, and impedance measurements indicate a higher resistance of the passive film in a fluoride-containing alkaline solution (which has been shown to extend the lifetime of the zinc electrode) compared to that in solution without fluoride ions.

- Raman spectroscopy studies of solutions having a wide range of Zn^{2+} and OH^- concentrations by Argonne National Laboratory (ANL) indicate only one dominant Zn^{2+} complex is present in aqueous Zn^{2+}/KOH solutions. The evidence suggests that Zn^{2+}-hydroxyl complexes, $Zn(OH)_x^{2-x}$, as opposed to ZnO^{2-}, are present in the alkaline solution.

- Sandia National Laboratory is exploring synthesis techniques to prepare sulfonated polyphenylene membranes that are stable in alkaline ferro/ferricyanide electrolytes. A material with a high ion-exchange capacity (>30 meq/g) was obtained by sulfonation with fuming sulfuric acid.

- A number of membranes (polyvinyl alcohol cross-linked with crown ether) have been fabricated by Brigham Young University. They exhibit conductivities that approached the target of 0.01 mho/cm, but the transference number for hydroxide ions in the membranes was only 0.71.

- Hybrid separators developed by Pinnacle Research Institute (PRI) appear to possess excellent selectivity to zincate ions, and their hydroxide-ion and water transport properties are not altered by the presence of ion-exchange groups.

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

- A traveling-stage videomicroscope was used by LBL to investigate the morphology of zinc electrodeposited from a flowing acidic electrolyte. The growth of large protrusions and the development of well-defined ridges are evident during electrodeposition.

- Illinois Institute of Technology (IIT) has observed that the growth rate of protrusions on a rotating cylinder electrode in 1 M $ZnCl_2$ (+3 M KCl) increases with the rotation rate to the power of approximately 0.6. Higher zinc halide concentrations and higher current densities also cause an increase in the growth rate of the protrusions.

- Brookhaven National Laboratory (BNL) has found that the presence of foreign metals (Bi, Pb, Cd) on the surface of zinc single crystals inhibited layer growth and promoted growth via a nucleation process during zinc deposition. Copper, on the other hand, did not inhibit layer growth and the kinetics of zinc deposition were accelerated.

- Lawrence Livermore National Laboratory (LLNL) has completed isopiestic measurements of the $ZnCl_2$-H_2O system over the concentration range 4.6749-13.143 mol/kg. These data will be used to calculate activity coefficients.

Molten-Salt Cells based on lithium alloy negative electrodes and metal disulfide positive electrodes can 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 found that the upper-plateau Li-Al/FeS_2 cell with LiCl-LiBr-KBr electrolyte at 397 °C showed an utilization capacity (at 50 mA/cm^2) of about 89% of theoretical through more than 300 cycles and 4000-h operation. Based on this performance, a 250-Ah monopolar cell is expected to achieve 175 Wh/kg at a 4-h rate and 200 W/kg at 80% depth-of-discharge.

- Gould, Inc. has observed that identical Li-alloy/FeS_2 cells containing LiCl-LiF-LiI electrolyte, which were cycled at 350 °C and 450 °C, lost upper-plateau capacity at the rate of 0.15% and 0.23% per cycle, respectively. These findings are preliminary,

but the two cells have accumulated 150 cycles over 4000 h and 64 cycles over 1700 h, respectively.

Improved Components for Alkali/Sulfur Cells, such as superior alternatives to the β''-Al_2O_3 ceramic electrolyte and high-temperature sulfur-polysulfide electrode used in Na/S cells and stable lithium-ion conductors for Li/S cells, are under investigation.

- A novel, low-temperature secondary cell has been developed at LBL which contains a liquid sodium negative, β''-alumina electrolyte, and a new positive electrode. The cell operates at 120-150 °C, and it can withstand freeze-thaw cycles without harm. Laboratory cells have been tested and show a specific energy of 80 Wh/kg.

- Rockwell International, Inc. is exploring fabrication techniques to reduce the large scatter in the strength of ZrO_2-toughened β''-alumina. The experiments indicate that a colloidal method, using a nonaqueous solution, helps to disperse the starting powder and allow classification of the powder to achieve the optimum particle size distribution for fabrication of the solid electrolyte.

- Rietveld analysis of the phase transformation and structure at 320 °C of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) solid solutions has been completed by the Massachusetts Institute of Technology (MIT). The results show no evidence for an order-disorder transformation in the sodium distribution. It is hoped that improved understanding of the NASICON structure will lead to similar materials that exhibit comparable sodium-ion conductivity and ease of fabrication, yet are stable to liquid sodium at elevated temperatures.

- ANL has completed evaluation of 24 soda-rich glasses in the soda-alumina-zirconia-silica system, and selected a glass with the composition (mol%) of 42 Na_2O, 8 Al_2O_3, 5 ZrO_2 and 45 SiO_2 for further testing in Na/S cells. This glass has an ionic conductivity of 7.1 x 10^{-3} $ohm^{-1}cm^{-1}$ at 300 °C, and its chemical stability in the cell environment is comparable to that of DOW glass and β''-alumina.

- MIT has observed that Ca-containing borate glasses remain highly conductive, in sharp contrast to the known depressing effect of Ca additions on alkali-ion transport in alkali-silicate glasses. This finding has technological importance since CaO

additions are believed to improve the durability of glasses in contact with lithium metal or its alloys.

- LBL has developed a lithium-chloroborate glass which is capable of supporting pseudo-steady-state current densities up to 15 mA/cm^2 for 15-20 h in a Li/S cell, but this glass lacks the necessary stability to withstand charge-discharge cycling.

- Stanford University is exploring the use of Li_2S-SiS_2 glasses as solid electrolytes. These materials have ionic conductivities comparable to those of the best known inorganic solid electrolytes. Preliminary evaluations (thermodynamic calculations and electrochemical measurements) of several ternary phases, Li-Si-S, Li-O-S and Si-O-S, have been completed.

- The method of restricted diffusion was used by LBL to determine differential diffusion coefficients of sodium ions in sodium polysulfide melts. The experimental data can be correlated by the expression

$$D = 0.153 \exp(-5.89 \times 10^3/T) \exp(5.30x_e)\ cm^2/s.$$

- Experimental measurements on the static-corrosion and dynamic-polarization behavior of materials in sulfur-polysulfide melts were completed by LBL, and the results were published in LBL reports (LBL-19518, LBL-20248, LBL-20249), and presented at the 1985 Fall Meeting of the Electrochemical Society in Las Vegas, NV.

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.

- Measurements at ANL indicate that an alloy with an approximate composition of Al-10 Mg plus 15 vol% SiC would fulfill most of the requirements for a container material for Na/S cells. This alloy would be lightweight, relatively inexpensive, and corrosion-resistant to polysulfides and sulfur.

- The factors influencing the adherence of Mo coatings (CVD deposition) on low-carbon steels were delineated in experiments at IIT. A temperature of 900-950 °C, system pressure of 2.5-3.0 kPa, and a slight excess of H_2 provided the optimum

conditions.

- A 40-μm thick Cr layer was successfully electrodeposited by ANL on Type 304 stainless steel from a molten-salt electrolyte containing 58 mol% LiCl-42 mol% KCl eutectic plus $CrCl_2$. Analysis indicates the Cr layer shows strong adherence to the stainless steel.

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

- Measurements at LBL show that Li_3N layers formed by reaction of Li with gaseous nitrogen are microporous. These layers were shown by impedance spectroscopy to be insufficiently protective in nonaqueous solution for use in rechargeable Li electrodes.

- Case Western Reserve University (CWRU) has completed assembly of the ultrahigh vacuum apparatus for investigations of alkali and alkaline-earth metals on metal substrates. Preliminary experiments indicate that clean alkali-metal films, free of carbon contaminants, can be produced in the apparatus.

- The University of Pennsylvania has found that $PbBr_2$, in addition to $MgCl_2$, form complexes with poly(ethylene oxide) (PEO). The lead halide-PEO complexes are the first polymeric electrolytes with divalent cations that have been reported. This work suggests that many salts of divalent cations and monovalent anions may form conductive complexes with PEO and related polymers.

- LBL is exploring the electroreduction of Mg from $Mg(BF_4)_2$ in propylene carbonate. This study shows that the presence of a few parts per million of moisture in the electrolyte prevents the formation of detectable amounts of Mg.

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.

- Mathematical models were developed at LBL to identify the physical phenomena that govern the performance of electrochemical systems. Models were developed that (i) simulate the behavior of Li-alloy/FeS_2 cells employing LiCl-KCl electrolyte, (ii) calculate the frequency response of a rotating-disk electrode, and (iii) calculate the concentration, potential, and current distribution in a thin-gap channel flow cell.

- The kinetic parameters for the aqueous sulfide-polysulfide redox couple, which is used as the counter electrode in several photoelectrochemical cells and has been proposed for use in redox cells, were measured by LBL. Exchange current densities of the order 1 mA/cm^2 were found, which are significantly higher than those reported previously.

- Electrochemical experiments at LBL indicate that repeated formation/reduction of a monolayer of oxide on gold did not change the structure of the surface; this is in direct contrast to the results obtained with platinum.

- Modeling studies by LBL on gas evolution at smooth electrodes indicate that the current density near the bubble/electrode interface is enhanced, which results from the local depression of the supersaturation potential in this region. This enhancement effect diminishes with increasingly sluggish kinetics, and it is seen to disappear completely in the limit of Tafel polarization.

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 (zinc/air, iron/air) cells; and novel alkaline zinc electrode structures, which could be used in either electrically recharged or mechanically recharged cell configurations.

- Recent experiments at LBL on the graphitization of carbon blacks indicate that there is a new family of graphitic material having particularly attractive BET-

area/iodine-adsorption ratios, and which appear to be nearly an order of magnitude better in corrosion resistance than acetylene black.

- Analytical measurements by CWRU indicate that heat treatment of organic macrocyles supported on carbon results in the decomposition of the macrocycle, but the pyrrole nitrogen is retained. This nitrogen provides binding sites for adsorbed transition metals, such as Co and Fe, with the catalytic activity due mostly to the metal in an atomic state of dispersion.

- Energy Research Corporation (ERC) has found a perovskite of the composition $La_{0.5}Sr_{0.5}CoO_3$ that can be operated as a bifunctional air electrode for 800 cycles at 10 mA/cm^2 (charge) and 20 mA/cm^2 (discharge). Its polarization characteristics are comparable to those of Westinghouse's technology.

- An investigation has been completed at LBL on the effect of potential fluctuations on the morphology of zinc electrodeposited on fluidized-bed and particulate zinc electrodes in alkaline electrolytes. In most cases the fluctuations have a marked effect on both macrostructure and microstructure. Investigations to date indicate that a fluidized-bed electrode might be most suitable for charging a zinc/air cell (depositing zinc) but that a moving-bed electrode would be more suitable for discharge.

- PRI was awarded a contract from a RFP on metal/air battery R&D issued by LBL during 1985. PRI will investigate methods to improve the performance of particulate zinc electrodes for Zn/air cells.

Aluminum/Air Battery R & D, managed by LLNL, is directed at improving cell components and solving system integration, problems, including the following: (i) air cathode development, (ii) hydrargillite crystallization and separation, (iii) integrated experiments involving a coupled cell/crystallizer, (iv) cell design, and (v) development of improved aluminum anodes. Major achievements of the program include:

- Experiments were performed at LLNL in which a single cell was run for over 5 h at 70 °C with 99.999% pure aluminum anode. The presence of stannate ions in solution, which is present to reduce Al corrosion, was found to deposit as tin on cell components (cell hardware and pump valves). This observation suggests that additives

other than stannate ions are required to suppress corrosion.

- Experiments at Eltech Systems Inc., Electromedia, Inc., and CWRU have identified Norit (Ultracarbon) containing 5-10% CoTMPP as a promising air cathode material that exhibit long life (over 3000 simulated-drive cycles*). The performance of these air electrodes in KOH electrolyte is approximately 240 mV higher (at 600 mA/cm^2) than the corresponding performance in NaOH electrolyte.

- Alcan International Ltd. has developed a proprietary aluminum anode which has anodic polarization characteristics similar to that of RX-808 (Reynolds alloy) and corrosion behavior approaching a target of 10 mA/cm^2 equivalent corrosion rate. Its polarization is not appreciably changed by operation at 80 °C or the use of KOH electrolyte, but the corrosion rate is somewhat increased under these conditions.

- Eltech has developed a new cell design, EL-2, to overcome many of the problems identified with the M-4 design. An improved modular cathode, better gasket sealing, and a better anode current-collection design were achieved.

- LLNL is exploring alternative methods to hydrocyclones for separation of hydrargillite. Theoretical calculations and preliminary measurements indicate that lamella settlers offer an attractive alternative to hydrocyclones.

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 demonstrated that the Pt catalyst loading in proton-exchange membrane fuel cells can be dramatically reduced by pretreating commercial Prototech electrodes with solubilized Nafion. Their performance was comparable to that of conventional electrodes, despite a Pt loading that is an order of magnitude lower.

* Not true vehicle driving cycles, but represents cycles for comparative test of electrode cycle life.

- LANL has concluded from studies using isotopic-labeled oxygen that methanol reforming on ZnO-CuO catalysts does not follow the cracking-shift route; instead methanol adds to an oxide vacancy, and in that position, reacts with lattice oxygen atoms to generate CO_2.

- Theoretical studies at LANL have been extended to Pt_3 molecules. These studies indicate that the three atoms are located at the corners of an equilateral triangle with an internuclear separation of 2.69 Å.

- Testing of a 20-kW fuel-cell system, which was delivered by ERC, was completed at LANL. The transient characteristics of the fuel processor were quantified. A time constant of about 15 s was recorded for a change in reformate temperature in response to a step change in the burner temperature.

- BNL is investigation the electrochemistry and characterization of metal-organic macrocycles. None of the 20 synthesized tetrasulfonated metal phthalocyanines (M-TsPc) exhibited interaction with C_1 compounds, which indicates that they are not active for compounds with C-H bonds.

- International Fuel Cells, Inc. (United Technologies Corporation) has concluded from thermogravimetric analysis and Mossbauer spectroscopy that the central FeN_4 group remained intact after heat-treatment of Fe-TMPP supported on carbon at 950 °C. This material was more active for oxygen reduction in H_3PO_4 than the cobalt analog.

- Hamilton Standard-Electrochemical concluded from their study on solid-polymer-electrolyte fuel cells that (i) the development of a low-cost, ion-exchange membrane that exhibits similar performance to Nafion for over 1000-h operation is feasible, and (ii) material costs for both the anode and cathode can be reduced by 50% while maintaining similar performance to a fuel cell containing noble-metal loadings of 4 mg/cm^2.

- The University of Virginia observed that an alloy of 25 at% Cr-75 at% Pt produced activity for O_2 reduction in H_3PO_4 that was comparable to that of Pt. However, the performance of the alloy never exceeded that of Pt, contrary to the results obtained

with dispersed alloy catalysts, which indicated higher activity after Cr addition to Pt.

- Oxygen reduction measurements in K_2CO_3 and KOH have been completed by LBL. The kinetic currents at 0.9 V (versus RHE) are 2 to 2.5 times higher in K_2CO_3 than in KOH at the same concentration. However, lower oxygen solubilities in carbonate electrolytes may lead to higher mass-transfer overpotentials in a fuel cell.

Planned Activities in 1986

New research projects planned include:

1. An RFP will be issued for research on novel concepts for rechargeable lithium cells.

2. Applied research on the characterization of components for secondary batteries.

Management Activities

During 1985, LBL managed 30 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:

- Sixth Meeting of the DOE Advanced Fuel Cell Working Group, LBL, Berkeley, CA, January 9-11, 1985.
- DOE/SNL/LBL/EPRI Lead Center Coordination Meeting, Washington, DC, January 22, 1985.
- Electrochemical Energy Storage Program Lead Center Review, Washington, DC, January 23, 1985.
- Review of Ceramatec's Programs on Beta"-Alumina and Related Technologies, Salt Lake City, UT, January 24-25, 1985.
- EPRI Na/S Battery Research Program, EPRI, Palo Alto, CA, February 5, 1985.
- Golden Gate Metals and Welding Conference, San Francisco, CA, February 12, 1985.
- Sodium Heat Engine Review, ANL, Argonne, IL, February 12-13, 1985.

- Annual Meeting of the AIME, New York, NY, February 24-28, 1985.
- Frontiers of Experimental and Theoretical Electrochemistry Workshop, LANL, Los Alamos, NM, February 25-26, 1985.
- Electric Vehicle Battery Review Meeting, Washington, DC, April 23, 1985.
- Spring Meeting of the Electrochemical Society, Toronto, Ontario, Canada, May 12-17, 1985.
- NRC Committee Meeting on Electrochemical Aspects of Energy Conservation and Production, Toronto, Ontario, Canada, May 16, 1985.
- Aluminum/Air Battery Review Meeting, Toronto, Ontario, Canada, May 17, 1985
- National Fuel Cell Seminar, Tucson, AZ, May 19-22, 1985.
- Beta Battery Workshop VI, Snowbird, UT, May 19-23, 1985.
- Electrochemical Energy Storage Program Lead Center Meeting, Washington, DC, July 10-11, 1985.
- Sixth Read Conference on Electrodeposition, University Park, PA, July 22-26, 1985.
- NRC Committee Meeting on Chemical Engineering Frontiers, Panel on Energy and Natural Resources Processing, Itasca, IL, July 31-August 1, 1985.
- NRC Committee Meeting on Energy Conservation and Production, Washington, DC, August 15-16, 1985.
- 20th Intersociety Energy Conversion Engineering Conference, Miami Beach, FL, August 18-23, 1985.
- 36th Meeting of the International Society of Electrochemistry, Salamanca, Spain, September 22-27, 1985.
- Fall Meeting of the Electrochemical Society, Las Vegas, NV, October 13-18, 1985.
- Aluminum/Air Battery Review Meeting, Las Vegas, NV, October 18, 1985.
- Seventh Battery and Electrochemical Contractors' Conference, Crystal City, VA, November 18-21, 1985.

Milestones for The Technology Base Research Project

Milestones accomplished in Fiscal Year 1985 by the TBR project include:

- LLNL initiated testing of an Al/air cell (M-4) that is coupled to a crystallizer. This test showed that the crystallizer design was adequate to obtain separation of crystal from the electrolyte flow stream. The major finding from this test is that the stannate ions (inhibitor to reduce Al corrosion) present in solution are reduced and precipitate as metallic tin on various components in the system.
- Testing of the M-5 cell design (500 cm) was completed by Eltech Systems Corp. This Al/air cell contained an anode of 99.98% Al and a cathode of CoTMPP. The cell operated at 1.21 V (200 mA/cm^2) at the start of testing in 4 N NaOH at 55 °C. The initial test demonstrated that the results with small cells (2.5-cm x 2.5-cm electrodes) can be correlated with data from larger cells (500 cm^2).

- Eltech Systems Corp. completed a new design (EL-2) for an Al/air cell that provided major improvements over the old design (M-5). Cell EL-2 demonstrated improvements in the sealing mechanism for the air cathodes, reliability of components, and ease of assembly of multi-cell stacks.

- A glass electrolyte with the composition (in mol%) 42 Na_2O, 8 Al_2O_3, 5 ZrO_2 and 45 SiO_2 has been selected by ANL for testing in Na/S cells. The chemical stability of this glass in Na/S cell environment is comparable to that of β''-alumina and Dow glass.

- A research program at United Technologies Corp. (UTC) seeks to reduce the cost of electrocatalysts for air electrodes in phosphoric acid fuel cells. Various organic macrocyclics were evaluated as possible alternatives to Pt for oxygen-reduction electrocatalysis. FeTMPP showed stable performance in half-cell tests, but its performance decayed badly in fuel-cell tests. Based on these results a decision was made not to pursue endurance testing of FeTMPP in fuel cells. Instead, it was decided to continue with studies to determine the cause of performance decay and to proceed with tests on the variations in electrode fabrication that are needed to improve the performance of electrodes containing organic macrocyclics.

- Hamilton Standard-Electrochemical has tested solid-polymer-electrolyte fuel cells with an active area of 0.05 ft^2. This cell size is adequate for laboratory tests, but is not a suitable size for cell stacks for use in a vehicle propulsion system where the active electrode area should be at least 1 ft^2. Despite the encouraging results obtained in this program, the progress to date did not warrant a scale-up of the cell from 0.05 ft^2 to 1 ft^2.

Acknowledgement

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Annual Reports

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

SUBCONTRACTOR FINANCIAL DATA - CY 1985

Subcontractor	Principal Investigator	Project	Contract Value (K$)	Duration (months)	Expiration Date	Status in FY 1986
EXPLORATORY RESEARCH						
Ambient Temperature Lithium Cells						
Duracell International,Inc.	A. Dey	Li/SO_2	1500	48	12-85	R
Alternative Sodium/Sulfur Cell Designs						
University of Tennessee	G. Mamantov	$Na/SCl_4(NaCl\text{-}AlCl_3)$	19	12	3-85	T
Dow Chemical Company	P. Pierini	Sodium/Sulfur	290	12	8-85	T
Thermally-Regenerative System						
Ford Motor Company	T.K. Hunt	Sodium Heat Engine	253	16	5-85	T
APPLIED SCIENCE RESEARCH						
Lawrence Berkeley Laboratory	E. Cairns, L. DeJonghe J. Evans, R. Muller, J. Newman, P. Ross, and C. Tobias	Electrochem. Energy Storage	1500	12	9-85	C
Alkaline Cells						
SRI International	M. Madou	Semiconductor Electrode	71	12	3-85	T
Argonne National Laboratory	J. Battles	Spectroscopic Studies	25	12	9-85	T
Brigham Young Univ.	D. Bennion	Zn/NiOOH Separators	77	12	7-85	T
Pinnacle Research	R. Yeo	Zn/NiOOH Separators	100	13	7-85	T
Zinc/Halogen Cells						
Illinois Institute of Technology	J.R. Selman	Zn Deposition	71	12	8-86	C
Brookhaven National Laboratory	J. McBreen	Zn Morphology	100	12	9-85	C
Lawrence Livermore Nat'l Laboratory	D. Miller	Transport Properties	65	12	9-85	C
Molten-Salt Cells						
Argonne National Laboratory	J. Battles	Molten-Salt Cells	330	12	9-85	C
Gould, Incorporated	H.F. Gibbard	Li/FeS_2	200	20	4-86	R
Stanford University	R. Huggins	New Battery Materials	300	12	11-85	C

SUBCONTRACTOR FINANCIAL DATA - CY 1985

Subcontractor	Principal Investigator	Project	Contract Value (K$)	Duration (months)	Expiration Date	Status in FY 1986
Improved Components for Alkali/Sulfur Cells						
Rockwell International, Inc.	F. Lange	Improved $\beta''Al_2O_3$	145	12	4-86	T
Massachusetts Institute of Technology	B. Wuensch	Superionic Conductors	83	12	7-85	C
Massachusetts Institute of Technology	H. Tuller	Li Conducting Glasses	99	12	5-86	C
Argonne National Laboratory	J. Battles	Glass Electrolytes	300	12	9-85	C
Corrosion Processes in High Temperature, High-Sulfur Activity Molten Salt						
Argonne National Laboratory	J. Battles	Polysulfide Containment	200	12	9-85	C
Illinois Institute of Technology	R. Selman	Corrosion Resistant Coatings	163	12	9-85	C
Argonne National Laboratory	J. Battles	Amorphous Coatings	50	6	3-86	T
Components for Ambient-Temperature Lithium Cells						
Case Western Reserve University	D. Scherson	Spectroscopic Studies	58	12	11-85	C
University of Pennsylvania	G. Farrington	Polymeric Electrolytes	82	12	2-86	C
AIR SYSTEMS RESEARCH						
Metal/Air Cell Research						
Case Western Reserve University	E. Yeager	Air Electrodes	213	12	3-86	C
Energy Research Corporation	M. Klein	Bifunctional O_2 Electrode	195	12	9-85	T
Pinnacle Research Institute	L. Morris	Zn/Air Battery	225	12	11-86	C
Aluminum/Air Battery R&D						
Lawrence Livermore Nat'l Laboratory	A. Maimoni	Al/Air Battery R&D	450	12	9-85	C
Eltech Systems Corporation	L. Gestaut	Al/Air Battery	600	24	1-86	C
Fuel Cell R&D						
Los Alamos National Laboratory	J. Huff	Fuel Cell R&D	784	12	9-85	C
Brookhaven National Laboratory	J. McBreen	Fuel Cell Research	290	12	9-85	C
United Technologies Corporation	J.A. Bett	Alloy Catalysts	627	24	4-85	T
Hamilton Standard (formerly G.E.)	J.F. McElroy	Solid Polymer Electrolyte	997	35	12-85	T
University of Virginia	G. Stoner	Alloy Electrocatalyst	82	28	1-86	T

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

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