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**Exploratory Battery Technology** 

**Development and Testing Report for 1986** 

Prepared by

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Sandia National Laboratories Albuquerque, New Mexico 87185 and Livermore, California 94550 for the United States Department of Energy under Contract DE-AC04-76DP00789





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# Exploratory Battery Technology Development and Testing Report for 1986

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# Abstract

Sandia National Laboratories, Albuquerque, has been designated as Lead Center for the Exploratory Battery Technology Development and Testing Project, which is sponsored by the U.S. Department of Energy's Office of Energy Storage and Distribution. In this capacity, Sandia is responsible for the engineering development of advanced rechargeable batteries for both mobile and stationary energy storage applications. This report details the technical achievements realized in pursuit of the Lead Center's goals during calendar year 1986. -

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# Acronyms and Abbreviations

ABS	Advanced Battery Systems
ADL	Analysis & Diagnostic Laboratory
ANL	Argonne National Laboratory
ANOVA	analysis of variance
BATSIM	Battery Simulation
BEST	Battery Energy Storage Test Facility
BET	Brunauer, Emmett, Teller method for determining particle surface area
BUMP	battery unit maintenance program
COMSAT	Communications Satellite Corporation
CPE	carbon-plastic electrode
CSPL	Chloride Silent Power, Ltd.
CVD	chemical vapor deposition
DMA	dynamic mechanical analysis
DOD	depth of discharge
DOE	Department of Energy
DSC	differential scanning calorimetry
DSEP	Dual Shaft Electric Propulsion Program
EDA	Energy Development Associates
EHP	Electric and Hybrid Propulsion (a branch of DOE OTS)
EPD	electrophoretic deposition
EPI	Eagle-Picher Industries
EPRI	Electric Power Research Institute
ER&E	Exxon Research and Engineering Co.
ERC	Energy Research Corporation
ETD	Exploratory Battery Technology Development and Testing Project
ETX	Electric Transaxle Experimental Test Vehicle Project
EV	electric vehicle
EVEM	Electric Vehicle Engineering Model
FACC	Ford Aerospace and Communications Corporation
FUDS	Federal Urban Driving Schedule
GVW	gross vehicle weight
HDPE	high-density polyethylene
HNEI	Hawaii Natural Energy Institute
HPO	polyolefin copolymer used in Exxon zinc/bromine battery
ICPV	individual cells within a common pressure vessel
IDSEP	improved DSEP
IEC	ion exchange capacity
IR	internal resistance; infrared analysis
JCI	Johnson Controls, Inc.
JPL	Jet Propulsion Laboratories
LBL	Lawrence Berkeley Laboratory
LL	load leveling
LMSC	Lockheed Missiles and Space Company
LPARL	Lockheed Palo Alto Research Laboratory
NBTL	National Battery Test Laboratory
NMR	nuclear magnetic resonance
OCV	open circuit voltage

# Acronyms and Abbreviations (continued)

OFED	DOE Office of Energy Storage and Distribution
OESD	Oale Didee National Laboratory
OKNL	DOE Office of Transportion Systems
015	DUE Office of Transporation Systems
PASTE	Photovoltaic Advanced Systems Test Facility
PB	designation for standard CSPL sodium/sultur cell
PFA	perfluoroacrylate
PP	polypropylene
PTFE	polytetrafluoroethylene
PV	photovoltaic
PVC	polyvinylchloride
RH	relative humidity
Redox	reduction oxidation
RELSIM	Reliability Simulator
S <sup>4</sup> D	seeded slurry solution spray-drying
SAE	Society of Automotive Engineers
SAIC	Science Applications International Corporation
SAM	scanning acoustic microscopy
SCE	Southern California Edison
S.E.A.	Studiengescellschafft fur Energiespeicher und Antriebssysteme
SEM	scanning electron microscopy
SERI	Solar Energy Research Institute
SES	stationary energy storage
SFUDS	simplified FUDS
SNL	Sandia National Laboratories
SPS	sulfonated polysulfone resins
TBR	Technology Base Research Project
TD	designation for a prototype CSPL sodium/sulfur cell (technology demonstration)
UK	United Kingdom
WTG	wind turbine generator

XPB Extended (larger capacity) PB sodium/sulfur cell

# Exploratory Battery Technology Development and Testing Report for 1986

# **Chapter 1. Aqueous Battery Development**

# Introduction

During 1986, the Exploratory Battery Technology Development (ETD) Project continued to support several aqueous-electrolyte advanced secondary-battery systems. These included zinc/bromine, nickel/hydrogen, and zinc/redox. In all cases, the development is carried out by industrial organizations through cost-shared contracts.

The largest program in this element is the Zinc/Bromine Battery Development with Energy Research Corporation (ERC). This \$5.1M program was initiated in September 1985. Originally intended to run for three years, the period of performance was extended, at no cost, to four years. The objectives of this contract were to continue the development of ERC's zinc/bromine core technology, which was acquired from Gould in 1982, and demonstrate a proof-of-concept 50-kWh stationary battery during the final contract year.

A second zinc/bromine activity was initiated with Johnson Controls, Inc. (JCI), which involved the testing and analysis of the Exxon Z30-A battery and the fabrication of a 20-kWh unit, designated Z20. This program was jointly funded by the DOE Office of Energy Storage and Distribution and the Office of Transportation Systems. JCI licensed the zinc/bromine technology from Exxon, which was previously supported by ETD.

During 1986, the prime-contract responsibility for nickel/hydrogen battery development transferred from Communications Satellite Corporation (COMSAT) to JCI. Previously JCI was the subcontractor to COMSAT in this effort. The main thrust of the nickel/hydrogen program continued to be the reduction of costs of terrestrial battery systems without compromising the demonstrated performance of nickel/hydrogen batteries for satellite applications. The major activities at JCI consisted of a statistically designed experiment to evaluate component and process variables in single cells, thermal management modeling, fivecell battery evaluations, and development of additional low-cost components and processes.

Lockheed Missiles and Space Corporation has been performing engineering development studies on the zinc/redox system since 1981. During 1986, an evaluation of several unresolved technical issues was completed. Issues that were addressed included low-cost membrane performance, zinc-electrode design, bipolarelectrode composition, and cell-performance modeling. An assessment was also made of the feasibility of providing ETD support for the next phase of the development program: the design and construction of multicell stacks. Based both on technical issues and available budget, the decision was made to not continue the ETDsponsored development of the zinc/redox technology after the existing contract expires in January 1987.

# Zinc/Bromine Battery - ERC

Energy Research Corporation is involved in a program to develop the zinc/bromine battery system for stationary energy storage applications. Two projects are currently underway in the development program. Technology development work is being done under a project supported by the U.S. Department of Energy through Sandia National Laboratories (SNL). A smaller project, supported by the Electric Power Research Institute (EPRI), examines design and commercialization issues specific to the utility load-leveling application. This section describes the work conducted in the SNL-supported technology development project. This work is summarized in Table 1-1.

The SNL project is a four-year effort culminating in the demonstration of the battery technology in 50-kWh prototype systems. The first year of the project centered on componentdevelopment work, electrochemical studies, and stack-hardware optimization. The second and third years of the project will be characterized by testing and optimization of multicell stacks (5-cell, 30-cell, and 52-cell). The fourth year work will involve the fabrication and testing of the 50-kWh systems.

The project was started in late September 1985, so the first annual report covered only the first three months of the work when many of the activities were just beginning. This second annual report will therefore describe activities conducted over the first 15 months of the project. Before discussing this work, a brief description of the battery system is presented.

# **Battery System Concept**

The battery stores energy by the electrolysis of an aqueous zinc bromide salt to zinc metal and molecular bromine. Zinc is plated as a layer on the negative electrode surface, while bromine is dissolved in the electrolyte. On discharge, the zinc and bromine are consumed, regenerating the zinc bromide salt.

The reactions occur in a bipolar electrode stack, which consists of a stack of flow frames into which the electrodes are bonded. The stack is fed with electrolyte from two (anolyte and catholyte) recirculation systems. The electrolyte is essentially the same in the two flow loops except for the concentration of dissolved bromine, which ranges from 5 to 13 g/l in the catholyte and is kept below 1 g/l in the anolyte.

Within each cell in the bipolar stack, the two electrolytes are separated by a porous separator membrane, which allows ionic transport between the half-cells but prevents bulk mixing of the electrolytes. Channels in the flow frames direct anolyte and catholyte past the proper side of each electrode. These channels are long, thin recesses in the flow frame. This configuration is used to provide high electrical resistance in the channels to limit shunt current losses in the bipolar stack.

To keep the catholyte bromine concentration in the 5 to 13 g/l range, an organic complexing agent is used to extract evolved bromine from the catholyte during charge. When the catholyte bromine level decreases on discharge, bromine is released from the complexing agent as an equilibrium between the two phases is maintained.

The complexing agent flows in a third recirculation loop in the system, contacting the aqueous catholyte in a static mixer as it returns to the storage tank. In the tank, the heavy immiscible bromine complex settles to the bottom in a separate phase.

The open circuit voltage of zinc/bromine cell is typically 1.75 V to 1.8 V, depending on catholyte bromine concentration. A typical charge voltage (at  $35 \text{ mA/cm}^2$  current density) is 2 V, and 1.6 V is a typical discharge voltage. Improving this voltaic performance and reducing coulombic and parasitic losses are major objectives of the development program. Additional objectives include the development of a low-cost system design and the demonstration of extended battery cycle life. A discussion of activities in the project in 1986 is presented below.

# **Component and Subsystem Development**

### **Bromine Electrode Development**

The ERC zinc/bromine battery utilizes a high-surface-area carbon felt flow-through electrode to support the bromine/bromide reaction. Two of the major drawbacks of the electrode have been buildup of the organic bromine complexing agent in the felt and a lack of material uniformity within batches of purchased materials.

During 1986, ERC developed procedures to produce carbon felt in-house. This allowed the application of quality control to both precursor and carbonized material, and facilitated the investigation of the effect of process variables on electrode performance.

# Table 1–1. Zinc/Bromine Technology Progress – ERC

### Component and Subsystem Development Superior performance of in-house felt attributed to reduced polybromide **Bromine Electrode** entrapment and improved flow distribution. Low loadings of RuO<sub>2</sub> catalyst lessen discharge polarization. Zinc Electrode Anolyte with higher Cl/Br ratio shows improved zinc-deposit morphology. New, PVC-based separator tested (Amer-Sil): lower polybromide Separator absorption, but increased crossover of electrolyte. Small-cell tests show new, Flourel-based gasket filler more durable than current gasket filler. Bromine Storage Subsystem Studies initiated on tank that will eliminate polybromide recirculation loop. Hardware Development New stack clamping assembly built: more even load distribution and lower Stack Assembly assembly cost (\$2 to \$3/kWh). End Electrode Large samples of coated copper-end electrodes produced; "primer" coating improved adhesion between carbon/plastic mix and copper insert. Flow Frame New flow-frame design allows charging at voltages up to 100 V and increases electrode active area to $1500 \text{ cm}^2$ . System Development Computer model of zinc/bromine battery system that estimates pressure System Modeling drops and shunt current losses used for next design of zinc/bromine battery. Battery Design and Testing Tests on SNL-5-2 (five-cell stack, 872-cm<sup>2</sup> electrodes, old leaf-spring stack assembly) show that zinc-stripping procedure is necessary and that anolyte cleaning improves coulombic efficiency. Tests initiated on SNL-5-3 (five-cell stack, 872-cm<sup>2</sup> electrodes, new clamping hardware) and SNL-5-4 (same as SNL-5-3 except no polybromide recirculation loop). Material Stability Battery flow-frame and piping materials narrowed to a few preferred grades of PVC. Carbon-plastic bipolar plates show excellent dimensional and weight stability; but excess bromine (100 g/l) causes some strength loss, and graphite identified as a source of iron contamination. Tests on 10-cm<sup>2</sup> cells show no significant physical changes in cell components after 100 cycles.

Optimization of the in-house felt electrode was tested on cells with 10 cm<sup>2</sup> and 20 cm<sup>2</sup> active electrode area. Variables examined included felt thickness, felt compression level (cathode gap thickness), carbonization temperature, and carbonization environment. The chosen baseline design was 0.30-cm felt thickness, 0.25-cm cathode channel gap, carbonizing at 1200°C in a nitrogen environment.

Several full-size single cells  $(872 \text{ cm}^2 \text{ active} \text{ area})$  were built with the in-house felt material. Voltaic efficiency (discharge voltage  $\div$  charge voltage) for these cells was typically 80% to 85%. Voltaic efficiency observed in cells and batteries with the purchased felt electrodes previously used ranged from 73% to 78%. The range in voltaic efficiency is primarily because of temperature variations that change electrolyte conductivity and electrode kinetics. Figure 1-1 shows charge/discharge curves for cells with purchased and in-house felt electrodes.

The improved performance of the in-house felt material is because of a number of factors. The fibers in the felt are narrower than those in the purchased material, so it has a larger specific surface area. The greater uniformity of the material results in improved flow distribution in the cathode, ensuring that flow is through (and not over) the felt. Testing has also indicated that polybromide entrapment is reduced in the in-house felt, probably because of the improved flow distribution.

Bromine-electrode catalysis was another area of development. Candidate catalyst materials were screened in short-term stability tests. Ruthenium oxide, perovskite, gold-black, and gold-palladium alloy catalyst materials were screened, and only the ruthenium oxide catalyst was found to be stable. Longer-term stability tests were initiated, and evaluation of cells with ruthenia-catalyzed carbon felt was begun.

Initial tests were conducted in  $10-cm^2$  cells with catalyst loadings from 0.14 to 2.7 mg/cm<sup>2</sup>. Performance improvement was observed, but not enough to justify the cost of the catalyst. A series of cells were then built using very low catalyst loadings. The cell designations and catalyst loadings are given in Table 1-2, along with a comparison of discharge polarization performance.



Figure 1-1. Voltage Performance of 872-cm<sup>2</sup> Single Cells with Purchased Felt (SC-1-23) and In-House Felt (SNL-1-2)

RuO <sub>2</sub> Loading mg/cm <sup>2</sup>	Estimated Catalyst Cost \$/kWh	Polarization @ 40 mA/cm <sup>2*</sup> mV	
		165	
0	-	105	
.068	1.32	109	
.034	0.66	101	
.017	0.33	66	
	RuO <sub>2</sub> Loading mg/cm <sup>2</sup> 0 .068 .034 .017	RuO2 Loading mg/cm2Estimated Catalyst Cost \$/kWh00681.32.0340.66.0170.33	Discharge PolarizationRuO2 Loading mg/cm2Estimated Catalyst Cost $\$/kWh$ Polarization $@ 40 mA/cm^{2*}$ mV0-165.0681.32109.0340.66101.0170.3366

Table 1–2. Catalyst Loading Level	and Estimated Catalyst Cost for
<b>Cells with Ruthenized Carbon-Felt</b>	Electrodes

\*Catholyte bromine concentration = 10 gm/1 Catholyte flow rate = 40 m1/min

An unexpected result from these tests (and subsequent duplicate tests) was that the cells with lower catalyst loading exhibited less polarization. Analysis of catalyzed felt samples by scanning electron microscopy showed some clumping of catalyst material at higher loading levels, which could result in less active catalyst area.

#### Zinc Electrode Development

The zinc-deposition process limits the loading level of battery stacks, or the amount of capacity that can be stored in a stack with a given electrode area. As more zinc is plated onto a substrate, the deposit becomes less dense, and deposit thickness increases to the point where electrical short circuiting is possible.

Shortly before the start of the current SNLsupported program, an electrolyte formation was developed that allowed discharge capacity density of 200 mAh/cm<sup>2</sup> with dense, uniform zinc deposits. Large single-cell testing conducted during this year was limited to repeated tests using this electrolyte to characterize deposit quality fully. The cells exhibited dense uniform plates, but with occasional small nodules growing up to the level of the separator. Typically about five to ten such nodules (about 2 mm to 3 mm in diameter) would be seen on an 872-cm<sup>2</sup> plate. The presence of these nodules limits battery stack cycle tests to the 170-mAh/cm<sup>2</sup> charge input level.

Most of the work conducted on zinc electrode development this year involved electrochemical studies on zinc-deposition kinetics. The objective of this work was to identify the set of kinetic conditions that promote dense, nondendritic zinc deposits.

The major area of investigation involved activation kinetics. When the kinetics of zinc deposition are fast, the deposition process is diffusion controlled, leading to dendritic or mossy deposits. It is desirable to shift the deposition process to activation control, with slower kinetics. If the shift is too great, hydrogen evolution can result. The focus of the kinetic studies was to identify the range of conditions in which both hydrogen evolution and dendritic deposition are avoided.

The major variable in these studies was electrolyte formulation, particularly the ratio of chloride and bromide ions in the electrolyte. Other investigators have shown that zinc deposition kinetics are faster in zinc bromide electrolytes than in zinc chloride electrolytes. This is attributed to the relative stability of different zinc halide complexes (J. McBreen, E. Gannon, "Zinc Electrode Morphology in Acid Electrolytes," Brookhaven National Laboratories Annual Report BNL 51705, July 1983). By adding metal chloride supporting salts to the electrolyte, the equilibrium of the zinc halide complex can be shifted toward formation of zinc chloride complexes, with a resulting slowing of zinc deposition kinetics.

The electrolyte formulations examined in the program included a high-chloride electrolyte (the new baseline) and a low-chloride electrolyte that was the previous baseline. High- and lowchloride electrolytes with reduced zinc bromide concentration (simulating depletion of zinc bromide during charge) were also evaluated. The higher chloride content of the current baseline electrolyte is believed to improve zinc deposit morphology more than the previous baseline.

The electrolytes with high chloride content exhibited higher nucleation overpotential and lower exchange current density in electrolytes with less than 2M zinc ion concentration. This slowing of kinetics becomes more pronounced as the chloride/bromide ratio increases with depletion of bromide ions. Observations from these experiments suggested that the high chloride/bromide ratio in the baseline electrolyte toward the end of charge may be causing some hydrogen evolution. Hydrogen evolution, in addition to reducing the coulombic efficiency of the deposit, impairs deposit quality in the areas of bubble formation.

A series of batches of experimental electrolyte formulations with lower chloride/bromide ratios than the present baseline has been made. The electrolytes will be tested in large single cells for evaluation of deposit quality with  $240-mAh/cm^2$  charge loadings.

### Separator Development

The separator presently used in zinc/bromine batteries at ERC is a porous, silica-filled polyethylene from W.R. Grace with the trade name Daramic. The separator material is cut to the size of the flow frames and the area outside the active cell area is filled with a silicone elastomer. The filled area acts as a gasket to seal flow channels and manifolds.

The bromine permeability of the separator is such that bromine diffusion into the anolyte causes a self-discharge rate equivalent to about 2  $mA/cm^2$ . This, combined with the voltaic resistance of Daramic (about 1  $\Omega \cdot cm^2$  for the 25-mil-thick material) makes the separator one of the more significant sources of energy loss in the cell. The pores of Daramic also tend to get filled with the bromine complexing agent, which increases both bromine diffusion and voltaic resistance. Studies conducted before the start of the SNL program indicated that Daramic may not be chemically stable in long-term stationary energy storage applications.

A more stable alternate material evaluated this year is Amer-Sil, a PVC-based film made by Amerace Corporation. Amer-Sil has a larger pore size than Daramic and is less prone to absorption of the bromine complex.

The first cell tests on Amer-Sil were 10-cm<sup>2</sup> cells in a flow system using the bromine complex to store evolved bromine. Electrolyte flow velocities in the small cell test loop were too low to expel the polybromide droplets formed during charge. As a result, the test results exhibited a high degree of variability from flow irregularities and bromine complex buildup within the cells.

A second series of cell tests was done without the bromine complex, using excess catholyte to keep bromine concentration in the 5 to 13 g/l range. The larger pore size of the Amer-Sil had the expected effect of increasing bromine diffusion and lowering voltaic resistance, but also led to an increase in bulk electrolyte crossover through the separator.

Characterization tests are underway to evaluate other commercially available separators for transport properties and chemical stability. The possibility of using Amer-Sil, with its good wetting characteristics and low polybromide absorption, as a laminate with a less porous material is also being evaluated.

Another development effort is centered on the gasket filler used outside the cell active area. The silicone presently used is known to have limited long-term stability when exposed to bromine and has been observed to leach into the uncoated active area of the separator. Several alternate filler materials have been evaluated for ease of application and sealing resiliency. A filler based on Fluorel (a fluorelastomer from 3M Corporation) was selected from screening tests and has been used successfully on small cells. Scale-up to 872-cm<sup>2</sup> cell separators is presently underway.

#### **Bromine Storage Subsystem**

As described above, evolved bromine is extracted from the catholyte and stored as a polybromide complex with an organic complexing agent. The stability of the complexing agent was demonstrated in work done prior to the SNL-supported project. The main limitations of the complexing agent are that it builds up in the carbon-felt bromine electrodes, and it increases system complexity by requiring a third recirculation loop.

To eliminate polybromide buildup in the felt electrodes, solid bromine storage agents are being evaluated. Amorphous carbon blacks, graphites, and solid quaternary ammonium complexing agents would be used in a packed bed in the catholyte recirculation loop.

Initial studies were done on graphite as a storage agent because of its low cost and chemical stability. A graphite bed was found to store 1 g bromine per 100 g graphite in equilibrium with a 10 g/l catholyte bromine concentration (50% state of charge). Cost of graphite as a storage agent would therefore be about \$50/kWh, which is excessive. Problems were also encountered in maintaining flow through the graphite bed: the graphite tended to clump and restrict flow. Studies are presently evaluating solid quaternary compounds that complex bromine in the same way as our baseline complexing agent but are solid at the temperatures used in the battery system.

To reduce system complexity, a new catholyte tank was designed that allows mixing and separation of the catholyte and polybromide within the tanks. This design eliminates the need for a third recirculation loop in the system. Catholyte leaving the stack is returned to the bottom of the tank and then bubbles up through a column of polybromide. Subsequent settling zones in the tank separate the two phases before the electrolyte reaches the pump suction port.

Initial tests are just beginning on the first prototype tank, which is being used with a fivecell stack. Sufficient contact has been established between the catholyte and polybromide phases to maintain transfer at the design rate throughout a full cycle.

### Hardware Development

#### Stack Assembly

The stack of flow frames is held together by compression applied to the stack by end plates and tie bolts. The clamping assembly used at the start of the program consisted of 2.5-inch-thick polypropylene end plates backed up by a 1/2-inch-thick steel strongback. To distribute force evenly over the stack area, leaf springs (2.5 inches wide) transferred the tie-bolt tension to the seal areas. The clamping assembly was identified as one of the more expensive components of the battery because of the large quantities of plastic, steel, and spring steel required.

During this year the clamping assembly was redesigned to provide more even load distribution and to lower the assembly cost. Leaf springs are no longer used, and rib members in the steel strongback now limit deflection and provide uniform clamping force distribution. Polyvinyl chloride (PVC) end plates (1/2 inch thick) between the strongback and flow frames provide the electrolyte flow connections. Belleville washers on the tie bolts ensure that proper tie-bolt tension is maintained during gasket relaxation and thermal expansion or contraction. Five-cell stacks using the new hardware have been sealed with less than 25% of the compressive load required by the previous clamping assembly. The cost of the end hardware in commercial systems has been estimated at 2 to  $3 \/kWh.$ 

#### **End Electrode Design**

The end-electrode current collector at each end of the stack needs to be conductive enough to distribute current evenly from a terminal over the electrode area. The bipolar plate material (a molded carbon/plastic mix) is not sufficiently conductive. Titanium end electrodes have been used because of the stability of titanium in the corrosive electrolyte. However, titanium is too expensive for commercial systems. End-electrode development work was done to produce a low-cost current collector. The feasibility of encapsulating a copper current collector with the carbon/plastic material was investigated. Initial attempts to mold the carbon/plastic mix with a copper insert were not successful because of poor adhesion to the copper. A "primer" coating was developed that, when applied to the copper before molding, produced good adhesion between the two materials. Large samples of the coated copperend electrodes were recently produced. Initial testing will be done in single cells to evaluate current distribution in the prototypes.

### Flow-Frame Design

The flow frames in the battery stack are injection-molded from polyvinyl chloride and provide  $872 \text{ cm}^2$  of active cell area. The frames were designed for 25-cell stacks and have flow-channel configurations that limit shunt currents sufficiently in stacks with up to 60 V total voltage.

A new frame design was developed that allows operation of stacks with up to 100 V total charge voltage. The frame design also provides for an increase in electrode active area up to 1500 cm<sup>2</sup>. Bids are presently being solicited for machined frame prototypes and an injection mold to make the parts. The frames have large electrolyte manifolds to reduce pressure drop in the manifold and ensure good cell-to-cell flow uniformity. Multiple sealing ridges around manifold ports and flow channels provide reliable gasket sealing. Frame-design calculations are described in the next section.

### System Development

### System Modeling

A computer model of the zinc/bromine battery system is being developed. Work conducted this year included the development of a model that estimates pressure drops and pumping power requirements for different flow frame and piping designs. The model also predicts shunt current losses in multi-cell stacks.

The model generated a frame design to replace the present  $872-cm^2$  electrode frames.

Various design configurations were evaluated. In all configurations, the flow channels were designed as long as possible (to reduce shunt currents) and as straight as possible (to reduce pumping power).

A "flow channel" is actually an array of parallel channels, each being 0.254 cm wide by 0.152 cm deep. Several of these channels are used (instead of a single, wider channel) to prevent the separator/gasket from collapsing into the channel. Using more channels reduces pumping power but increases shunt currents. For any given frame design, there is an optimum number of channels where the sum of the shunt current and pumping losses is minimized.

The shunt-current estimation assumed the frames were built into a 52-cell stack, with an average voltage (over a 12-h charge/discharge cycle) of 94 V. The maximum shunt discharge current was calculated by adding up the leakage currents of the individual cells. This maximum current (seen only in the center cells of the stack) was used to calculate the ampere-hour capacity loss over the 12-h cycle. The 83.3-V nominal stack discharge voltage was used to calculate the watt-hour energy loss. This analysis assumes that the capacity loss in the center cells, where the drain is greatest, limits the entire stack on discharge.

Calculations were done for electrode sizes of 1000 to 6000  $cm^2$  active area. The 6000- $cm^2$  electrode frames had about half the energy loss (as a percentage of rated capacity) as the 1000- $cm^2$  frame. This is primarily because the driving force for shunt currents (stack voltage) does not increase with scale-up, while the available channel length (for shunt current reduction) does increase.

It was not desired to scale up the battery hardware significantly at this point. Therefore, an electrode frame size of  $1500 \text{ cm}^2$  was chosen for the next hardware procurement. 52-cell stacks built with these frames will have a rated capacity of 25 kWh, with a shunt current loss of 660 Wh and pumping energy requirement of 560 Wh over a full cycle.

The model is being expanded to include calculations of bulk electrolyte crossover (through the porous separator) and liquid level changes in the electrolyte tanks. The model will then be used in system simulation studies to assist in the development of a system control strategy.



Figure 1-2. Cycle Performance of Five-Cell Stack SNL-5-2

#### **Battery Design and Testing**

Testing was conducted on SNL-5-2, a fivecell stack with 872-cm<sup>2</sup> electrodes and the leafspring stack assembly system. The stack contains the in-house felt electrodes. Figure 1-2 shows coulombic, voltaic, and energy efficiencies for the battery over 118 cycles of testing. Cycles were run with 5-h charges at 0.30 A (172  $mAh/cm^2$ ), followed by a 30-A discharge to a 6.0-V cutoff. After each discharge, an additional 5-A discharge was usually conducted, followed by an open circuit self-discharge of residual zinc. For cycles 20 through 24, this was not done in order to evaluate the need for the stripping procedure. Coulombic efficiency fell to as low as 42%. Battery performance was recovered after resuming the zinc-stripping procedure.

Coulombic efficiency for SNL-5-2 was initially low because of an unusually high hydrogen evolution rate. After cycle 54, the anolyte was filtered through activated carbon filter cartridges. Coulombic efficiency increased to about 87% and remained stable. Testing is continuing on SNL-5-2. Testing has also recently begun on two new stacks, SNL-5-3 and SNL-5-4. Both stacks use the new clamping hardware developed in the program, and stack sealing was achieved with about 25% of the compressive force needed to seal stacks with the leaf-spring hardware. Stack SNL-5-3 is otherwise identical to SNL-5-2. Stack SNL-5-4 uses intratank mixing of catholyte and polybromide, and does not have a polybromide recirculation loop.

#### Material Stability

Material stability studies that evaluate the chemical and electrochemical stability of battery components are underway. Candidate plastic materials of construction (for flow frames, piping, etc.) are being evaluated in immersion tests at both room and elevated temperatures for dimensional and weight stability. The immersion solutions are analyzed for impurities leaching from the plastic and for pH stability. Final material selection has not yet been made, but the studies have narrowed the list of candidate materials to a few preferred grades of PVC. Immersion studies are also being conducted on the carbon-plastic bipolar plate. Dimensional and weight stability for the plate are excellent; however, some strength loss has been observed in electrolyte solutions with excess bromine (100 g/l). The graphite used in the plates has been identified as a source of iron contamination, and purer graphite materials are being evaluated.

A group of  $10-cm^2$  cells is on cycle test to evaluate the electrochemical stability of cell components. Selected cells are removed from the test after a specified number of cycles. The components are then analyzed by optical and electron microscopy, BET surface area, conductivity (bipolar plate), and transport properties (separator). The first set of cells was tested after only 100 cycles, and no significant changes in appearance or properties were observed.

# Zinc/Bromine Battery - JCI

Johnson Controls, Inc. (JCI), has successfully completed its work on the Zinc/Bromine EV Battery Testing and Fabrication Contract (95-0808). The contract involved two major tasks:

- testing of a 30-kWh zinc/bromine battery (Z30-A), and
- fabrication and testing of a 20-kWh lowprofile zinc/bromine battery (Z20-low profile).

Midway through the contract, the scope of the Z20-low profile test program was expanded through a contract extension. At that time, two additional tasks were added: the evaluation of new electrode formulations designed to reduce warpage and the analysis of the performance and ease of application of new activation layers.

The primary objective of the program was to demonstrate the performance capabilities of the zinc/bromine system for EV applications. Secondary objectives included the identification of battery design and/or material problems specific to high-voltage zinc/bromine systems, the testing and analysis of shunt-current protection and thermal-management subsystems to be applied toward subsequent design efforts, and the comparison of the 20- and 30-kWh battery configurations. The achievements of this program are summarized in Table 1-3 and are discussed below.

# Battery Testing

# Z30-A

Battery Z30-A consisted of two 124-cell stacks (190 V) connected in parallel. Z30-A had previously been built and tested at Exxon Research and Engineering Company (ER&E), with additional testing at Ford Motor Company. Testing at Ford included Federal Urban Driving Schedule (FUDS) cycling using the Ford Electric Transaxle Experimental Test (ETX-I) vehicle on a dynamometer with the battery off-board. Before its arrival at JCI, Z30-A had completed 94 cycles and had been disassembled and shipped between test locations twice.

JCI conducted power tests, constant current discharge tests, and shutdown/stand-loss tests. Significant declines in both capacity and power performance from previous tests were observed. One cell group exhibited a high charge voltage and an early drop in discharge voltage, which is indicative of poor electrolyte flow, most likely the result of adhesive blockage in the electrolyte channels.

Continuing declines in performance and increasing problems with electrolyte leakage led to the teardown of Z30-A after 108 cycles. The observed capacity decline was traced to adhesive blockage and electrode warpage, both of which disrupted the uniformity of electrolyte flow distribution and caused dendritic zinc shorting. The decline in power performance was attributed to blistering of the carbon-paper activation layer, degradation of those layers that did not blister, and severe corrosion of the exposed terminal electrode screens. Physical properties of representative polymeric samples from all battery components were carefully analyzed for degradation. Although declines in molecular weights, tensile strength, and other physical properties were observed, no related operating failures, for example, embrittlement or cracking, were observed.

The results of the Z30-A testing and teardown confirmed the direction for subsequent

# Table 1–3. Zinc/Bromine Technology Progress – JCI

<b>Battery Testing</b>		
Z30-A	Testing terminated after 108 cycles because of poor performance.	
	Capacity decline traced to adhesive blockage and electrode warpage; power-performance decline attributed to blistering of carbon-paper activation layer and electrode-screen corrosion. No failures in polymeric materials.	
Z20-Low Profile	Typical efficiencies (3-h discharge rate): 72% coulombic, 81% voltaic, and 58% energy; testing discontinued after cycle 76 because of direct short from electrolyte leak and dendritic zinc shorting.	
	Peak power declined rapidly as battery discharged.	
	Tests on efficiency versus discharge rate show need for a well-designed thermal-management subsystem.	
	Extremely low voltages during discharges following open-circuit stand periods not satisfactorily explained.	
Comparison of Z30-A and Z20-Low Profile	Z20 attained slightly higher efficiency because of reduced shunt-current losses.	
	Z30-A peak power does not drop off as rapidly as that of Z20 does.	
Electrode Development		
Analysis of Electrode Formulations	Two HDPE-based carbon-plastic electrode formulations demonstrate excellent conductivity and warpage resistance.	
Heat Pressing of Carbon Cloths	Procedure perfected for heat pressing carbon cloths into HDPE substrate.	

zinc/bromine research and development efforts at JCI. The test period provided an important transition from working with smaller laboratory-scale batteries (1 kWh) to large application-specific battery systems. The experience proved to be a great advantage during the subsequent assembly and testing of Z20-low profile.

### Z20-Low Profile

The Z20-low profile battery consisted of two 78-cell stacks (120 V) connected in parallel. Most of the components for the system were provided by SNL through ER&E and were of the same two-piece Z design as those belonging to Z30-A. Since part of the purpose of the Z20 test was to provide a comparison of the lower-voltage Z20 versus the higher-voltage Z30-A configurations, efforts were made to keep the two systems as similar as possible. However, based on the Z30-A experience, several minor design changes were made in areas that were expected to eliminate reliability problems without biasing the performance comparison.

Z20-low profile was assembled at JCI. Initial problems were encountered with high cross-flow within the adhesive-sealed battery stacks, but these problems were overcome. The stacks were free of external leaks and had normal cross-flow when testing was initiated.

Testing of Z20-low profile at the 3-h discharge rate resulted in typical efficiencies of 72% coulombic, 81% voltaic, and 58% energy.

Figure 1-3 displays a history of the efficiencies for 3-h rate discharges.

Peak-power tests were performed at depths of discharge (DOD) ranging from 0% to 80%. The peak power is calculated as the power at the end of a 30-s pulse for which the pulse current is set to cause the battery voltage to equal 2/3 of the open circuit voltage.

Figure 1-4 displays the results of two sets of power tests. The peak power was very good at 0% DOD, but it declined rapidly as the battery was discharged. A slight decline in power performance was also observed with cycle life. Although these factors raise some concerns about the performance of the carbon-paper activation layer, several uncontrolled factors related to the treatment of those layers prior to the assembly of Z20-low profile may have contributed to their poor performance.

Table 1-4 compares the efficiencies for discharge rates ranging from one to five hours. As expected, reduced bromine diffusion and shunt current losses improve coulombic efficiency as the discharge rate is increased, while higher internal resistance (IR) losses decrease voltaic efficiency as the discharge rate is increased. The drop in coulombic efficiency for the 1-h rate discharge can be attributed to a corresponding rise in electrolyte temperature caused by the higher discharge rate. The higher temperature increased the rate of bromine diffusion across the separator. This result



Figure 1-3. Efficiency versus Cycle Number for Z20 at 3-h Rate

emphasizes the need for a well-designed, thermal-management subsystem for the zinc/bromine battery.

# Table 1–4. Effect of Discharge Rate onZ20 Efficiency

		Efficiency (%)			
_	Rate	Coulombic	Voltaic	Energy	
5	hour (27 A)	68.3	85.6	58.1	
3	hour (45 A)	71.6	81.4	58.2	
1	hour (135 A)*	66.3	74.1	49.1	

\*Electrolyte temperature rose to 40°C

An unanticipated issue was encountered during shutdown/stand-loss tests. Extremely low voltages were observed during discharges following open-circuit stand periods. Extensive tests were performed to attempt to trace the source of the voltage decline. Simple explanations such as gas entrapment in the stacks and poor electrolyte flow were quickly eliminated. Keeping the stacks flooded during the stand and



Figure 1-4. Z20-Low Profile Power Tests

flushing the excess second phase out of the stacks prior to the stand recouped normal discharge behavior. Several mechanisms for the observed behavior have been postulated, but none of them satisfactorily explains all the observations.

A small electrolyte leak that dripped onto the terminal connection of one stack, coupled with a defect in the insulative coating on an assembly bolt, led to a direct short that caused the failure of one of the two battery stacks after 74 cycles. Although testing was continued with the second stack, it failed during cycle 76. Subsequent teardown of the second stack traced the cause of failure to dendritic zinc shorting caused by the poor electrolyte distribution that resulted from electrode warpage.

#### Comparison of Z30-A and Z20-Low Profile

Figure 1-5 compares the energy-efficiency histories for Z30-A and Z20-low profile. The slightly higher efficiencies attained with Z20 can be attributed to reduced shunt current losses for the lower-voltage Z20 stacks. Figure 1-6 provides a comparison of the initial peak power behaviors for Z30-A at ER&E and Z20-low profile at JCI. The Z30-A data are normalized to a 20-kWh basis to provide a fair comparison. The Z30-A peak power does not drop off as rapidly as that of Z20 although both batteries used carbon-paper activation layers.

The results of the configuration comparison do not suggest the superiority of one configuration over the other with regard to the zinc/bromine system in general. The Z design was originally optimized for the 78-cell (Z20) configuration, thus it would be expected to provide better overall performance in its intended configuration. However, component design changes can readily be made to optimize the system for higher- or lower-voltage configurations.

### **Electrode Development**

#### Analysis of Electrode Formulations

Results of the analysis of two new carbonplastic electrode formulations are presented in Table 1-5. These formulations were intended as a check of the reproducibility of previous high-



Figure 1-5. Efficiency versus Cycle Number for Z20 and Z30-A at 3-h Rate



Figure 1-6. Power Comparison of Z30-A and Z20

Identification		Composition Specified (%) Actual (%)		Four-Point Resistivity (Ω•cm)				
100091W*	· .							
	HDPE Ketjenblack Glass	62 16 22	59.68 17.24 23.08	1.45				
100090W*	<b>i</b> .							
	HDPE Ketjenblack Glass	64 17 20	63.72 16.28 19	1.74				
*Electrode expansion (in bromine vapor):								
100091W 100090W	- 1.96% - 2.5%	÷ · ·						

# Table 1–5. HDPE–Based Electrode Samples

density polyethylene-based (HDPE) materials that had displayed good physical properties. Both materials demonstrated excellent conductivity and warpage resistance as compared to the present electrode materials that have typical resistivities between 5  $\Omega$ ·cm and 10  $\Omega$ ·cm and expansion of 6% in bromine vapor.

### Heat Pressing of Carbon Cloths

Initial attempts at heat pressing carbon cloths into HDPE backbones yielded bromine electrodes that performed poorly on accelerated polarization tests. These results indicated that the higher pressures required to press the cloths into the HDPE backbone, which was a higher melt viscosity than the polypropylene (PP) backbones used previously, may crush or tear the carbon fibers in the cloths. Subsequent attempts that used a lower pressure and higher temperature for the press step yielded results equivalent to those obtained with PP. Little degradation in the performance of these electrodes was observed after 500 cycles at current densities of up to 100  $mA/cm^2$ .

### Conclusions

The Z30-A and Z20-low profile test programs provided encouraging results regarding the potential use of the zinc/bromine battery in EV applications. The efforts also helped identify and clarify several design issues that require further attention. The program has helped provide direction for the zinc/bromine research and development efforts being pursued at JCI.

Stack sealing and electrode warpage will continue to be the main areas of focus for these efforts. Development of improved cathode activation layers, electrolytes, and separators will also be approached as critical issues. An improved understanding of battery behavior during and after extended open-circuit stand periods should be pursued, and variations of the operational procedures during these stand periods need to be considered. Data generated from the Z30-A and Z20 shunt-current-protection and thermal-management subsystems can be used to develop new subsystem designs that provide performance and reliability improvements.

In summary, the program was successful both in demonstrating the potential for zinc/bromine batteries in EV applications and in providing additional insight into the issues that must still be overcome in order to develop the zinc/bromine system to the level of performance that will be required for commercialization. The experience gained through the program has helped to clarify the direction of subsequent development efforts at JCI and is expected to provide a significant advantage in the new design efforts being pursued under the zinc/bromine EV development program that was recently awarded to JCI through Sandia National Laboratories.

# Nickel/Hydrogen Battery - COMSAT/JCI

Work continued at Communications Satellite Corporation (COMSAT) Laboratories and Johnson Controls, Inc. (JCI), to develop a sealed, nickel/hydrogen battery for deep-discharge, terrestrial applications. The technical effort on Contract 51-5767 was completed in September 1986 and battery 4, the final deliverable on the contract, was received at Sandia during October 1986. A final report on this effort was printed in early 1987 as SAND87-7061 (Dunlop, J. D., W. O. Gentry, et al., Design and Development of a Multi-Kilowatt Hour Hydrogen/Nickel Oxide Battery).

Research was performed to find ways to reduce the cost of the nickel/hydrogen battery system without unduly sacrificing performance. Major cost-reduction contributions were the development of a 70-mil thick positive (nickel) electrode, reduction of the materials cost for negative electrodes, and the reduction of fabrication costs for positive electrodes. In addition, a cost study was completed on a 15-kWh nickel/hydrogen battery design. Progress in nickel/hydrogen technology by COMSAT and JCI is summarized in Table 1-6 and is discussed below. Evaluation results on the nickel/hydrogen technology are discussed in Chapter 3 (Nickel/Hydrogen Testing at SNL).

# **Component Cost-Reduction Studies**

#### 70-Mil Positive Electrode

The most important contribution to cost reduction was the development of a 70-mil-thick positive electrode that performs well. Previously, 32-mil-thick positive electrodes were used. With 70-mil-thick positive electrodes, seven cell modules are used instead of the 10.5 used with the 32-mil-thick positive electrodes. The new design requires one-third fewer negative electrodes, screens, and separators. Furthermore, the capacity (Ah) and energy density (Wh/cm<sup>3</sup>) is 45% greater.

### **Reuse of KOH for Positive Electrode**

Experimental studies on the reuse of KOH showed that:

- The reuse of KOH does not impair cycle capacity.
- An electrochemical reduction step can replace the formation and characterization steps.
- Electrochemical reduction can be used with lithiated electrodes.

These findings are discussed in detail below.

Currently, the potassium hydroxide solution for forming and characterizing the positive electrodes is used once and then discarded. Therefore, reuse of the solution was evaluated. Electrochemical reduction was found satisfactory for removing nitrates from an electrode. It was also found that there was no capacity reduction with reused KOH if the reduction process was employed.

To determine whether costs could be further reduced by substituting the reduction process for the entire formation-characterization step, a 2 X 3 ANOVA (analysis of variance) experiment

# Table 1-6. Nickel/Hydrogen Technology Progress - COMSAT/JCI

#### Component Cost Reduction Studies

70-mil Positive Electrode	70-mil positive electrode developed that requires one-third fewer components than the 32-mil electrode. Seven-cell modules instead of 10.5 in same size case, yielding a 45% increase in energy density.		
Reuse of KOH for Positive Electrode	Studies show that KOH can be reused without impairing cycle capacity.		
	Studies show that electrochemical reduction can replace the formation and characterization steps and can be used with lithiated electrodes.		
Negative Electrode	Two experimental cells fabricated without Gore-Tex wet-proofing laye which represents 25% of the negative-electrode materials cost.		
Experimental Cells			
	Cells were built to test 70-mil positive electrode, negative electrode without Gore-Tex backing, and use of KOH and LiOH in the electrolyte.		
	Initial performance of non-Gore-Tex cells comparable to Gore-Tex cells.		
Design of Battery 4			
	Common-pressure-vessel-with-individual-cells approach selected for battery 4 because of ICPV design flexibility, design simplicity, and improved heat transfer.		
	Initial performance fully meets expectations.		
Multi-kWh Battery Cost Study			
	Cost study of a 15-kWh battery (based on May 1986 technology) shows costs at lowest production level are 15% less than those of the 1984 benchmark study.		
	A \$235/battery cost reduction realized by changing from pure nickel to a nickel-coated steel screen and by streamlining plaque preparation.		

was designed. The data show that this substitution is possible.

In parallel with these reduction studies, experiments on the effect of lithium hydroxide in the electrolyte on cell performance were in progress. It was decided to determine if there was any interaction between the reduction process and lithiated electrodes. A second 2 X 3 ANOVA experiment was designed to check three lithium oxide levels in two categories: reduced and unreduced (characterized) electrodes. The resulting capacity measurements and coulombic and energy efficiencies showed no statistical difference between the two types of electrodes.

#### **Negative Electrode**

The negative electrode is multilayered: the front face is the teflonated catalyst (platinum supported on carbon); the center a currentcollecting grid; and the back a microporous wetproofing layer (Gore-Tex). The hydrogen reaction on the front face constitutes a threephase interface of gas, electrolyte, and solid catalyst sites. This electrode is fabricated by rollcompacting a mixture of the supported carbonplatinum catalyst, Teflon powder, and a bulking agent to produce a very thin catalyst film. This film is subsequently laminated to one side of the current-collecting grid. The Gore-Tex layer is laminated to the opposite face.

Removal of the Gore-Tex wetproofing layer was studied since it accounts for 25% of the materials cost in the negative electrode. No effect on electrode performance was anticipated from removing the Gore-Tex layer. Two experimental cells (20 and 22) were fabricated without a Gore-Tex backing on the negative electrodes. Initial performance for these cells was comparable to that of the cells having Gore-Tex backing. However, SNL testing has shown the capacity of cells 20 and 22 has declined somewhat (Nickel/Hydrogen Testing at SNL, Chapter 3). These two cells were delivered to SNL and are now being evaluated.

### **Experimental Cells**

New cell components and design changes were evaluated in experimental cells (Table 1-7). The top objective in testing these cells was to show that the 70-mil-thick positive electrode could meet performance expectations. The next objective was to reduce material cost for the negative electrode by eliminating the Teflon wetproof backing and by implementing the lowercost electroformed current-collecting grid. The combination of these two changes significantly

# Table 1–7. Design Variables of Experimental Nickel/Hydrogen Cells

	Positive		24	Cell Design*					
<u>S/N</u>	Electrode Thickness (mil)	<u>Negative</u> Gore-Tex	Electrode Substrate	Number of Modules	Reser- voir	Flat Bottom	KOH (molar)	Electrolyte LiOH (molar)	Vol. (cc)
17	32	N	screen	10.5	Y	N	9.8	0	250
18	70	Y	electro- formed	7	Ν	Y	9.3	1.0	300
19	70	Y	electro- formed	7	Ν	Y	9.3	0	300
20	70	N	electro- formed	7	Ν	Y	9.3	1.0	300
21	70	Ν	electro- formed	6	Y	Ν	9.3	1.0	300
22	70	Ν	electro- formed	7	Ν	Y	9.3	1.0	300
23	70	Y	electro- formed	7	N	Y	7.9	1.0	300

\* All cells are back-to-back with a screen between positives and with the peripheral seal around each module. Separators are asbestos except for S/N 21, which uses two KT layers.

reduced the cost of negative electrode materials. Cell design changes included the peripheral seal construction and the elimination of the reservoir.

Figure 1-7 shows an assembled cell with the following key features:

- The outside dimensions of the polypropylene container are 14 cm wide, 19 cm high, and 6 cm deep. The container wall thickness is 0.2 cm. This container makes up one section of a standard sixcell, injection-molded, lead-acid battery container that has mud wells that create additional volume for use as an electrolyte reservoir.
- The cover of the cell is heat-sealed to the case, and a gas-permeable plug is provided for hydrogen flow into and out of the cell.

• Threaded negative and positive stainlesssteel terminal posts are used with stainlesssteel hex nuts.

Figure 1-8 shows the electrode stack components used to make up one module in this back-to-back design. Two positive and two negative electrodes, along with the two asbestos separators, make up one module. The module, referred to as peripheral-seal design, is held together by two gas screens that are heat-sealed around the periphery of the electrodes. With the thick (70-mil) positive electrodes, seven of these modules are used to make one cell compared to the 10-1/2 modules needed for cells with the thinner (32-mil) positive electrodes. The completed cell is then assembled into a boilerplate pressure vessel. The individual cells are discussed below.



Figure 1-7. Experimental Cell

Cell 17 was constructed without the Gore-Tex backing on the negative electrode. Otherwise, it is similar to cells 15 and 16, the last two cells delivered to SNL under the previous contract.

Cells 18 and 23 were similar, providing a baseline design for SNL evaluation. Cell 18 was constructed with thick positive electrodes formed in KOH with lithium additive. In addition, this cell incorporates the peripheral seal concept with a flat bottom case. This cell was activated with electrolyte containing lithium hydroxide. Cell 23 was activated with electrolyte containing 7.9 Molar KOH + 1 Molar LiOH, representing a reduction in KOH concentration from 9.3M KOH used previously.

Cell 19 was constructed with thick positive electrodes formed in KOH with lithium additive and activated with 9.3M KOH electrolyte without lithium additive. Except for the lack of lithium in the electrolyte, this cell was identical to cell 18.

Cells 20 and 22 have negative electrodes without the Gore-Tex backing. Except for the



Figure 1-8. Electrode Stack Components

lack of Gore-Tex, these cells were identical to cell 18.

Cell 21 was constructed the same as cells 20 and 22 except that it has the new W. R. Grace potassium titanate material for separators. The nonuniformity in the thickness requires the use of a double layer to avoid shorting through thin areas. Because of the additional separator thickness, only six modules could be fit into the cell case. Since cell 21 does not represent the preferred design of seven modules with a single layer of separator, it was recommended that cell 21 not be delivered to SNL and that delivery of a potassium titanate cell should await the more uniform separator product anticipated from a pilot run of the material.

The performance of the cells built with the thick positive electrodes has been very encouraging. This improved performance of the thicker electrodes is particularly evident when compared to the performance of cell 17 with the thinner electrodes. With the thicker electrode, the volume of the positive electrode in the cell is increased by 42% and has been accompanied by a 39% increase in capacity to 1.0 V. Therefore, all of the increase in active material within the electrode is being utilized.

### **Design of Battery 4**

At the Third Quarter Design Review at SNL held on February 6, 1986, a decision was made to use the individual-cells-within-a-commonpressure-vessel (ICPV) design approach for building battery 4. This constituted a major design change from the previous baseline design, which was a six-cell monoblock with the through-the-partition weld. There are many advantages to this new ICPV design approach, particularly the ability to select system designs of 6, 12, or 24 V as well as better heat transfer from the cell case to the pressure-vessel wall.

Other advantages include simplicity of design and flexibility. The battery becomes a number of individual cells contained within one pressure vessel, the individual cells can be connected in series or parallel, and bypass protection of individual cells is provided, if desired. The building block for this system becomes an individual cell rather than a six-cell monoblock.

The baseline cell design of cell 23 was selected for this battery. A 145-Ah, five-cell battery was assembled, as shown in Figure 1-9. The cells were spaced about 1/2 inch apart with corrugated metal spacers placed between to prevent bulging of the cell cases and also to allow intercell cooling by means of free convective heat transfer. This assembly of five cells, corrugated spacers, and end plates was bound together with two nylon straps. The battery was mounted on a 3/32-inch brass cold plate with copper water tubing soldered to its underside. The plate has perforations that line up with the corrugated spacers to allow convection currents to flow up through it. A rectangular frame fits over the top of the battery and bolts it to the cold plate.

The cold plate was mounted into the vessel using the same technique proposed for the multikilowatt-hour vessel design discussed below. The battery was completely assembled on the cold plate and the plate then slid into the vessel on rails, providing an opportunity to test this assembly concept. The assembly was instrumented with 12 thermocouples to generate sufficient data on the temperature distribution throughout the five-cell battery pack so that the thermal model could be verified with this new design approach.

Electrolyte was added to battery 4, and it was then assembled into a pressure vessel. After the initial vented cycle, the pressure vessel was sealed, and standard capacity cycles (charge at 12.5 A for 16 hours, discharge at 25 A, coolant fluid at 10°C) were performed. The measured capacity was 140 Ah to 5 V (1 V per cell), which is quite good and fully meets expectation. Battery 4 has been delivered to SNL for life-cycle testing and evaluation.

# Multi-kWh Battery Cost Study

The objectives of the cost study on the nickel/hydrogen battery are to

- determine if the cost goal of \$375 kWh for a multi-kilowatt hour nickel/hydrogen battery can be achieved,
- identify areas that, because of their cost implications, warrant further development, and
- provide benchmarks against which later studies can be measured.



The design of the battery and its fabrication were fixed by the state-of-the-art of nickel/hydrogen technology as of May 1986. As a consequence, this cost study does not reflect the individual cell concept. The design was based on conservative engineering judgment of the lowest cost permutation of the developments available that would not significantly degrade the performance of the resulting product.

The multi-kilowatt-hour battery system selected for this study is nominally rated at 15 kWh. It consists of a single boiler-plate pressure vessel designed to operate with a hydrogen atmosphere cycling between 50 and 230 psig. Inside the pressure vessel are 15 series-connected battery modules. Each battery module contains six series-connected cells in a lead-acid battery case. The cells are joined by means of a Ushaped intercell connector. The positive electrodes are 70-mil-thick, sintered nickel plaque on a nickel-plated iron screen. The plaque is electrochemically impregnated with cadmiumdoped nickel hydroxide. The negative electrodes are Teflon-bonded, platinized carbon on an electroformed nickel screen. There is no wetproof backing. The separators are a proprietary, asbestos-free, inorganic material. The electrolyte proposed for use is 25 wt % potassium hydroxide in a 1N lithium hydroxide solution.

Costs of the 15-kWh battery (in dollars per kilowatt hour) were determined for production levels of 72, 270, and 1,024 units per year, fixed by the rates of three different bottleneck processes in the manufacturing. The results of the 1986 cost study update are shown in Figure 1-10, along with the previous 1984 benchmark study. As a result of the past two years of research and development, the cost at the lowest production level has been reduced 15%, to \$1,451/kWh.

Cost reductions were made possible by:

- The change from the pure nickel substrate used in the 1984 battery to a nickel-coated steel screen.
- Streamlining plaque preparation by reducing the aging time of the slurry from overnight to four hours. (This, combined with the change to a nickel-coated steel screen, reduced the cost of nickel plaque in the positive electrodes by \$235 per battery.)
- Using an electrochemical reduction step to clean the impregnated electrode of entrained nitrates. (This achieved a significant reduction of nickel electrode cost.)
- Reducing the width of the nickel electrode tabs. (This achieved an additional small saving.)



Figure 1-10. Consumer Cost of 15-kWh Battery (1986 Costs)

# Nickel/Hydrogen Battery - JCI

In September 1986, the prime-contract responsibility for nickel/hydrogen battery development became Johnson Controls' (JCI). The goal for the next eighteen months is to assemble a 24-V, 7-kWh nickel/hydrogen battery for testing and evaluation at Sandia. To do that, JCI's Advanced Battery Business Unit plans to:

- conduct a statistically designed Analysis of Variance, or ANOVA, experiment to confirm that four component and process variables developed earlier in the program can be used in commercial terrestrial batteries without degradation of the properties found so attractive in aerospace cells;
- update the model for thermal management of the nickel/hydrogen battery for use in designing terrestrial batteries without active cooling;
- assemble a five-cell battery to verify the results of the ANOVA experiment and to test the thermal model on a scale closer to that of the final battery; and
- continue the research and development of low-cost components and processes for manufacturing terrestrial nickel/hydrogen batteries that will be cost competitive with lead-acid batteries in long-term energy storage applications.

In the first four months of this effort, JCI has begun the ANOVA experiment, continued its research on the components of the battery, and delivered an experimental cell for testing at Sandia National Laboratories. Progress in 1986 is summarized in Table 1-8 and is discussed in detail below.

### **Component and Process Variables**

The four variables (and their interactions) that are to be evaluated in the statistically designed experiment are the concentration of the potassium hydroxide in the electrolyte, the number of modules per battery cell, the form of the gas-diffusion screen between the negative electrodes, and the design of the electrolyte reservoir and associated cell details. Developments in each of these four areas have shown a pronounced effect on the cost of the nickel/hydrogen battery.

The electrolyte concentration will be varied in the experiment over a very wide range: 16% to 40% KOH. The other three variables will each be evaluated at two levels. A total of 16 full-sized cells will be tested.

The test parameters are the electrochemical efficiencies of the cells over approximately 200 twice-a-day cycles. The test regimes being followed are discharges to 1.00 V at rates of C/3 to C/6, followed to recharging to 80% or 100% of theoretical capacity at the same rates.

Preliminary data from the experiment indicate that the performance of the terrestrial battery will not be degraded by using the lessexpensive elements.

# **Experimental Cell**

The experimental cell delivered to Sandia contained a number of innovative design modifications. First, the number of modules in the cell was increased from seven to nine by using a larger cell case, which increased the cell capacity 40 Ah. Second, to improve the electrolyte management within the cell, the reservoir volume was increased by removing the gas diffusion screen between the positive electrodes and replacing it with an absorptive material. Gas diffusion was ensured by slightly grooving the back-to-back nickel electrodes. Third, the negative electrodes were prepared by a low-cost, proprietary process. Fourth, the form of the gas diffusion screen between the negative electrodes was changed. Finally, the electrolyte was modified by reducing the KOH concentration and incorporating an additive to improve the cell's performance at higher temperatures, a well-known shortcoming of the nickel/hvdrogen battery.

Each of these modifications had been investigated previously in sub-size cells and then, in more detail, in full-size cells in order to demonstrate their potential.

Figure 1-11 shows the behavior of the cell C144 during the preliminary cycle testing at an ambient temperature of 30°C done at JCI. In

# Table 1-8. Nickel/Hydrogen Technology Progress - JCI

Component and Process Variables

Four design parameters targeted for statistical evaluation: KOH in the<br/>electrolyte, number of modules per cell, form of negative-electrode gas<br/>diffusion screen, and electrolyte reservoir design.Experimental CellExperimental cell, incorporating cost-reduction design, shows no<br/>degradation of efficiencies or loss of capacity during preliminary cycling.Cost ReductionsPlatinum loadings on negative electrode reduced from 8.0 mg/cm² to 0.60<br/>mg/cm².Sintering negative electrode reduces required platinum loading by a factor

of three.

Presently, nickel/hydrogen battery costs are estimated to be \$930/kWh (commercial quantities); \$375/kWh considered an attainable goal.



Figure 1-11. Cell C144 Capacity and Efficiency During Preliminary Cycling

contrast to earlier cells tested at this temperature, the performance of this cell showed no degradation of the efficiencies or loss of the capacity with cycling.

Figure 1-12 shows the earlier experimental cell geometry, the white cell (the new geometry), and the boiler-plate pressure vessel the cells are tested in.



Figure 1-12. Earlier Experimental Cell, White Experimental Cell, and Pressure Vessel

### **Cost Reductions**

One of the obviously high-priced materials in the nickel/hydrogen battery is the platinum catalyst in the negative electrode. To reduce that cost, it first was necessary to develop a laboratory test that would predict the electrochemical behavior of the electrodes at discharge rates expected in a terrestrial application. The test adopted was a measurement of the polarization resistance of a miniature electrode. Results showed that a polarization resistance of 6  $\Omega \cdot cm^2$  or less would lead to a well-functioning electrode. In an attempt to reduce the platinum cost, platinum-black was replaced with a commercially available platinum-on-carbon catalyst. The performance of electrodes with 0.45 mg/cm<sup>2</sup> of this material proved to be essentially the same as that of electrodes with 8.0 mg/cm<sup>2</sup> of platinumblack. Based on this finding, a loading of 0.60 mg/cm<sup>2</sup> for the negatives in the early cells and batteries was used.

A simple sintering operation on the electrode was found to significantly improve performance. As the data on Figure 1-13 show, the platinum loading on a sintered electrode can be reduced by a factor of three and yet have the same polarization resistance as a standard (nonsintered) negative electrode.

Over the life of this project, the cost of a terrestrial nickel/hydrogen battery has steadily and progressively decreased. As the research, development, and engineering efforts continue, the cost reductions should also continue. Today the battery could be made available, if manufactured in commercial quantities, at a price of \$930/kWh--a cost that on a life-cycle basis is competitive in long-life applications with lead-acid batteries. The programmatic goal JCI has set for itself, \$375/kWh, is challenging but not unreachable.

# Zinc/Redox Battery - Lockheed

Development of the zinc/redox battery was initiated in 1977 by scientists at Lockheed Missiles and Space Company (LMSC). The battery's technology is based on solid storage of both charged and discharged active materials. On charge, zinc is electrodeposited on the negative electrode; on discharge, it is stored as sodium zincate. The active positive electrode materials (sodium ferrocyanide and ferricyanide) are stored as precipitates. Storage of solids results in a compact but more complex process compared to other flow battery systems. The open circuit voltage of a zinc/redox cell is 1.74 V. The working voltage at 35 mA/cm<sup>2</sup> is approximately 1.6 V. This battery system is intended for bulk electrical energy storage applications. The system features good electrical efficiency, relatively high cell voltage, near-ambient temperature operation, low toxicity with biodegradable reactants, and potentially long cycle life.

A major advantage of this technology over many of the other advanced batteries may be related to the low toxicity of the reactants and products. An important consideration for any large battery system is the impact that a major spill of electrolyte would have upon the environment. The zinc/redox battery contains 20% sodium hydroxide (the only toxic component), zinc oxide, sodium ferrocyanide, and sodium ferricyanide. These latter three chemicals are all biodegradable, which means that with dilution of the sodium hydroxide, disposal within the community sewer system is possible. Safety requirements for the employee are projected as being similar to those for a normal chemical laboratory. Furthermore, because toxic gases or fumes are not generated, plant ventilation will not be required.

The results obtained during the Phase V development contract are briefly presented in this section. These results are summarized in Table 1-9. This contract funded a portion of the Lockheed activities from 1 November 1985 to 31 January 1987 that specifically involved characterizing the performance of low-cost membranes, identifying the key zinc-electrode parameters that affect half-cell performance, developing a suitable composite bipolar-electrode material, and continuing cell performance modeling studies. These particular activities were identified at the end of the Phase IV contract as being prerequisites for a multicell development effort.

## Membrane Studies

The performance in single cells of several low-cost membrane materials is very encouraging. RAI Research Corp. was contracted through SNL to formulate a matrix of 22 different membrane formulations utilizing styrene and alpha-methylstyrene grafts upon base films of PTFE and PFA (polytetrafluoroethylene and perfluoroacrylate). In addition, Springborn Labs was also contracted to formulate several sulfonated polysulfone (SPS) membranes (see Chapter 4, Membrane Development for Zinc/Redox Batteries).



Figure 1-13. Polarization Performance of Catalyst BD5087 Negative Electrodes (Standard and Sintered) versus Platinum Loading
#### Table 1–9. Zinc/Redox Technology Progress – Lockheed

Membrane Studies	
	Two membranes composed of an alpha-methylstyrene graft upon a PTFE base film have logged over 700 cycles with energy efficiencies above 80%; projected cost is \$5-7/ft <sup>2</sup> , versus \$28/ft <sup>2</sup> for Nafion membranes.
	Testing initiated on SPS membranes (lower in cost than alpha- methylstyrene/PTFE membranes).
Bipolar Electrode Development	
	Nickel-containing substrates in zinc electrode shown to reduce coulombic efficiency.
	Problems with electrodeposition of zinc onto plastic electrode not overcome; further studies needed to define the cadmium-coating process.
	Cost studies proposed for an alternative iron bipolar electrode coated with nickel on the redox side and cadmium on the zinc side.
Cell and System Modeling	
	Saturation concentration of ferrocyanide shown to be strongly dependent upon the concentration of ferricyanide.
	The cell-performance model developed during Phase IV enhanced; good agreement with experimental charge/discharge data.

The membranes selected by Lockheed for continued studies are both based upon alphamethylstyrene. RAI membrane 1164-259-125 is a 35% alpha-methylstyrene graft upon a PTFE base film. This membrane is currently still functioning adequately in a cell that has logged 754 consecutive 70-mAh/cm<sup>2</sup> cycles. Results obtained included a mean energy efficiency of 82.6  $\pm$ 4.4%, a voltaic efficiency of 88.8  $\pm$  1.0% and coulombic efficiency of 93.0  $\pm$  4.6%. A similar 40% alpha-methylstyrene graft, RAI 1164-259-16, currently has 711 consecutive cycles. Its efficiency results are also very good, with a mean energy efficiency of  $83.0 \pm 3.1\%$ , a mean voltaic efficiency of  $88.9 \pm 1.0\%$ , and a coulombic efficiency of  $93.4 \pm 3.5\%$ . Life-cvcle testing of cells with these membranes is continuing. The projected costs of these membranes is  $5-\frac{7}{ft^2}$ . This compares with the baseline Nafion membranes costing \$28/ft<sup>2</sup>, a very significant and needed cost reduction.

Because the projected cost of the RAI materials may still be too high, the performance of the intrinsically very inexpensive sulfonated polysulfone materials is still being investigated. However, the membranes made on a laboratory scale at SNL have been subject to pinhole defects. Testing of the SPS membranes manufactured by Springborn was started just as the contract expired, and results are therefore not yet available.

#### **Bipolar-Electrode Development**

The identification of a suitable bipolar electrode material is very critical to the eventual design and construction of a cost-effective multicell battery stack. Because of cost considerations, it would be preferable to base this electrode on a conductive plastic. However, in order to better understand the plating process, a study was first completed to determine the key parameters affecting zinc deposition on metal electrodes. Zinc electrode half-cell coulombic efficiency was shown to be highly dependent upon substrate composition. Steel type 4130, with low chromium and nickel content, yields zinc coulombic efficiencies ranging between 93% and 96%. Stainless steel alloy 301, containing 7% nickel and 17% chromium, yields zinc coulombic efficiencies that rapidly decline approximately 10% from the nominal 90% to 95%. The presence of a nickel strike on the stainless steel substrate was identified as the cause of this problem. This finding indicates that nickel-containing substrates should be avoided.

Good results were demonstrated in Phase IV when conductive plastics were used as a redox electrode current collector in contact with a felt electrode. However, extreme difficulties were encountered when zinc was electrodeposited onto plastic electrodes. Studies were performed to identify the key bipolar-electrode parameters by focusing on the cyclic deposition of zinc upon plastic composite electrodes comprised of carbon loaded, graphite-fiber-loaded, or nickel-coated graphite-fiber-loaded ryton, kynar, and polysulfone.

The best results to date were with a 50 wt % loading of graphite fiber in ryton. A cell using this as the zinc substrate could be cycled only 86 times with a low energy efficiency of 72.8  $\pm$  6.7% (using the expensive Nafion N-117 membrane). Failure was because of zinc plugging of cell exit channels, probably from the mossy, nonadherent nature of the zinc formed during deposition.

All of the plastic composites studied to date have been prepared by a simple sanding operation prior to cadmium plating. This procedure may not be sufficient to remove the external plastic barrier formed during thermoprocessing operations. Therefore, further studies are required to define the cadmiumplating process, with the emphasis placed on the preparation of the composite substrate before cadmium plating.

Because problems with plastic electrodes have not been overcome, Lockheed now feels that the suitability of using an iron bipolar-electrode plate that is coated with nickel on the redox side and cadmium on the zinc side should be investigated. The performance of this material may be adequate and is cost competitive.

# **Cell and System Modeling**

The cell and system models developed by Prof. Selman and his associates at the Illinois Institute of Technology have provided valuable data on how a zinc/redox battery operates. Specific accomplishments are summarized in the following paragraphs.

The electrode potential of the redox electrode has been measured in saturated solutions of ferrocyanide in 2N NaOH with varying amounts of ferricyanide. The saturation concentration of ferrocyanide has been shown to depend strongly on the concentration of ferricyanide. Sodium ferricyanide crystals in equilibrium with dry air are in the trihydrate form.

The cell-performance model developed in the Phase IV report has been extended so that it is now capable of predicting cell voltage, temperature, and concentrations in a charge/discharge cycle, in addition to predicting the effects of all design parameters, including flow rates, solid/liquid ratio, and cell and crystallizer dimensions. Although the current distribution along the cell is assumed to be constant, the refined model can be incorporated easily in case the cell performance deviates significantly from selected experimental data because of reactant depletion (for example, at end of charge).

Performance predictions using the cyclingcell model have been compared with selected experimental charge/discharge data. With small adjustments to the equilibrium cell potential, good agreement was achieved. Further work to incorporate hydrogen evolution at the zinc electrode as a source of current inefficiency is necessary. Models for shunt currents in a bipolar battery design have been developed and are ready to be incorporated into an overall battery model.

## **Program Status**

The Phase V final report (R. P. Hollandsworth, et al., Zinc Redox Battery Development Phase V. Lockheed Missiles and Space Company Report, LMSC-F183059, April 1987) contains a comprehensive summary of the status of the zinc/redox technology, its remaining problems, and a brief description of a program Lockheed proposed for the development of a multicell stack module. In addition to the results from technical studies performed under joint DOE/Lockheed sponsorship, this report includes economic and marketing information obtained solely by Lockheed. Copies of the report are available upon request (contact J. W. Braithwaite, Sandia National Laboratories, P. O. Box 5800, Albuquerque, NM 87185).

Although several core technology issues have not been completely resolved at this time (for example, bipolar electrode material, membrane materials, hydrogen recombination technique, solids-handling technique), the development of multicell modules was viewed by DOE and Lockheed as the goal of next contract phase. A critical examination of this technology was performed in late 1986 at SNL that showed the program should be continued if it is desirable to have a nontoxic flow system under development that is an alternative to the zinc/bromine technology. Ultimate performance of the competing flow systems was viewed to be comparable, but life-cycle costs appear to be a major disadvantage of the zinc/redox system. Because of this lack of identifiable technical and economic advantages plus the complete unavailability of funding for such a major development program, the decision was made to discontinue DOE support for the zinc/redox technology at this time.

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# Chapter 2. Nonaqueous Battery Development

# Introduction

The objective of this ETD activity is to support the development of nonaqueous secondary-battery technologies that have the potential to satisfy the requirements of mobile and stationary energy-storage applications. In 1986, this effort focused exclusively on the sodium/sulfur system. Programs were supported through development contracts with industrial participants and another national laboratory. The contracts with the industrial participants were cost-shared.

The following programs were supported in 1986: Sodium/Sulfur Core Technology Development at Chloride Silent Power, Limited (CSPL); Sodium/Sulfur Battery Development at Science Applications International Corporation (SAIC); Beta"-Alumina Electrolyte Development at Ceramatec; and Posttest Analysis of Sodium/Sulfur Cells at Argonne National Laboratory (ANL).

The CSPL program addressed sodium/sulfur core technology development in the areas of electrolyte research and development, materials development and qualification, cell development, cell and module testing, and posttest analysis. The program, which was initiated in September 1985 as a three-year effort, was modified this year to run through August 1989. Stationary battery engineering and testing will be addressed during the final contract year. However, SAIC, under subcontract to CSPL, has begun modeling battery systems.

Through a series of contracts, Ceramatec has developed techniques to improve the properties of beta"-alumina electrolytes. During this past year, a program was initiated to evaluate these improved electrolytes in sodium/sulfur cells. The following electrolytes were fabricated for characterization and in-cell evaluation: Ceramatec's standard zeta process, the seeded slurry solution, spray-dried process, the zirconiatoughened process, and the yttria-stabilized zirconia-toughened process.

ANL conducted posttest analysis on eight sodium/sulfur cells fabricated by Ford Aerospace

& Communications Corporation (FACC). Five cells were electric vehicle (EV) designs, two were stationary designs, and one was a satellite design. Three of the EV cells were removed from the ETX-I sub-battery, which was previously tested by Ford Motor Company under a DOE/Office of Transportation Systems program.

Sodium/sulfur technology continued to make steady progress in 1986. High-quality beta"-alumina electrolytes were produced using a variety of cost-competitive starting materials and process techniques. Full-size electrolytes incorporating zirconia toughening were produced and evaluated in sodium/sulfur cells. CSPL also demonstrated improved cell reliability by accumulating over 76,000 cycles on 204 PB cells with no failures.

# Sodium/Sulfur Battery Development - CSPL

This program, sponsored by the Department of Energy (DOE), commenced on 16 September 1985 at Chloride Silent Power, Limited, Runcorn, England. The Core Technology and Battery Engineering Program was intended to be parallel to a program sponsored by the Electric Power Research Institute (EPRI). The EPRI contract, to develop and construct a 500-kWh sodium/sulfur battery for the Battery Energy Storage Test Facility (BEST) facility commenced in December 1985, but was substantially reduced in content on 14 February 1986. Plans to construct a 500-kWh battery were deferred.

At the request of the Sandia National Laboratories the Core Technology and Battery Engineering Program was extended by one year to reduce the annual program costs. This was achieved by deferring the construction of the main contract deliverable, a 100-cell battery, into a fourth year, while maintaining the three-year time frame for the Core Technology Task 1 activities. The objective of the program is to advance the state of the art of sodium/sulfur technology in components, cells, and small batteries. The program is divided into two tasks:

- Task 1 Core Technology Research and Development
- Task 2 Battery Engineering and Testing

Task 1 is devoted to research and development in the areas generic to both stationary and electric-vehicle applications of sodium/sulfur batteries. Major emphases of the program are performance, reliability, safety, and cost.

The following subtasks are part of Task 1:

- Subtask 1.1 Electrolyte Research and Development
- Subtask 1.2 Materials Development and Qualification
- Subtask 1.3 Cell Development
- Subtask 1.4 Cell Testing and Posttest Analysis (Results are discussed under Subtasks 1.3 and 1.5.)
- Subtask 1.5 Module Development and Testing

Work on the Task 2 effort, design and building of batteries for stationary applications, was not due to commence during the first year of the contract. However, Science Applications International Corporation, under subcontract, modeled battery systems and the effect of cell design on system behavior. This work is discussed later in this report (Sodium/Sulfur Battery Development - SAIC).

The sodium/sulfur battery development program is cost shared between DOE and CSPL. CSPL also has a UK-funded electric vehicle program, the aim of which is to demonstrate a 3.5-ton urban delivery van in a road trial.

The CSPL Core Technology R&D progress is discussed below. Specific accomplishments are summarized in Table 2-1.

# Background

The CSPL sodium/sulfur cell design strategy is based on a family of cells designated PB cells. Two specific sizes are currently being tested: a 45-mm diameter by 45-mm high cell called PB and a 45-mm diameter by 110-mm high cell called the Extended PB (XPB). The cells have central-sodium electrodes and are based on identical components as far as possible, particularly the seal designs.

The XPB has been proposed for stationary applications and the PB for electric vehicle (EV) applications, although it is intended to develop a generic technology. This generic technology will enable the commercialization of optimized cell designs, which are close in size to those for which a data base has been established. Selection of cell size is a complex issue that interacts with battery voltage, battery capacity, cell reliability, vertical dimensions of the battery bay, and costs.

CSPL has a long-term technology data base from the central sulfur 150-Ah NaS7 and 30-Ah technology demonstration (TD) cells. These designs have now been tested for more than 4600 charge/discharge cycles. Technology from these cells has been incorporated into the PB cell design that has achieved maximum lives in excess of 1000 charge/discharge cycles.

# Core Technology Research and Development

Progress was made in all subtasks of Task 1. The availability of a reliable PB cell, with stable and predictable performance, permitted excellent progress in the module subtask. The reliability of the PB cell was improved during the year. A group of 204 PB cells was tested for up to 850 cycles. A total of 76,681 cell cycles was recorded in these cells, four cell strings, modules, and a 120-cell battery before the first cell failure occurred. The reduction of infant mortality has considerable significance for overall batteryreliability predictions.

The power characteristics of 24-, 20-, and 15-cell modules were examined. These tests confirmed that the PB design is capable of delivering 89 W/kg sustained power at the battery level. Lives in excess of 750 charge/discharge cycles were achieved, using a 1-h discharge/2-h recharge regime on a 24-cell module. The regimes examined during the year also included 3-h discharges combined with charge periods between 5 h and 1 h, 35-min discharge, and discharge on simplified and normalized Federal Urban Driving Schedule (FUDS) cycles.

A 120 PB cell battery was constructed and tested on a 4.5-h discharge/7-h charge regime for 250 cycles. Cycle 250 was performed on 31 December 1986 and no cell failures had been recorded up to that time. The battery capacity and resistance were stable within the limits predicted.

The objective of Task 1 is to carry out the basic research, cell development, cell testing, materials studies, quality control, and computer modeling required to support a battery program directed to the fabrication of the final deliverable, a 100-cell XPB battery, and also to advance generic sodium/sulfur technology for both utility and EV applications. The issues of performance, reliability, safety, and cost are specifically addressed.

#### Electrolyte Research and Development

**Production Scale-Up.** The electrolyte made by CSPL is deposited in the green state by electrophoretic deposition (EPD) from an alcohol slurry. This process has been shown to provide a consistently high-quality beta"-alumina electrolyte, but unlike some other technologies employed by CSPL, there is no prior industrial background to which reference can be made. Thus much of this subtask was concentrated on developing the technology for scaling up production to pilot-plant levels. All the process steps needed to manufacture 450 shapes per week were installed and commissioned. The total number of Grade I (i.e., zero-defect) ceramics produced per year increased from 390 in 1985 to 3600 in 1986, the majority being manufactured in the last three months. The capital equipment was purchased by CSPL under its UK-funded contract, but the underlying technology development was funded by the SNL Core Technology Program.

CSPL's beta"-alumina is manufactured by the route shown schematically in Figure 2-1. Scaleup of the processes to produce slurry of the correct quality and quantity was accomplished by the introduction of larger equipment. This includes powder-processing equipment, mediumcapacity vibromills, and a large batch-sintering furnace. Installation was followed by validation trials in which the new product was compared to the old.

Powder and slurry quality were assessed by X-ray diffraction, particle-size analysis, chemical composition, and water concentration in the alcohol. A Microtrac particle-size analyzer, acquired during the past year, capable of analyzing the powders and slurries without the need for complicated dispersing techniques, proved especially important in establishing process control. Experiments to investigate rotary calcination of the powder indicated the need for further development.

Reclamation of the amyl alcohol was studied, and small batch trials conducted. Alcohol is routinely dried on the equipment shown in Figure 2-2. Reclamation of both alcohol and the solids content of the slurry are key objectives for reaching commercially viable cost targets. The recycling of alcohol was successfully attempted and further trials using multiple recycling of alcohol are planned. Utilization of the powder in EPD was increased from 30% to 50% by a new slurry-reclamation technique.

Improvements in powder processing were effected, with a reduction in calcination time from 24 h to 5 h and a reduction in milling time from 16 h to 5 h.

At the start of the year, a change was made from a single-chamber EPD rig to one with four chambers. Following its successful commissioning, over 1000 ceramic shapes were deposited. A 12-chamber rig was then designed and constructed. Comparison of ceramic deposit weights on the three rigs showed that the standard deviation was reduced from 5.1% on the single-chamber rig to 3.0% on the 12-chamber rig. The standard deviation on a single pallet of 12 shapes was 1.1% of the deposit weight. Increasing the number of chambers per pallet does not introduce any drawbacks in yield and quality, and further increases in the pallet size are considered feasible.

A two-hearth, lifting-hood sintering kiln was purchased under the parallel EPRI contract. During the year, this was successfully commissioned, and 9000 ceramic shapes were sintered.

# Table 2–1. Sodium/Sulfur Core Technology R&D Progress – CSPL

Electrolyte R&D

Production Scale-Up	Larger equipment introduced for electrolyte production by EPD from an alcohol slurry; product from this new equipment analyzed.
	Reclamation of amyl alcohol successful; EPD powder utilization increased from 30% to 70%; calcination time reduced from 24 h to 5 h; milling time reduced from 16 h to 5 h.
	Increased uniformity in ceramic deposit weights from new 12-chamber rig.
	Grade I (zero-defect) ceramic production increased by almost an order of magnitude to 3600 in 1986.
Second-Source Alumina	New alumina source for electrolyte adopted that produces a higher- strength ceramic at half the cost of the original source.
Zirconia-Toughened Beta"-Alumina	Moisture-sensitivity problems encountered during testing have identified the need for improved manufacturing techniques.
	Electrolytes with high beta"-alumina content also show greater moisture sensitivity.
XPB Ceramics	4-chamber rig converted for production of XPB ceramics.
	Studies show that by next year good reclamation of materials can be achieved for production of XPB ceramics.
Acoustic Nondestructive Evaluation	SAM nondestructive evaluation shown to be as accurate as dye-penetrant testing, but faster scanning techniques needed and method of examining cylindrical surfaces must be established.
Materials Development and Qualification	
Alpha-Alumina-to-Beta- Alumina Glass Seals	Freeze/thaw testing shows that aluminoborate glass has greater resistance to sodium diffusion than aluminoborosilicate glass; cell tests have begun on aluminoborate glass joints.
Metal-to-Alpha-Alumina Seals	MkIII seal developed that combines the MkII (the CSPL proprietary sodium seal) and MkI (aluminum/chromized mild-steel sulfur-electrode seal) technologies; initial exposure trials show an improvement in corrosion stability to $Na_2S_3$ .
Sodium Electrode	XPB sodium wick delivers 460 mA/cm <sup>2</sup> , exceeding the 250 mA/cm <sup>2</sup> target.
Sulfur Electrode	Sulfur-electrode performance, in EV discharge cycles, has been demonstrated in both the PB and XPB designs; 300-unit-per-week production target exceeded.

# Table 2-1. Sodium/Sulfur Core Technology R&D Progress - CSPL (Continued)

Materials Development and Qualification (Continued)

Containment	Cell container coated with a proprietary chromized coating tested for 1500 cycles judged superior to duplex chromizing layer presently used.
	3200 PB cans chromized during year; 100-container-per-run capacity established for chromizing PB cans; 250-container-per-run trials completed.
Cell Development	
Reliability Development	A group of 204 cells (consisting of individual cells, cell strings, cell modules, and a 120-cell battery) accumulated 76,681 cell cycles before the first cell failure.
Performance	Performance of 204-cell group consistent and reliable.
Freeze/Thaw	Cell freeze/thaw test facilities installed; module freeze/thaw test facilities close to completion.
	30 freeze/thaw cycles completed in fully charged state; no detected change in open-circuit voltage.
Cell Fabrication and Terminations	Low-resistance termination design validated by 250 cycles in a 120-cell battery and 600 cycles in a 4-cell string, and by high-current testing.
Cell Safety	Tests on the standard PB MkII design show reactant leakage can occur and that cell-to-cell propagation is possible.
	Latest design shows improved cell safety performance: no reactant leakages during the first nine tests.
XPB Development	MkII seal design modified and welding technology for the sodium filling/sealing operation improved.
	Five XPB cells cycling; five failed because sodium blocked electrode feed hole.
	Theoretical capacity is 34 Ah to 1.9 OCV or 41 Ah to 1.76 OCV.
Module Testing	
	All modules achieved more than 200 cycles without any cell failures.
Module 1 (20 cells)	Tested termination methods and intercell insulation intended for future EV batteries. No cell failures at 207 cycles $(3-h discharge/5-h charge)$ when removed from test.
Module 2 (24 cells)	Testing a variety of extreme charge/discharge regimes. One cell failure after 774 cycles; still cycling.
Module 3 (15 cells)	Accommodates the electrical requirements of a dynamic cycling rig; it has successfully completed 1352 FUDS cycles.

# Table 2-1. Sodium/Sulfur Core Technology R&D Progress - CSPL (Continued)

### Module Testing (Continued)

Module 4 (24 cells)	To be used for experiments with inverter loads and pulsed switching.
Module 5 (24 cells)	To be used for freeze/thaw cycling.
Module 6 (36 cells)	Used for safety tests: three cells suffered reactant leakage. This module did not have improved safety features.
Module 7 (36 cells)	To be used for safety tests; this module does have improved safety features.
Module 8 (24 cells)	For vibration testing; has undergone the tests with no obvious signs of damage.
Module 9 (120 cells)	Completed 250 cycles without any cell failures. More 120-cell batteries proposed for construction in 1987.



Figure 2-1. CSPL Electrolyte Production Route

The production rate from the electrolyte department was increased as shown in Figure 2-3. The graph shows the monthly output of Grade I ceramics. Grade I quality requires a total absence of defects on visual and dye-penetrant testing, as well as fulfillment of all dimensional tolerances. A Grade I ceramic is shown in Figure 2-4. It is considered that the use of Grade I ceramic in the PB cell experiments is partly responsible for the dramatic decrease in infant mortality. The monthly yield of Grade I ceramics is shown in Figure 2-5, expressed as a threepoint moving average.

Second-Source Alumina. A commercial objective of CSPL is to identify alternative sources of raw materials in order to dual-source and, where possible, reduce cost. At the start of 1986, several new sources of alumina were investigated, and one was selected for batch trials. The preferred material was half the cost and produced a higher-strength ceramic, improving it from 185 N/mm<sup>2</sup> to 240 N/mm<sup>2</sup>. Processing yield and microstructure were also found to be superior. Twelve cells were tested, as a scoping trial, for the second-source alumina. The results were as follows: one cell was removed from testing after 69 cycles; and eight cells reached 396 cycles, one cell reached 448 cycles, and two cells reached 511 cycles. These eleven cells continue to be tested. Since June 1986, all cells manufactured have contained electrolyte manufactured with the new source material.

Zirconia-Toughened Beta"-Alumina. The addition of zirconia to beta"-alumina to improve its mechanical properties has been studied for several years at CSPL. A group of eight CSPL technology demonstration (TD) cells containing various zirconia beta"-alumina formulations had logged 900 cycles at the start of the year. One cell, containing 3% of a nonpreferred zirconia formulation, failed after 949 cycles.

The remaining seven cells completed between 1800 and 1860 cycles without failure by the end of the year. These cells contain preferred zirconia sources, close to the preferred addition level. The cell capacities and resistances are shown in Figure 2-6.

The ceramic from the failed cell was recovered by posttest analysis and strengthtested. The posttest strength was 224 N/mm<sup>2</sup>. This is the estimated strength of a virgin tube of the same formulation, based on data from strength versus zirconia-addition levels. The absence of strength degradation is indicative of good electrolyte stability in the cell environment.

The combination of second-source alumina and a preferred formulation for zirconia toughening produced a C-ring strength of 340 N/mm<sup>2</sup>. This combination was tested in a PB cell scoping trial but was found to be extremely moisture sensitive, resulting in poor cell performance and low reliability.

A third option for zirconia-toughened beta"-alumina was tested in 14 PB cells. Six cells showed good performance, eight had high resistance, resulting from moisture uptake during storage. Although more effective storage conditions have subsequently been introduced, the relationship between improved mechanical properties and increased moisture sensitivity may necessitate the use of improved manufacturing techniques if zirconia-containing electrolytes are to be used.

In a special experiment, attempts were made to identify the cause of degradation of both beta" and beta"/zirconia electrolytes in storage. Electrolytes were stored in various conditions from 0 to 100% relative humidity (RH) for periods of up to 200 days. It was difficult to establish a systematic dependence of properties such as resistivity, strength, wetting behavior and in-cell resistance as a function of storage time and condition. It was, however, possible to conclude that beta"/zirconia ceramics were significantly more moisture sensitive than beta", although certain formulations could be stored for up to 100 days at up to 25% RH without degradation of electrical or microstructural properties.

Six electrolytes with a high beta"-alumina content (98%), induced by over-firing, were tested in TD cells. One cell was removed from testing after 98 cycles; one cell failed after 1349 cycles; and four cells reached 1806 cycles. The latter cells continue to be tested. Three of the cells exhibited high resistance, possibly because the beta" content resulted in greater moisture sensitivity than usual.

**XPB Ceramics.** When the 12-chamber EPD rig was commissioned, the four-chamber rig was converted so that ceramics for XPB cells could be deposited. The XPB has a ceramic of the same diameter as the PB but of 101 mm length. The release of the four-chamber rig from production enabled a variety of deposition trials to be attempted. Approximately 100 XPB ceramics of reductor is indicative of second course slumine second course slumine mulation for recomm domain of 140 more restor to 1 F6-con course to be extrated for a to be extrated for a to be extrated

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Figure 2-2. Alcohol Drying Facility



### Figure 2-3. Monthly Output of Zero-Defect Ceramics



Figure 2-4. Comparison of Zero-Defect Ceramic (left) and Defective Ceramic (right)



Figure 2-5. 3-Point Moving Average of Zero-Defect Ceramic Yield During 1986



Figure 2-6. Capacity and Resistance versus Cycles for High-Zirconia TD Cells

standard formulation were manufactured, and a number of tubes were deposited from experimental formulations in order to examine the influence of suspension concentration and deposition voltage. These preliminary studies were aimed at enhancing the understanding of the processes, in addition to optimizing output from the plant. In addition, XPB deposits were obtained using reclaimed alcohol, reclaimed powder, and reclaimed suspension in an effort to improve the materials utilization to near 100%. Good quality shapes were obtained with slight modifications of processing parameters, and the reclamation process is expected to develop into the production standard during the coming year.

Acoustic Nondestructive Evaluation. A preliminary evaluation of scanning acoustic microscopy (SAM) as a potential nondestructive evaluation method for the electrolyte was conducted. Two samples of electrolyte were supplied to VG Semicon for analysis on an ASM/100 microscope. With a slow scan (approximately 7 min), the instrument was able to distinguish clearly between good- and poorquality ceramic previously characterized by dyepenetrant testing. This is the first positive result obtained from any of the acoustic nondestructive evaluation techniques, and the method warrants further evaluation. However, it is not yet clear if sufficient resolution is obtainable on fast scans or if the technique is useful for examining cylindrical surfaces. To be generally suitable for production-line inspection, faster examination on both the flat end and cylindrical surface will be required.

#### Materials Development and Qualification

The major objective of this subtask is to qualify cost-effective candidate materials for cell and system design. The subtask includes the following activities: alpha-alumina-tobeta"-alumina glass seals, alpha-alumina ceramicto-metal seals, sulfur- and sodium-electrode design, and sulfur-electrode containment.

A materials-durability data base had been established before the start of the Core Technology program. This was based on CSPL's NaS7, 150-Ah design that contained materials and materials combinations pertinent to the present PB family of cells. These cells have continued cycling during the year, and the increased maturity to the data base is shown in Table 2-2.

Alpha-Alumina-to-Beta"-Alumina Glass Seals. A glass joint is used to seal the alphaalumina seal header hermetically to the beta"-alumina. The preferred glass formulation has been tested in cells for over 3800 cycles totaling over 30,000 hours. However, resistance to freeze/thaw cycling is a necessity for commercial applications. This was investigated by means of high-temperature sodium exposure, combined with freeze/thaw cycling. The vulnerability of the glass joint to freeze/thaw results from the diffusion of sodium into the glass. This modifies the surface of the glass and changes its expansion coefficient so that spalling occurs during cool down.

Two compositions were included in the trials: the preferred aluminoborosilicate and an aluminoborate glass. The trial consisted of exposure to sodium at 400°C with two thermal cycles to room temperature. It indicated that the aluminoborate has greater sodium resistance, although diffusion of barium into the beta"-alumina is a concern. Cell tests have commenced with glass joints made from aluminoborate glass.

Metal-to-Alpha-Alumina Seals. The ceramic-to-metal electrode seals of a sodium/sulfur cell are critically important components. CSPL pursued two electrode-seal approaches during the year, one which was all UK-funded and one funded by Sandia. Both are thermocompression bonds. While the CSPLfunded seal, known as MkII, has produced low infant mortality in a large number of cell tests, it has been shown to be vulnerable to corrosion by sodium trisulfide (Na<sub>2</sub>S<sub>3</sub>). The other seal, designated MkI, is based on the use of a deformable aluminum ring between the alphaalumina header and a chromized seal top cap. After a parametric study of bonding conditions, thermal top-cap cycle, and strength testing, chromized mild steel was selected for the metal top cap of the sulfur electrode seal. The strength variation between options was 10-fold. Chromized, 0.5-mm-thick mild steel was one of the stronger and more durable under thermal cycling conditions.

In October 1986, a review of the ceramic-tometal seal design was held. After consideration of the thermal cycling, sodium and sulfur exposure trials at 400°C, cell test, and posttest

	10/10/85		12/31/86		
	Cycles	Hours	Cycles	Hours	9 10
Electrolyte Comp.	2603	21384	3960	32328	
Glass Comp.	2603	21384	3960	32328	
Thermocompr. Seal Mats.	3278	27024	4646	37968	
Sodium Electrode Design	2603	21384	3960	32328	
Sulfur Electrode Design	2987	24696	4336	35640	
Secondary Protection	2987	24696	4336	35640	

#### Table 2–2. Component/Materials Durability Data Base

analyses, a hybrid seal design was selected for further development. This combined the CSPL proprietary sodium seal with the aluminum/chromized mild-steel sulfur-electrode seal. This seal, designated MkIII, is shown in Figure 2-7. The presence of aluminum prevents the glass seal being made after the ceramic-tometal sealing operation because of the difference in the aluminum and glass melting temperatures. This necessitates mechanical loading of the base of the electrolyte during the bonding process, unless a self-loading jig is used, which reacts the load on the alpha-alumina header. A jig was designed and used to make a small number of hermetic seals. The economics of this manufacturing route are being evaluated.



Figure 2-7. Seal Sub-Assembly of Mark III Cell

Exposure trials to  $Na_2S_3$  at 350 °C showed an improvement in the corrosion stability of the MkIII design over the MkII design. These trials were incomplete at the time of writing.

Sodium Electrode. The design of the sodium electrode interacts strongly with the safety of the sodium/sulfur cell. In order to minimize the sodium immediately available for reaction after ceramic fracture, the sodium is contained within a light inner container. In the XPB design, this also acts as a wicking device to ensure wetting up the length of the ceramic. In sodium-sodium cell testing, a wick design delivered 460 mA/cm<sup>2</sup> before sodium depletion occurred. This exceeds the 250 mA/cm<sup>2</sup> target for utility applications.

Sulfur Electrode. The performance of the present CSPL sulfur electrode has been validated in both the PB and XPB designs. The PB design has been shown to be capable of meeting the most demanding EV discharge cycles in module tests. However, high-rate module testing indicated that the maximum recharge rate was limited to 2 h, beyond which polarization voltage caused trip-out of the charger.

The design of the CSPL sulfur electrode remained the same as that used previously, a composite of carbon and alumina fiber arranged so that only alumina contacts the electrolyte. Alumina fiber channels are arranged radially to transport reaction products rapidly. This design has now been tested for 4400 cycles.

Other work on the sulfur electrode was limited to validating an effective way of making sulfur electrodes at 300 units per week. This target was exceeded by the end of 1986.

Containment. The present method of making the sulfur-electrode containment resistant to corrosion by sulfur and sulfides is to form a duplex chromizing layer on a mild steel can. The duplex layer consists of an outer chromium carbide layer on an interlayer of iron-chromium alloy. During the year, a cell container coated with a proprietary coating completed 1500 cycles in a PB cell. When compared to the duplex chromized coating operated for the same cycle life, the proprietary coating was judged to be in better condition, and a further trial has been planned. Seal top caps with the proprietary coating were successfully bonded to alphaalumina in the MkIII seal configuration. It is therefore possible to make a cell in which all the sulfur electrode containment is protected by this proprietary coating.

A total of 3200 PB cans were chromized in 64 batches during the year. Midyear, the transition was made from coating in the vendor's laboratory to a larger production furnace. This was successfully accomplished, and a capacity of 100 containers per run was established. Trial runs on even larger tooling, capable of batch sizes of 250, were completed. These were successful, apart from some slight variations of coating thickness.

Optimization of the process conditions was carried out, and the carbide thicknesses were increased to 10  $\mu$ m. This represents the limit for the carbon availability of the present raw material used for the cans. Some further work on pre- and post-carburizing was carried out to study the potential of this technique for creating a thicker coating. This work is continuing.

#### **Cell Development**

The objective of this subtask is to develop cell designs for both stationary and motive power applications and to establish the cell performance, reliability, safety, cost, and freeze/thaw survivability. The reduction of infant mortality is a specific item in the contract where substantial progress was made. Progress in cell development is reported below.

**Reliability Development.** During the year, the experiment to compare cell size and reliability has continued, funded partly by the parallel

EPRI contract that ended in July 1986. The reliability data from this experiment are shown in Table 2-3. The NaS7 and TDC cells are 150-Ah and 30-Ah central-sulfur designs, respectively. Direct comparison of the NaS7 and TDC data can be made as the design features are matched. The life data confirm a statistically significant ceramic size effect.

Figure 2-8 shows the percentage of all experimental PB cells that have failed within the first 250 cycles and indicates the trend towards lower infant mortality of the PB-sized cell. No cells have been censored from the data, which include all the PB cells submitted for test, including MkI, MkII, and MkIII designs.

The reliability of the PB design, which at the start of the year was 435 cycles with a shape parameter of 3.0, has improved significantly this year. A group of 204 cells with a slightly modified proprietary seal (PB MkIIA) were placed on test in a variety of experiments commencing between March and August. The test configurations included 36 single cells, a 4-cell string, 20- and 24-cell modules, and a 120-cell PB battery. The group accumulated a total of 76,681 cell cycles before the first cell failure. One cell failed at 562 cycles (from the 36-cell population) and another at 774 cycles (in the 24-cell module). At this time, three other cells, which had exhibited rising resistances, were removed. These had completed 474, 589, and 610 cycles and, at the time of removal, had resistances approaching double their minimum value. The failures at 562 cycles and 774 cycles were judged on the grounds of non-faradic behavior. Thus, at least two failure modes are implicated in the five failures. Table 2-4 shows the 95% confidence limits and mean estimates for the Weibull parameters of the above five data points.

These parameters reflect the trend towards low incidence of early failure in the PB designs and PB-sized electrolytes. At the time of the first failure in the 204-cell population, the product of cell-cycles was as shown in Table 2-5.

**Performance.** The consistency and repeatability of PB cell performance is demonstrated in Figure 2-9, which plots the capacity and resistance vs. cycles for a 36-cell population. This performance typifies what was obtained in all 204 cells in the group. These cells contain sulfur electrodes that are approximately 3.5 g below the target sulfur weight because they

					Weibull (10 Analy	0/01/86) /sis
Cell Type	Electrolyte Length (mm)	No. o Cycling	of <u>Cells</u> Failed	Cycles Completed	Characteristic Life (Cycles)	Shape Parameter
NaS7	580	alies de lan Dan 31. co	12	2731	68513282574	0.540.861.36
TDC	120	5	10	3346	152028715423	0.580.981.68

#### Table 2-3. Electrolyte Length and Cell-Life Comparison

alumina in the MKHI seal configuration to another therefore possible to make a cell in which all the suffur electrode containment is protected by this proprietary castore

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Figure 2-8. Infant Mortality Improvement of PB Cells

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% OF CELLS

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FAILING

BEFORE 250 60 .

50

40

30

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cell development is reperted helow Reliability Direfanment. During the plan, the experiment in compute cell size and reliability has continued. fouried real oby the parallel

Table 2-4. Weibull I MkIIA PB Cell Populati	Parameters of on	the
Weibull Charact. (cycles)	71511671907	
Weibull Shape Parameter	1.84.511.4	

	diase in the	Cell-Cycles
Experiment	Cycles	Product
120-Cell Battery	250	30,000
20-Cell Module	207	4,140
24-Cell Module	773	18,552
4-Cell String	500	2,000
36-Cell Experiment	Various	21,989
and the second		76,681

were manufactured on development tooling. The sulfur loading on a group of experimental cells was increased to 26 g, the target weight. After 350 cycles, these cells are delivering 10.1 Ah at the 3-h rate, which is 83% of theoretical to 1.9 OCV. With a cell weight of 119 g, this is equivalent to 170 Wh/kg of *delivered* energy density. Both the energy and power performance of the PB cells are discussed more fully under Subtask 1.5, Module Development and Testing.

**Freeze/Thaw.** The ability to freeze/thaw a battery is an important design criteria for the commercial product. During the year, automatic freeze/thaw facilities for testing cells were installed, and facilities for freeze/thaw testing modules are close to completion. Freeze/thaw cycling of three PB MkII cells and a MkIII cell has commenced. These cells completed 30 thermal cycles between room temperature and 350°C in the fully charged state. No change of open circuit voltage was detected. It is proposed to continue these tests at different levels of discharge, with performance testing between levels.

Cell Fabrication and Terminations. Effective termination of cells to complete battery interconnections is an important program objective. A secure, low-resistance termination must be made between the base of a cell and the sodium electrode current collector of the next cell in the series string. An additional requirement is that the space taken by the termination should be minimized. Such a design was established and used in the module designs and the 120 PB cell battery. This design was validated by 250 cycles in the 120-cell battery and 600 cycles in a four-cell string as well as continuous high-current testing at 30 A (equivalent to the 20-min rate). Microscopic analysis of containers after cell testing has not revealed any enhanced degradation of the chromized layer from the termination welding process. Real-time weld monitoring of the termination process was installed and successfully incorporated into the assembly procedure.

Cell Safety. During 1986, in preparation for the building of larger assemblies of cells, the safety effort was substantially increased. Deliberate failure of the standard PB MkII design in both individual cells and cells contained in a 36-cell module indicated that reactant leakage was occurring and that cell-tocell propagation was possible. Several enhanced safety features were designed and tested for both cell safety and electrical performance. Initially problems were encountered with rising cell resistances, but these were overcome by the introduction of getters to the sodium electrode. Cell safety performance was improved with the latest design, and no reactant leakages occurred during the first nine tests on the new design. The design is to be incorporated in a 36-cell module for further safety evaluation.

**XPB** Development. A major objective of the contract is to progress the family concept of PB cells based on generic core technology. Such a strategy will improve the ability to design cells for application-specific requirements, without moving away from a design data base. The 110-mm-long XPB cell is currently targeted for stationary utility applications, but a high-volume EV application could require (and justify) an intermediate, specific size between PB and XPB. The selection of cell size depends on system voltage requirements, space, and cost. There may also be trade-offs in the production engineering aspects of cell construction. For example, the depth-to-diameter ratio that can be achieved in deep drawing the containers will be a major influence in the cost, size, and manufacturing route of that component.



Figure 2-9. Resistance versus Cycles and Capacity versus Cycles (% to 1.9 OCV) for PB Cells

deep drawing the containers will be a majo influence in the cost, size, and manufacturing routs of that controngat. Before commencing the development of the XPB cell, it was necessary to eliminate some of the reliability problems that were being encountered with the PB cell. This was partly solved by the introduction of modifications to the MkII seal design, combined with improved welding technology in the sodium filling/sealing operation.

An initial scoping trial of ten cells is illustrated in Figure 2-10. These contained two gettering options, one of which proved unsatisfactory and caused cell failure because of blocking of the sodium-electrode feed hole. The status of the five cells cycling at the end of the year is shown in Table 2-6.

Other work on the XPB has included the introduction of a four-chamber EPD rig for electrolyte manufacture (Figure 2-11) and a design study to examine the optimum sulfur loading. A maximum of 74 g of sulfur can be used in the present electrode diameter. This gives a theoretical capacity of 34 Ah to 1.9 OCV or 41 Ah to 1.76 OCV. The design is sulfur-limited.

#### Module Testing

The objective of this subtask is to develop and test submodules of larger battery designs in order to explore the interactions of cell interconnection strategy and to test groups of cells in application-specific requirements. Other objectives are to study the effect of cell-failure interactions and the effect that varying cell performance has in an interconnected group of cells.

Individual Modules. The improvement of cell reliability achieved during the year enabled significant progress to be made with modules of PB cells. All the modules placed on cycle testing during the year achieved more than 200 cycles without any cell failures. A 120-cell PB battery was introduced in a program revision in March and commenced testing in July. The battery achieved 250 charge/discharge cycles by the end of December, and no cell failures were recorded. The modules that were tested during the year are summarized in Table 2-7.

Module 1 consisted of 20 cells arranged in five parallel strings of four cells, using the termination methods and intercell insulation intended for future EV batteries. The module was cycled for 207 cycles on a regime of 3-h discharge/5-h charge before removal to make space for other modules. At the time of removal, no cell failures had occurred.

Module 2 consisted of 24 cells arranged in six parallel strings of four cells. The module was used to explore a variety of extreme charge/discharge regimes and completed 773 1-h/2-h charge cycles by the end of the year. A cell failure occurred on 1 January 1987. This module was subjected to a variety of other cycling regimes including 5-, 4-, 3-, 2-, and 1-h recharge times combined with discharge times down to the 35-min rate. Polarization effects at the 1-h recharge rate prevented full recharge and 2 h is regarded as the limit of the present cell design. (Graphs of the 5-h/3-h and 1-h/2-hcharge/discharge cycling regimes are shown in Figure 2-12.) The power of the module was also measured at various levels of discharge, and the specific power outputs are plotted in Figure 2-13.

Module 3 was configured with three parallel strings of five cells to accommodate the electrical requirements of a dynamic cycling rig. This computer-controlled rig can subject a module to many charge/discharge profiles, depending on the software used. The module was operated on both normalized and simplified FUDS cycles as well as a conventional 3-h/5-h discharge/charge regime. During the year, it completed 51 conventional cycles and a total of 1352 FUDS cycles. The FUDS cycles were a mix of normalized and simplified, both of which are equivalent to 32 normal cycles. The FUDS cycle is shown in Figure 2-12.

Module 4 was constructed during the year but not warmed up. It is intended to be used to explore the effects of inverter loads and pulsed switching. A further module (module 5) was constructed and made ready for freeze/thaw cycling.

Two modules, consisting of 36 cells, were constructed for safety testing. The first (No. 6) was subjected to 23 consecutive cell failures by overvoltaging. Twenty cells failed benignly, but three suffered reactant leakage. The cells did not contain all the preferred safety features so that the effect of reactant leakage onto other cells and module hardware could be studied. The test reinforced the need for further development of the cell safety performance that had commenced before the module test. A second 36-cell module (module 7) was under construction by the end of

# Table 2-6. XPB Cell Status (12/31/86)

			Ene			
Resistance mΩ 350°C	Specific Resistance $\Omega \cdot cm^2$	Corrected Resistance*	% Theo to 1.9 V	Specific Energy Wh Kg <sup>-1</sup> Delivered	Cycles Complete	
17.4	1.75	1.37	89	152	162	
18.4	1.82	1.44	89	147	129	
14.8	1.41	1.03	90	157	129	
15.8	1.47	1.09	88	146	129	
24.7	2.61	2.18	90	152	74	
	Resistance mΩ 350°C 17.4 18.4 14.8 15.8 24.7	Resistance $m\Omega$ $350^{\circ}C$ Specific Resistance $\Omega \cdot cm^2$ 17.4 $1.75$ $18.4$ 18.4 $1.82$ $1.41$ 15.8 $1.47$ $24.7$ 261	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

\* The resistance of the cells is measured near the end of discharge when the contribution of the steel current collector is a significant proportion of the total. The figures in the Corrected Resistance column are estimates that assume an aluminum collector was used. Two of these corrected resistance values are close to those of the best PB cells. The use of aluminum current collector is being investigated.



Figure 2-10. Batch of XPB Scoping Cells



Figure 2-11. EPD Rig for XPB Ceramic Deposition

Module	No. of Cells	Array (Volts)	Wh*	No. of Cycles	Cycle Regime**	Remarks
1	20	5 × 4 (8)	400	207	3/5	Removed, zero failures
2	24	6 × 4 (8)	480	773	1/2	Power pulse testing (controller simulation)
3	15	3 × 5 (10)	300	1352	FUDS	51 cycles, 3/5, 32 of FUDS
4	24	6 × 4 (8)	480		3/5	Pulse switch/inverter effects
5	24	6 × 4 (8)	480	-	-	Awaiting warm up freeze/thaw
6	36	9 × 4 (8)	-	-	-	Safety
7	36	9 × 4 (0)	-	-	1	Safety
8	24	8 × 4 (0)	-	-		Dummy - Vibration testing
9	120	15 × 8 (16)	2400	250	4.5/7	Zero failures at 250 cycles

# Table 2-7. 1986 Module Builds

\* Nominal delivered Wh \*\*Discharge hours/recharge hours



Figure 2-12. Charge/Discharge Regimes of PB Cell Modules

the year. This module contains cells with improved safety features, developed under Subtask 1.3 (Cell Development).

Module 8 was constructed with cells containing all the standard metal and ceramic components except sodium and sulfur. These were replaced by silicone oils of similar physical properties. The module was subjected to vibrational testing on the equipment shown in Figure 2-14. In the absence of a vibration specification relevant to a 3.5-ton battery-driven vehicle, a UK military specification for batteries was used. This is a more severe regime than that expected to be experienced in a road vehicle. The frequency chosen was 35 Hz with an amplitude of 1.2 mm for 2 hours. This produced a maximum acceleration of 6.3 g. During the test, the module received 2 X 10<sup>6</sup> cycles, and no obvious signs of damage were noted.

120-Cell Battery. A battery consisting of 120 PB cells was constructed and commenced testing in July 1986. The battery, shown in Figure 2-15, was configured as shown in Figure 2-16 to give a 16-V output. The weight was 18.4 kg, and the external dimensions were 255 mm X 245 mm X 187 mm. The battery completed 250 cycles of 4.5-h discharge/7-h recharge on 31 December 1986. An in-cycle voltage versus Ah plot is shown in Figure 2-17 for cycle 250. No cell failures have occurred. On cycle 292, the battery completed 64 6-min simplified FUDS (SFUDS) cycles. Each SFUDS cycle removed 2 Ah and supplied approximately 0.32 Ah of recharge so that a total of 129 Ah was discharged and 30 Ah was replaced as simulated regenerative braking. The discharge rate during the SFUDS cycle was 10% below that required, and software adjustments are to be made in the controller program.

In order to explore the improved reliability of cells, further 120-cell batteries have been proposed for construction in 1987. The use of this larger cell population reflects the need to discriminate improvements in infant mortality.

#### **Battery Engineering**

Task 2 was not scheduled to commence in the reporting period. However, much of the Science Applications International Corporation subcontract was directed towards modeling battery systems and the effect of cell design on system behavior. This is discussed in the next section, Sodium/Sulfur Battery Development -CSPL.

A preliminary design study of the battery configuration is planned for the forthcoming year so that the XPB module designs can closely match the requirements of the 100-cell XPB battery and the future utility requirements.

# Sodium/Sulfur Battery Development - SAIC

Science Applications International Corporation (SAIC) is a subcontractor to CSPL on the Battery Engineering and Testing Program. The SAIC effort consists of four major tasks:

- Cell/battery statistical analysis. A Weibull-based Monte Carlo computer program has been written to evaluate the effects of cell failures on a variety of battery network configurations.
- Cell freeze/thaw model and test. Realtime X-ray radiography has been tested and proven a viable tool for imaging sodium and sulfur electrode levels, and sulfur-electrode structure. Examining the internal structure during freeze/thaw cycling is important for determining the mechanisms of stress generation leading to electrolyte failure.
- Cell performance modeling. A computer program has been written that calculates cell temperature, voltage, resistance, and capacity as a function of time and charge/discharge rate. CSPL PB cell data have verified the computer model.
- Cell component material study. The tensile stress state on the interior surface of the chromized cans was measured; switch materials and designs for failure protection were investigated.

Significant progress has been made in each task. The progress on these tasks is discussed below and is summarized in Table 2-8.







Figure 2-15. 120 PB Cell Battery



Figure 2-16. Electrical Configuration of 120 PB Cell Battery



# **Cell/Battery Statistical Analysis**

To gain insight into the behavior of series/parallel arrays of cells under various operating conditions, two battery-simulation computer programs have been written:

- Battery Simulation (BATSIM), which simulates in detail a small group of cells, and
- Reliability Simulator (RELSIM), which provides generalized reliability data for the entire cell population of a load-leveling facility.

These programs are used extensively for reliability analysis, electrical-network simulation, battery-maintenance simulation, structural analysis, and thermal analysis. BATSIM and RELSIM, along with other related programs, are described below.

# Table 2-8. Sodium/Sulfur Battery Modeling Progress - SAIC

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Cell/Battery Statistical Analysis	
BATSIM	Models how cell characteristics and failure modes affect battery current, voltage, and capacity; can simulate up to 25 X 25 cell arrays.
	Simulation runs show significant back currents through failed cells, dramatically shortening discharge time through parallel cells. This highlights the need for a reliable open-circuit-failure switch for parallel arrays.
RELSIM	Forecasts the available capacity of a battery under the influence of cell failures.
	Various cell- and module-replacement strategies evaluated to optimize cell utilization.
BUMP	Simulates the periodic replacement of battery subunits.
Thermal Models	Model of an entire 10-MWh heating/cooling zone of a unit building developed.
	Detailed model of heat transfer and fluid dynamics within a single module developed to determine optimum cell spacing within a cell bank.
Cell Freeze/Thaw Model and Test	
	Instrumentation and techniques to perform real-time X-ray radiography of hot sodium/sulfur cells under charge/discharge conditions were completed.
Cell Performance Modeling	
	Electrical simulation model of PB/XPB cell used both as a cell-design tool and as a cell-characteristics subroutine for BATSIM.
	Except for small differences in open-circuit voltage, good agreement with PB cell data achieved.
Cell Component Material Study	
	High residual tensile stresses detected on the inside surface of chromized cans.
	Busbar materials, demountable high-temperature electrical connectors, and fusible-link materials identified for in-depth evaluations.

#### BATSIM

BATSIM determines how individual cell characteristics and failure affect battery current, voltage, and capacity. The state of each cell in the array can be observed during any charge/discharge cycle.

BATSIM (Figure 2-18) accomplishes this by integrating three interactive tasks that predict cell-failure location and time (statistical-analysis subroutine), determine battery/cell temperatures (thermal-analysis program), and provide characteristics of operating cells (cellcharacteristics subroutine). The BATSIM master network program cycles the battery and tracks all current flows, voltages, and cell data. A detailed discussion of BATSIM follows. The cell characteristics subroutine is also discussed below, in the section on cell performance modeling.



Figure 2-18. Module Computer Modeling Method

All cells are assigned properties. A randomnumber generator assigns cell resistance before and after failure. Other cell characteristics (open circuit voltage, initial capacity, and Weibull parameters) are presently assigned constant values. Cells fail according to Weibull statistics and a uniform random-number generator, and circuit analysis is then performed.

Once a cell has failed, it is assigned a new resistance (see above), and its voltage is zeroed. The circuit-analysis subroutine then reads a load-versus-time profile and iterates the total module output current until the required load is reached. The program is terminated when any cell's capacity drops below 0.0 Ah since overdischarge would result in  $Na_2S_2$  precipitation and permanent cell damage. In the case of highresistance failed cells, the battery must be recharged immediately after discharge to prevent overdischarge from self-discharge.

All the major elements of BATSIM have been written and exercised. Module simulation runs have begun on 10 X 10 arrays, with distributions of cell resistance before and after failure. The internal discharge caused by failed cells is being qualified. The present size limit of the simulator is 25 X 25 cells, though it may be expanded to 300 X 50 cells. Simulations of 5 X 5 and 10 X 10 cells have been run based on cell data from CSPL.

The BATSIM results show significant back currents through failed cells, dramatically shortening the discharge time of cells in parallel. For example, a recent 10 X 10 cell simulation at charge/discharge cycle number 1000 showed one row with no failures and one row with 4 out of 10 failed cells. The row with 4 failures was fully discharged while the row with no failures still had 96.5% remaining capacity. This highlights the need for a reliable open-circuit-failure switch for parallel arrays.

Figure 2-19 shows the module simulator results. Reverse currents in the failed cells drain the capacity from parallel cells. This map, done 0.1 h after the beginning of discharge, shows most of the PB cells with a large fraction of their 8.5-Ah capacity. Internal loop currents from cell failures lower the battery voltage from 10.1 V to 9.45 V.

#### RELSIM

The RELSIM program forecasts the available capacity of a battery under the influence of cell failures. The program steps through charge/discharge cycles and fails cells according to the Weibull statistics (for the number of cells to fail) and a uniform random-number generator (to decide which cells to fail).

The mode of cell failure is approximated. In the parallel case, all cells are assumed to fail open circuit; closed-circuit failure is assumed in the full-series case. Thus, there is no accounting for loss in capacity from bank self-discharge. (BATSIM accurately models battery selfdischarge.)



Figure 2-19. Electrical Schematic of Module Simulator Results for CSPL PB Cells

The RELSIM output is in tabular form: each row of data represents a time step. Presently, percentage of failed cells and remaining battery capacity are of greatest interest. These data, presented graphically, are useful for contrasting the performance of various battery configurations. Figure 2-20 shows the effects of cell arrangements and cell failure on the capacity of a 40-MWh battery composed of 65-Wh cells. These curves represent the maximum capacity achievable; actual capacity is based on the DOD possible in each cell and is therefore less.

RELSIM has evaluated various cell and module replacement strategies to optimize cell utilization. The reliability results have been used to compare the cost of replacing cells and blocks of cells versus the addition of cells.

#### **Other Programs**

**BUMP.** The battery unit maintenance program (BUMP) simulates periodic replacement of 40-MWh units comprising a 120-MWh battery. BUMP can simulate the replacement of any size subunit to any size battery RELSIM can model. BUMP searches the capacity-versus-time output from RELSIM until the desired replacement capacity is found. BUMP then replaces the first unit by adding the capacity of the new unit less the remaining capacity of the replaced unit. The remaining capacity of each unit is calculated from a linear fit of the capacity degradation curve along with an array that tracks the unit's age. The battery then continues to degrade until replacement capacity is reached, at which time



Figure 2-20. Network Configuration Comparison

the next unit is replaced. This procedure continues until the desired life of the battery is reached.

At this point, BUMP calculates the average capacity (based on the area under the capacityversus-time curve) and compares it to the desired average capacity. The replacement capacity is then iterated, and the program reruns until the desired average capacity is reached. Finally, the curves for unit degradation and unit replacement are plotted.

Thermal Models. Thermal modeling of a load-leveling battery has been accomplished on two levels:

- Model of an entire 10-MWh heating/cooling zone of a unit building. This was developed for use as a design tool for the thermal management system of an EPRI load-leveling facility.
- Detailed model of heat transfer and fluid dynamic phenomena within a single module. This model accounts for convection, conduction, and radiation between cells and from cells to the container wall.

Both these models utilize the TSNAP program, a nodal analysis program for solving transient and steady-state problems. TSNAP calculates cell and air temperatures, air flow rates, and air pressure drops. The detailed model of the single module used these results to determine the optimum cell spacing for adequate air velocities and heat-transfer coefficients without undue pressure drop through the cell bank. TSNAP allows cell temperature to be determined for different rates of charge and discharge. This is important because cell resistance varies with temperature, and hence, its I<sup>2</sup>R heat generation varies with current and temperature.

#### **Cell Freeze/Thaw Model and Test**

A literature survey was performed. The cell design and literature base indicate that the phase transformations taking place in the sulfur electrode are the cause of tensile stresses in the electrolyte. Data on supercooling of polysulfides indicated that they would undercool variably as much as 100 °C before phase transformation begins.

Mechanisms have been postulated based on constrained expansion of the sulfur electrode on heat-up. Recent evidence from Sandia indicates that a failure has occurred on cool down. The SAIC program has focused on real-time radiography of hot sodium/sulfur cells under charge/discharge conditions as a way of obtaining needed data to understand the freeze/thaw problem. The movement of materials in the sulfur electrode is of particular interest. To date, cells have been radiographed cold, and several features identified with computer edgeenhanced real-time radiography using 70 KV Bremsstrahlung radiation and a linear scanning X-ray imaging system. These images have shown the sodium/beta"-alumina wetting angle, sodium level, sulfur level, wicking channels in the sulfur electrode, and seal integrity. An oven has been designed and ordered to perform these tests hot while measuring the cell capacity and voltage. Changes inside the cell during charge and discharge will be evaluated and an attempt made to relate them to stresses in the ceramic electrolytes.

# **Cell Performance Modeling**

An electrical simulation model of the PB and XPB cells was developed for use both as a cell design tool and as a cell-characteristics subroutine for the battery-module simulation program (see Cell/Battery Statistical Analysis). The objective of the program is to model cell behavior, in particular electrical/thermal interaction within the electrodes and electrolyte. A block diagram of the program is shown in Figure 2-21.

The program calculates cell component resistances (ionic and electronic) at each time step through charge and discharge based on the input physical characteristics of the cell. The sodium and sulfur levels are calculated during charge/discharge to determine the wetted electrolyte area for resistance calculations. The program then determines the open circuit voltage as a function of temperature and state-of-charge from Gupta and Tischer's data. The model also includes algorithms for cell resistance rise and capacity loss versus cycles.

The model-generated cell parameters are compared with PB cell test data at various statesof-charge in Figure 2-22. Except for the small differences in open circuit voltage, the model agrees very well with PB cell data. This type of data will be used in battery module simulation.

#### **Cell Component Material Study**

This task was designed to assist CSPL in materials-related issues for the cell or battery. Evaluation of chromized cans has shown high residual tensile stresses on the inside surface. The C-ring closing indicated stresses as high as 10,000 psi, based on a simple beam bending analysis.

Materials of the Nitnol memory metals were surveyed as possible high-temperature thermal fuse materials. The transition temperatures were much lower than the 350°C sodium/sulfur cell operating temperature. Fusible links appear superior as thermally activated fuses. SAIC has developed a multiplexed current-driven fusiblelink approach for cell protection. A battery materials requirement survey by SAIC this year indicates that busbar materials, demountable high-temperature electrical connectors, and fusible-link materials need in-depth evaluations for advanced batteries.

# Development of Beta"-Alumina Ceramic Electrolyte - Ceramatec

One of the remaining major obstacles to commercialization of the sodium/sulfur battery is the demonstration of acceptably high reliability. Reliability is affected by a number of factors, including system and cell design, corrosion of the cell container, and failure of the beta"-alumina electrolyte. Electrolyte failure, one of the most critical reliability factors, depends on a number of properties: composition, density, flaw population, variability, and fracture toughness.

Because beta"-alumina tubes are brittle, they are prone to failure under various conditions and mechanisms. Failure may be electrolytic in origin, or it may result from mechanical stresses. In either case, failure initiates at flaws such as cracks, voids, pores, large grains, or impurity inclusions. While some of these defects are intrinsic, most are introduced during electrolyte processing.

Ceramatec currently fabricates beta"-alumina electrolyte tubes by isostatic pressing, and processes the precursor powders by the zeta process. This is a dry-powder process in which alkaline salts are calcinated and mixed with alpha-alumina and then milled into a powder product. Zeta-process electrolytes have high mass density, a fine-grained microstructure, and high intrinsic conductivity.

However, the zeta process does have some disadvantages:

- It is both equipment and labor intensive.
- The powder is nonflowable, which makes minimization of defects during mold filling and elimination of them during isostatic pressing and sintering difficult.
- The many processing steps increase the likelihood for entrapment of impurities and inclusions in the green body, which can eventually result in defects in the sintered body.

Seeded slurry solution, spray-drying (S<sup>4</sup>D) is an alternative single-step route to powder preparation. Here various alkaline salts are mixed with alpha- and beta"-alumina seeds to form a slurry solution, which is then dried in a



Figure 2-21. Block Design of File/Module Interaction



Figure 2-22. Cell Performance Model versus PB Cell Test Data

conventional spray dryer. This process produced flowable powders suitable for isostatic pressing from inexpensive alpha-alumina sources. The seeding technique catalyzes conversion to the beta"-alumina phase during sintering and produces electrolytes of controlled grain size with excellent electrical and mechanical properties.

S<sup>4</sup>D is attractive because:

- The expensive milling and calcination operations are eliminated.
- The number of processing steps is reduced substantially, minimizing the likelihood of powder contamination during handling.
- The flowable powder introduces fewer and smaller defects during the forming operation, and defects are eliminated more readily during the reactive sintering process.

Toughening of beta"-alumina has been pursued to improve its mechanical properties. There are several toughening techniques, the most important of which is transformation toughening, where fine particles of zirconium oxide are dispersed into the beta"-alumina precursor powder. During sintering at around 1600°C, zirconia is present as an insoluble second phase with a tetragonal crystal structure. Upon cooling to below 1200°C, the surrounding beta"-alumina matrix metastably constrains the zirconia particles in the tetragonal phase. The propagating crack transforms the tetragonal phase to the low-temperature monoclinic polymorph, causing a 4% volume expansion. This transformation in turn absorbs energy from the propagating crack, and the volumetric expansion places the material surrounding the crack under compressive stress. These combined mechanisms arrest crack growth.

Strength and toughness attainable by this process depend critically on the amount of metastable, transformable tetragonal phase within the sintered body, which in turn depends on the zirconia particle size and content of stabilizing dopant. In beta"-alumina toughened with unstabilized zirconia, only particles below a critical size transform in the presence of a propagating crack. Larger particles transform during cooling following sintering and therefore do not contribute to transformation toughening. Table 2-9, which summarizes comparative data on electrolytes prepared from zeta-process,  $S^4D$ , and zirconia-toughened powders, shows that the  $S^4D$  and zirconia-toughening processes substantially improve beta"-alumina electrolytes.  $S^4D$  is clearly the preferred choice from the standpoint of cost, processing simplicity, impurity control, and physical properties. And zirconia can be easily incorporated into  $S^4D$  to further improve physical properties.

At the beginning of 1986, S<sup>4</sup>D and zirconiatoughening processes were routinely producing high-quality electrolyte tubes with consistent out-of-cell properties. The next step was to test these electrolytes in sodium/sulfur cells.

## **Program Objectives**

The specific objectives under this program for 1986 included the following: 1) sodium/sulfur battery technology transfer; 2) cell test facility augmentation; 3) development of a test plan for comparing the performance of S<sup>4</sup>D and zirconiatoughened electrolytes against standard zetaprocess electrolytes in sodium/sulfur cells; 4) electrolyte fabrication and characterization; 5) sodium/sulfur cell fabrication; and 6) qualification-cell testing. Items 1, 2, part of 5, and 6 were accomplished under Ceramatec funding. These tasks are discussed below and are summarized in Table 2-10.

#### **Technology Transfer from FACC**

As part of the license agreement between Ford and Ceramatec, the transfer of sodium/sulfur battery technology from Ford Aerospace and Communications Corporation (FACC) to Ceramatec was completed. This was accomplished through the transfer of extensive documentation including detailed engineering drawings, manufacturing and inspection instructions, internal technical memoranda, test data and computer models, extensive interviews and discussions with Ford personnel, and acquisition of a former Ford employee. Designs for the following state-of-the-art cells were transferred: two electric vehicle cells, two utility load-leveling cells, an energy-storage cell, and a satellite cell. In addition, CARBAT-I, ETX, and

Process*	Density (g/cm <sup>3</sup> )	Resistivity @ 300°C (Ω•cm)	K <sub>IC</sub> (MPa∙m <sup>1/2</sup> )	Burst Strength (Mpa)	Shape Factor	_
Zeta	3.23 (0.02)**	4.43 (0.29)	2.2 (0.2)	131 (16)	6.81	
S <sup>4</sup> D	3.22 (0.02)	3.94 (0.46)	2.2 (0.2)	154 (12)	13.2 (2.0)	
Toughened Unstabilized S <sup>4</sup> D	3.42 (0.01)	4.79 (0.45)	3.6 (0.2)	167 (34)	4.9 (0.3)	
Toughened Stabilized S <sup>4</sup> D	3.42 (0.01)	5.09 (0.25)	2.9 (0.3)	159 (23)	6.8 (0.8)	

## Table 2–9. Properties of Beta"-Alumina Prepared by Various Processes

\* The alumina source for the zeta process was Baikowski CR-30. Reynolds RCHPDM was used for the others.

\*\*Standard deviation

100-kWh load-leveling battery designs were transferred.

**Test Plan Development** 

A test plan was developed to fabricate electrolytes according to the following processes:

- zeta (seven electrolytes)
- seeded slurry solution, spray-drying (S<sup>4</sup>D) (eight electrolytes)
- unstabilized zirconia toughening (eight electrolytes) and
- partially stabilized zirconia toughening (eight electrolytes).

After processing, the electrolytes are to be assembled into sodium/sulfur cells, and the cells will be tested under cyclic conditions.

The cell chosen as the electrolyte test vehicle was the Ford EH-2A cell. The electrolyte in this cell has a 25-mm OD, is 220 mm long, and has a wall thickness of 1.4 mm. The theoretical capacity of the cell (sulfur limited) is 48 Ah. At

# Cell Test Facility Augmentation

In support of this program, Ceramatec undertook an expansion and upgrade of the sodium/sulfur cell testing facilities. When completed in early 1987, this facility will be capable of testing 20 single cells at a time. It will be computer operated and will allow cell operation under a variety of regimes including constant current and constant power discharges. In addition, a variety of parametric tests can be performed. The system will be protected against power outages by a diesel generator with automatic starting and crossover switching equipment to provide power to the cell furnaces, thus avoiding unintentional freezing of cells. A number of hardware and software redundancies have been incorporated to prevent damage to cells as a result of testing equipment malfunctions.
### Table 2–10. Beta"-Alumina Technology Progress – Ceramatec

Technology Transfer from FACC

Transfer of sodium/sulfur battery technology from FACC completed.

Cell Test Facility Augmentation

Computer-operated test facility with 20 single-cell capacity to be completed in early 1987.

#### **Test Plan Development**

Fabrication plans completed for standard zeta process and S<sup>4</sup>D process, in addition to unstabilized zirconia-toughened and partially stabilized zirconia-toughened formulations; Ford EH-2A cell chosen as electrolyte test vehicle.

Proposed test regime: constant current cycling to full-rated DOD during which cell capacity and IR measured; visual, dimensional, and mechanical property tests after cycling.

### Electrolyte Fabrication and Characterization

Tubes of the four electrolyte types fabricated and characterized.

Sodium/Sulfur Cell Fabrication

12 qualification cells fabricated under internal funding at an FACC facility.

44 electrolyte-characterization cells fabricated, but 11 electrolytes broke during assembly. Primary problems: misalignment of the electrolyte/header assembly and moisture problems with unstabilized zirconia.

**Qualification Cell Testing** 

Five of the cells underwent cycle testing and exhibited erratic behavior at increased current densities.

After 250 cycles, two cells removed to for posttest analysis.

a temperature of  $350^{\circ}$ C and discharge rate of C/3, the rated cell capacity is 41.5 Ah.

The test plan calls for cells to be cycled at constant currents to the full-rated depth of discharge. During testing, the voltage across each cell, the temperature of each cell, and the current through each cell will be measured. From these data, the cell capacity and internal resistance will be computed. Two cells from each of the four groups will be taken off test after 288 cycles (2 months), 576 cycles (4 months), and 864 cycles (6 months).

After cycling, the cells will be cooled, carefully dismantled, and the beta"-alumina electrolyte will be recovered. Each electrolyte will then be subjected to a series of visual, dimensional, physical, and mechanical-property tests. These tests will include the following:

- visual observations for apparent flaws using reflected and transmitted light
- dimensional measurements (diameter, wall thickness)
- density
- axial ionic resistivity
- microstructure (using light and electron microscopy)
- hoop strength by burst-testing of 2-cm rings and
- residual stress measurements using strain gauges.

By terminating the cell tests before electrolyte failure occurs, it is anticipated that it will be possible to determine whether any forms of slow, time-dependent electrolyte degradation are occurring and what other conditions may be developing over time, such as progressive accumulation of container corrosion products, which may eventually lead to electrolyte degradation and failure.

## Electrolyte Fabrication and Characterization

Electrolyte tubes were fabricated using each of the four designated processes (zeta,  $S^4D$ , unstabilized zirconia toughened, and stabilized zirconia toughened) and were characterized for microstructure, mass density, ionic resistivity, burst strength, and dimensional characteristics. The average densities, resistivities, burst strengths, shape factors, and fracture toughnesses (determined by double-cantilever beam tests of bar samples of the same materials) are shown in Table 2-9. Sufficient electrolytes were fabricated to yield 11 electrolytes of each type to allow for losses during cell assembly.

### Sodium/Sulfur Cell Fabrication

Prior to fabricating the cells in which the four electrolyte modifications were to be tested, Ceramatec fabricated 12 sodium/sulfur cells under internal funding to demonstrate competence at building and testing cells. The cells were fabricated according to FACC specifications for EH-2A electric vehicle cells by Ceramatec personnel at the Ford facility in Newport Beach, California. All 12 cells were then shipped to Salt Lake City for testing. Initial testing of these cells is discussed in the next section (Qualification Cell Testing).

Following the initial evaluation of the qualification cells, fabrication of the cells for electrolyte evaluation was initiated. These cells were fabricated using chromium-plated E-Brite containers rather than chromium-plated 410 stainless steel containers, as called for by the Ford EH-2A cells specification. The reason for using the E-Brite was that it was believed to be a more corrosion-resistant and more uniformly corroding material than 410 stainless steel. It would, therefore, be a more desirable material for these tests in which reduction of all extrinsic factors that may contribute to degradation of the electrolyte have been reduced to a relatively low and constant level.

The fabrication of 33 sodium/sulfur cells has been completed. During the course of cell assembly, 11 of the electrolytes broke. Six of the broken electrolytes were electrolytes toughened with unstabilized zirconia, one was toughened with partially stabilized zirconia, two were S<sup>4</sup>D electrolytes, and two were zeta-process electrolytes. Fabrication and assembly of these electrolytes is summarized in Table 2-11.

Six electrolytes (two zeta process, one S<sup>4</sup>D, one toughened with partially stabilized zirconia, and two toughened with unstabilized zirconia) broke during the operations in which the electrolyte/header assembly was pressed into the cathode container and the compression rings were installed. All six were broken circumferentially just below the headers, suggesting that the breakage was due to misalignment of either the electrolyte and header assembly or the assembly press.

The other five electrolytes broke at various times after cell assembly. One electrolyte toughened with unstabilized zirconia broke while being stored in a vacuum bell jar prior to the first bake-out operation. One electrolyte toughened with unstabilized zirconia broke in the furnace during the first bake-out. Two electrolytes (one S<sup>4</sup>D and one toughened with unstabilized zirconia) broke in the furnace during the bake-out after filling the cells with sodium. Another electrolyte toughened with unstabilized zirconia broke just as it was being removed from the filling station after being filled with sodium.

In reviewing the numbers and types of electrolytes that failed during cell assembly and the circumstances under which they failed, two problems were evident: misalignment of the electrolyte/header assembly in the cell and a larger than average number of failures of electrolytes toughened with unstabilized zirconia. The problem of fracture caused by misalignment was due primarily to an inadequate specification of electrolyte-to-header alignment in the EVEM-1 (Electric Vehicle Engineering Model) cell design. The problem can be solved by tightening the alignment specification and the qualitycontrol procedures used to check the alignment.

The problem with the unstabilized zirconia toughened electrolytes appears to be one of aging of the toughened material and is a more difficult problem to solve. It has been shown that partially stabilized zirconia undergoes some aging of mechanical properties and that the aging process is affected by the presence of moisture (K. Kobayashi, H. Kuwajima, and T. Masaki, "Phase Charge and Mechanical Properties of  $ZrO_2-Y_2O_3$ Solid Electrolyte After Aging," Solid State Ionics, 3/4, 1981, pp 489-493). The problem may be greatly exacerbated in beta"-alumina structure. If this is the case, much more stringent handling procedures and further optimization of the material are required in order to allow successful utilization of the unstabilized zirconiatoughened electrolytes outside of a laboratory environment.

### Qualification Cell Testing

Five of the twelve qualification cells were installed in Ceramatec's cell-test equipment and heated to 350 °C at the Ford prescribed rate of less than 15 °C/h to avoid thermal shock. The cells were subjected to an initial conditioning cycle by discharging them at 0.5 A to a depth of discharge of 42 Ah and then recharging at 0.5 A to a voltage limit of 2.3 V. The unrecoverable capacity was 6 Ah or 12.5% of the theoretical capacity.

Following the conditioning cycle, the cells were subjected to the test conditions shown in Table 2-12. Attempts were made early in the test to accelerate the test by operating the cells at current densities higher than the design current densities of 14 A for discharge and 7 A for charge. Doing so resulted in rather erratic behavior of the cells. The depth of discharge at the end of charge and discharge for cell \$306 is shown in Figure 2-23. Figure 2-24 shows the cycle average resistance for the same cell. These data are typical of those observed in the other four cells. After reducing the currents to design values, both the cell resistances and capacities stabilized at values that were consistent with data obtained during testing of similar cells at FACC.

After 250 cycles, two of the cells were brought to the top of charge by trickle charging and were then cooled to room temperature for posttest dissection and evaluation. The primary purpose for dissecting these cells was to develop a method for extracting the electrolytes from the cell without damaging them so that extensive, posttest characterization and analyses of the electrolytes could be performed.

						When Broken		
Process	Number Fabricated	Number Broken	Number Remaining	Header- Cathode Assembly	Before First Bake-Out	During First Bake-Out	After Filling with Na	
Zeta	11	2	9	2	-	-	-	
S4D	11	2	9	1	-	-	1	
Unstabilized Toughened S <sup>4</sup>	11 D	6	5	2	1	1	2	
Stabilized Toughened S <sup>4</sup>	11 D	1	10	1	-	-	-	

### Table 2-11. Fabrication and Assembly of Characterization Electrolytes

### Table 2–12. Test Conditions For Qualification Cells

Cycle Range	Current Discharge/Charge (A)	Voltage Cutoff Discharge/Charge (V)	Timing Discharge/Charge (h)	
1-2 3-11 12-25 26-78 79-277	$\begin{array}{ccccc} 1.0 & 1.0 \\ 14.0^* & 7.0^* \\ 21.0^* & 10.5^* \\ 28.0^* & 14.0^* \\ 14.0^* & 7.0^* \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccc} 42.0 & 42.0 \\ 3.0 & 6.0 \\ 2.0 & 4.0 \\ 1.5 & 3.0 \\ 3.0 & 6.0 \end{array}$	

\*Independent test variable changed +Lower cutoff limit independently adjusted for each cell to obtain an open circuit voltage at the end of discharge of 1.75 V.



Figure 2-23. End of Charge and Discharge Capacities versus Cycles for Cell S306



Figure 2-24. Internal Resistance of Cell S306

### Posttest Examinations of FACC Sodium/Sulfur Cells - ANL

Specialized facilities maintained at Argonne National Laboratory are used to examine selected sodium/sulfur cells. This effort supports battery development through studies of cell-failure mechanisms, morphological changes in the sulfur electrode, and the performance of cell hardware. In 1986, examinations were conducted on eight cells fabricated by (FACC). Five cells were designed for electric vehicle propulsion:

- Three cells (VB220, VB215, and VB230) were studied as part of a failure analysis conducted on the ETX-1 sub-battery.
- Two cells (VB023 and VB024) were from a group of cells that were inadvertently overdischarged.

The remaining three cells were for other purposes:

- Two cells (LL181 and MKD01) were developed for utility load leveling.
- One cell (AEC02), designed for satellite applications, was operated at Wright Aeronautical Laboratories.

Key posttest findings are discussed below and are summarized in Table 2-13.

### Failure Analysis of the ETX-1 Sub-Battery

A major accomplishment of this year's effort was establishing the underlying causes for a cellstring failure in the FACC ETX-1 sub-battery. This module consisted of four strings of 29 EVtype cells each. The cells are vertically oriented and closely packed in a hexagonal pattern, as shown in Figure 2-25. The module was wellcharged at Ford Dearborn prior to being cooled for shipment to ANL for further testing. At a temperature of about 160°C, a large decline in the voltage for the first string signaled the development of a multicell short circuit. The module was cooled to ambient temperature without further incident, and the affected cellstring was disassembled at ANL by Ford personnel as part of the repair effort to make the balance of the module operational. The ANL analysis combined module data for the cooldown period, nondestructive tests, and tear-down examinations of selected cells to reconstruct the probable sequence of events involved in the failure.

#### **Nondestructive Examinations**

Inspection of the cells from the damaged string provided the first insights on how the shorted condition developed. Only cells VB215

Failure Analysis of the ETX-1 Sub-Battery	
Nondestructive Examinations	
	Only the 5th (VB215) and 21st (VB220) cells showed visible damage: VB215 developed a vertical split in its container; the end-cap weld on VB220 was cracked.
	Voltage measurements corroborate hypothesis that VB215 leakage initiated cell failure and short-circuited the next 20 cells.
	X-ray radiography showed extensive electrolyte fragmentation and indentations in internal safety tubes in VB215 and VB220.
	Electrode levels of affected cells measured by X-ray radiography indicate current passed during self-discharge was minimal.
Tear-Down Examinations	
VB230	Tear-down of lowest-voltage cell of affected group confirms radiographic evidence of minimal current flow through shorted cells; all but obviously damaged cells recoverable.
VB215	Fragmentation near base of beta"-alumina tube allowed sodium and sulfur to react directly, forming sodium monosulfide, with a molar volume more than two times greater than molten sulfur, which exerted expansionary forces that eventually lead to cell rupture.
VB220	Same failure mechanism as VB215, though not as severe.
Reconstruction of String Failure	
	Polysulfide seeped from the vertical rupture in VB215, made contact with the 25th cell in the string, and the resultant short circuit induced a partial discharge of the intervening cells.
	$Na_2S_5$ coating on beta"-alumina electrolytes of intervening cells prevented deep discharge in all cells except VB220.
Individual Cell Analyses	
LL181	The findings on this Mark-IID cell voluntarily terminated after reaching performance goals (1825 days, more than 2500 cycles) are as follows:
	• Positive electrode mostly sulfur, some Na <sub>2</sub> S <sub>5</sub> , and some NaAlS <sub>2</sub> (from aluminum-gasket corrosion).
	• Extensive corrosion along unprotected section below compression seal and along gaps between C-shaped electrode halves; limited corrosion where chromium layer applied.
	• NaCrS <sub>2</sub> deposit (from corrosion of chromium plating) covered beta"-alumina surface, adversely affecting cycle life.

### Table 2-13. Posttest Examinations of FACC Sodium/Sulfur Cells - ANL

### Table 2-13. Posttest Examinations of FACC Sodium/Sulfur Cells - ANL (Continued)

Individual Cell Analyses (Continued)	
MKD01	The findings on this Mark-IIE cell terminated after 508 days/578 cycles because of low capacity are as follows:
	• Spallation of protective CVD-molybdenum coating contributed to extensive corrosion of the cell container.
	• Corrosion affected sulfur electrode: 35% sulfur (vs. 80% to 90% typical); sulfur depletion greatest where corrosion greatest.
VB023 and VB024	The findings on these two overdischarged ETX cells are as follows:
	• 90% sulfur in sulfur electrode.
	• High concentrations of Fe and Cr adjacent to beta"-alumina electrolyte; cause of high Fe concentrations unresolved.
AEC02	The findings on this satellite cell that failed during heat-up are as follows:
	• Separation in sodium seal probably occurred during welding of the aluminum terminal for the sodium electrode.
	• Gasket portion of the aluminum ring dislodged when the sulfur seal was formed.



Figure 2-25. Top View of the ETX-1 Sub-Battery. Note the failed cells and short-circuit path (solid loop) in the damaged string (top).

and VB220, cells 5 and 21, respectively, showed visible damage. Swelling had occurred in the lower sections of both stainless-steel containers until breaches developed. For cell VB220, the end-cap weld was completely cracked over 220° of arc. For cell VB215, a vertical split in the container was 7 cm long and 2 cm across at its widest point. Sodium polysulfides leaked through the rupture in cell VB215, and some of this material was encrusted around the base of cell VB202, the 25th cell in the two-row string, located adjacent to VB215. From these observations, a working hypothesis was formulated: 1) the failure of cell VB215 and its subsequent leakage initiated the string failure, and 2) the short-circuit involved the next twenty cells in the string.

Voltage measurements on the cold cells added support to this scenario. The failed cells, VB215 and VB220, had no measurable voltage, a clear indication that internal short-circuits had developed within these two cells. The voltage data for the other cells are listed in the third column of Table 2-14 and could be classified into three groups related to their positions in the cell string. The cells prior to cell VB215 had an average voltage of 1.287 V. The cells after VB215 up to and including cell VB202 (but excluding cell VB220) ranged between 0.219 and 0.627 V and averaged only one-third of the voltage for the first group. These results were consistent with the postulated short-circuit event. The group from the end of the string also had low voltages and averaged 0.527 V. Apparently these cells also underwent a discharge event, but no recorded data or external evidence existed for a second short-circuit or a continuation of the first short-circuit to the end of the string. Possibly the low-voltage condition developed in these cells inadvertently, during disassembly of the sub-battery.

X-ray radiography was used to evaluate the internal condition of these cells and to estimate the relative state of charge for the cells affected by the short circuit. The two failed cells showed extensive fragmentation of the beta"-alumina electrolytes and indentations in internal safety tubes. This damage was most severe in the regions corresponding to container swelling. In cell VB215, the safety tube was completely drained of sodium, and in cell VB220, the sodium level was only a fraction of its normal height. For the other cells, the internal cell components appeared to be in excellent condition. Measurements of the sodium and sulfur (or sodium polysulfide) levels are summarized in the final four columns of Table 2-14. Both levels were quite similar for the three cell groupings. The mid-string cells, for example, had mean group levels of 21.9 cm (s.d. 0.947 cm) and 15.3 cm (s.d. 0.600 cm) for the sodium and sulfur levels, respectively. The mean group levels for the cells at the beginning of the string were both within 0.7 standard deviations of the midstring values. The comparable electrode levels for cells with normal voltages and the cells with low voltages indicated that the current passed during the self-discharge event was minimal.

### Tear-Down Examinations

Cell VB230. A tear-down examination of cell VB230, the cell with the lowest voltage in the group of affected cells, confirmed the radiographic evidence of minimal current flow through the shorted section of the cell string. Axial and radial sections of the positive electrode revealed that the active material in the positive electrode was 85% to 90% sulfur, a typical quantity for a charged cell. Most of the sodium polysulfides were located in a 20 to 30  $\mu$ m band adjacent to the beta"-alumina, also a typical condition for a charged cell. This band was composed of two layers. X-ray diffraction identified the thicker outer layer as a metastable form of sodium pentasulfide (Na<sub>2</sub>S<sub>5</sub>), but attempts to establish the composition of the 2- to  $5-\mu m$  inner layer were unsuccessful. In view of the 150°C to 160°C temperature range that existed during the failure event, it seemed probable that the sulfur was still molten, but the sodium pentasulfide had cooled to a solid film on the electrolyte tube. The sodium ions transferred through the electrolyte would be restricted from reaction with the sulfur and forced to react with the sodium-pentasulfide film. Such a solid-state reaction would be expected to occur at a very low rate. The lower polysulfides formed at the interface would reduce the cell voltage without a significant effect on the bulk of the electrode. On the basis of this examination and the nondestructive test results, it appeared highly probable that all but the obviously damaged cells were recoverable.

Position	Cell	Voltage <sup>a</sup>	<u>Sodium</u>	<u>Level<sup>b</sup> (cm)</u>	<u>Sulfur L</u>	<u>evelc_(cm)</u>	
in String	I.D.	(V)	Mean	Std. Dev.	Mean	Std. Dev.	
02 03 04	VB225 VB221 VB216	1.437 1.530 0.893	21.3 21.9 21.2	0.000 0.047 0.047	16.7 14.7 15.8	0.943 0.471 1.247	
Averages		1.287	21.4	0.379	15.7	1.002	
06 07 08 09 10 11 12 13 14 15 16 17 18 19 20 22	VB221 VB210 VB209 VB208 VB206 VB205 VB197 VB196 VB195 VB235 VB232 VB230 VB229 VB224 VB222 VB214	0.420 0.421 0.627 0.321 0.510 0.454 0.511 0.480 0.430 0.477 0.395 0.219 0.397 0.404 0.461 0.490	22.4 23.8 22.2 22.4 22.0 20.8 20.8 22.3 22.2 22.6 23.5 20.4 20.8 20.8	0.047 0.000 0.047 0.000 0.047 0.047 0.047 0.000 0.047 0.000 0.000 0.000 0.000 0.047 0.047 0.047	15.3 14.5 14.9 15.9 15.5 14.9 15.7 15.3 15.6 16.0 15.2 13.8 15.8 16.4 15.9 15.1	0.986 0.816 0.837 1.133 1.354 1.367 1.344 0.629 0.975 0.408 1.027 2.376 1.109 0.534 1.170 1.397	
23 24 25	VB207 VB203 VB202	0.532 0.483 0.514	22.3 21.8 21.6	0.000 0.000 0.047	15.5 15.4 14.8	0.957 1.455 1.181	
Averages		0.450	21.9	0.947	15.3	0.600	
26 27 29	VB198 VB194 VB231	0.550 0.523 0.507	21.2 21.0 21.4	0.000 0.047 0.047	16.3 15.4 16.5	0.553 0.975 2.160	
Averages		0.527	21.2	0.200	16.1	0.586	

### Table 2-14. Cell Voltages and Electrode Levels for Cells from the Failed String of the ETX-1 Sub-Battery

The cold voltages were measured with a high-impedance ( $\approx 10^{13} \Omega$ ) circuit consisting of a digital voltmeter connected to a voltage follower. a

The sodium level was measured to the nearest 0.1 cm from the base of the cell to the solidified meniscus in the safety tube on each of three different radiographs. The sulfur level was derived from six estimates of the height where the positive electrode density declined below 70%. ь

с

Cell VB215. A comprehensive post-mortem was also conducted on cell VB215 to identify the factors responsible for the container breach that led to the string failure. Sections of the cell revealed numerous electrolyte fragments that were too small and displaced (with some missing near the breach) to attempt to locate the source of electrolyte failure. The safety tube was nonuniformly compressed and flattened into a nearly elliptical cross-section with the major axis pointing towards the rupture. Sodium polysulfides filled what was once the sodiumfilled annulus between the beta"-alumina and sodium tubes. Figure 2-26 depicts the distribution of the six different and often overlapping phases found in the bottom onethird of the cell. Nonstoichiometric sodium monosulfide (≈67.5 at % Na) was present in regions of severe swelling, such as the ring of bulges that was oriented at 60°C from the cell axis and that intersected the rupture near its midpoint. The breach region contained a mixture of sodium disulfide in sodium tetrasulfide, but much of the lower one-third of the cell contained a mixture of stoichiometric sodium monosulfide (Na<sub>2</sub>S) and sodium tetrasulfide  $(Na_2S_4)$ . Above the rupture, an abrupt transition to globules of sulfur in a matrix of sodium tetrasulfide and sodium pentasulfide was observed. Sulfur was not found elsewhere in the cell. On the ruptured side, the  $Na_2S_4$ - $Na_2S_5$  field continued up the electrode but did not completely supplant the Na<sub>2</sub>S-Na<sub>2</sub>S<sub>4</sub> field until the middle of the cell was reached. Periodic patches of sodium monosulfide and sodium disulfide  $(Na_2S_2)$  were still found in the upper  $Na_2S_4$ - $Na_2S_5$  phase field adjacent to fractures in the electrolyte.

A reasonably detailed description of the events following the electrolyte failure was interpreted from the composition and distribution of the sodium polysulfides. The positive electrode undoubtedly contained a high sulfur content, like cell VB230, prior to the electrolyte failure. The intense fragmentation noted near the base of the beta"-alumina tube resulted in much of the initial reaction occurring in the lower section of the electrode. Fast-reaction centers developed in localized areas where sodium was

easily accessible to the sulfur and formed sodium monosulfide as a solid phase (m.p.  $\approx 1180$  °C). The molar volume of this compound is 2.34 times greater than the molar volume of molten sulfur at 150°C. Continued formation of solid polysulfides was dependent upon renewing the supply of sodium to the outer surface of the electrolyte while the heat liberated by this exothermic reaction kept any nearby sulfur and newly formed, higher polysulfides in the molten state. Eventually the sodium monosulfide reached the cell exterior and exerted expansionary forces on both the container and the opposing electrolyte/safety-tube structure. These stresses induced more fractures in neighboring regions of the electrolyte and opened new pathways for sodium to reach the electrolyte surface. In this manner, solid monosulfide formation progressed around the electrolyte with each subsequent reaction center roughly located on a plane anchored by the initial center.

The cell container continued to form a ring of bulges until it ruptured. The breach permitted the molten components of the electrode to leak out. Judging by the melt composition found near the breach, the exit temperature was somewhat higher than 235°C to provide time for the melt to flow down the container, past the insulating partition between cell rows and into contact with cell VB202. The data for the string voltage indicated that four hours elapsed from the time that the electrolyte in cell VB215 failed until the multi-cell short circuit was formed.



Figure 2-26. Sketch of the Lower Section of Cell VB215. Shade patterns denote the locations of different phases.

Cell VB220. This cell, the other cell to bulge and breach, was also examined to further understand the swelling of the mechanism. Like cell VB215, fragmentation of the electrolyte, especially towards the base, was too severe to locate the initiation site. Stoichiometric and nonstoichiometric sodium monosulfide occupied essentially all of the lower quarter of the electrode. The adjoining section of the container had two separate rings of bulges. The safety tube was indented in the region corresponding to the upper bulge ring. This ring marked a transition to sulfur and higher polysulfides, such as sodium pentasulfide. In fact, sulfur was the predominant phase in the upper half of the cell.

From this morphology, it was apparent that initial monosulfide formation developed about 7 cm from the base of the cell. The propagation of fast reaction centers around the electrolyte occurred in a plane almost perpendicular to the axis of the cell. The resultant bulges in the container were insufficient to breach the container wall but were effective in creating a "plug" of sodium monosulfide that sealed off the top three-fourths of the cell. Sodium in the upper annulus reacted locally, but additional sodium from the safety tube did not penetrate the solid plug. The reaction became confined to the lower quarter of the cell. An additional bulge ring formed about 4 cm above the base of the cell, but ultimately the expansionary forces were directed axially. As the reaction advanced downward, swelling of the end-cap ensued until the weld failed. Minimal leakage occurred because conversion of the lower electrode section to sodium monosulfide was essentially complete. In fact, excess sodium remained isolated in the safety tube.

#### **Reconstruction of the String Failure**

The information gained from the nondestructive tests and the cell analyses led to the following reconstruction of the failure event. The module had cooled to about 160°C when the electrolyte fractured in the fifth cell of the first string. Different sodium polysulfides formed from the still-molten sodium and sulfur. Sodium transference through the fractured electrolyte was nonuniform, and reaction in the lower part of the cell included the formation of solid sodium polysulfides. Continued formation caused expansion of the container until a vertical rupture developed. The heat of reaction maintained higher sodium polysulfides in the molten state. The higher polysulfides seeped out and eventually contacted cell 25 in this two-row string. The resultant short circuit induced a partial discharge of the intervening cells in the string. Fortunately, a solidified film of sodium pentasulfide coated the beta"-alumina tubes and prevented a deep discharge. All but one of the twenty affected cells were considered recoverable. The only cell to fail during the selfdischarge was cell 21 in the string. The failure of the electrolyte in cell 21 again led to swelling that breached the container. Differences in the location and the degree of solid-polysulfide formation, however, minimized leakage from the cell and did not cause any additional shortcircuits.

It should be noted that other cells from other strings in this module had electrolyte failures that did not result in container swelling. Furthermore, swelling that results in breaching and leakage is a statistically rare event. However, as the failed string demonstrated, the consequence of cell swelling can be greatly magnified when individual cells are configured into battery arrays. Design improvements are needed to limit the quantity on sodium available to any one section of the cell or to redirect and accommodate the formation of sodium monosulfide within internal areas of the cell. Ford Aerospace addressed modifications needed to eliminate cell swelling in future generations of cells in a now completed program.

### Individual Cell Analyses

Descriptions of the individually examined cells and key posttest findings are summarized in Table 2-13. These results are more fully discussed below.

#### Cell LL181

Cell LL181 represented a milestone achievement in that it completed the goal of 2500 cycles for a load-leveling cell with good capacity and performance. Sulfur was the main constituent in the positive electrode of this charged cell and accounted for 80% of the phases found in the 90%-dense middle portion of the cell. Metastable forms of sodium pentasulfide formed a thin layer over the surface of the electrolyte tube and also existed as discrete globules midway through the electrode thickness. The sulfur concentration diminished to less than 50% of the phases present in both the highporosity ( $\approx 50\%$ ) upper sections and the fully dense bottom section. Sodium pentasulfide and sodium aluminum sulfide (NaA1S<sub>2</sub>) made up the differences in these sections of the electrode. The latter phase formed because of the complete corrosion of the aluminum gasket, a component of the container seal that is not essential to maintaining the seal. Particle aggregates of sodium aluminum sulfide, occupying 10% of the electrode volume, were primarily concentrated in the regions beneath the seal and at the base of the container and were always encapsulated in sodium pentasulfide matrix.

Corrosion of the cell container was also evident in this long-lived cell. The unprotected section below the compression seal showed a 75% reduction in thickness, and further corrosion would have ultimately perforated the container. (Newer cells have a plated layer of chromium applied up to the container rim.) In general, the chromium layer applied to the balance of the container showed a fairly uniform 40% reduction in thickness, but two vertical rows of corrosion pits that penetrated into the substrate were present along the separations between the Cshaped electrode halves. Elimination of these gaps should extend container lifetimes well beyond five years. The corrosion scale on the chromium plating was 30  $\mu$ m thick, but much of this corrosion product had migrated to the electrolyte and formed a porous deposit of sodium chromium sulfide (NaCrS<sub>2</sub>) that covered 75% of the beta"-alumina surface. As shown in Figure 2-27, average deposit thickness is almost linearly dependent on cycle life for cells tested at 325°C.

The condition of the other hardware components ranged from good to excellent. Aluminum compression seals and the glass seals retained their integrity with minimal degradation. The electrolyte tube featured only mild discoloration on the sodium side. The protective coating on the end-cap showed no visible deterioration.



Figure 2-27. Thickness of NaCrS<sub>2</sub> Deposits on the Beta"-Alumina Electrolyte from Cells Tested at 325°C.

#### Cell MKD01

Cell MKD01, a Mark-IIE cell voluntarily terminated because of low capacity, used a chemical vapor deposition (CVD) of molybdenum as the protective coating on the cell container. The examination identified degradation of this coating as the cause for the progressively lower capacity of this cell over its operational history. The coarse-grained coating and damage to the substrate during the deposition process contributed to extensive corrosion of the container. Reaction with the electrode melt produced a 5- $\mu$ m layer of molybdenum disulfide  $(MoS_2)$  over the surface and along the grain boundaries of the coating. Intergranular corrosion loosened individual grains and permitted direct substrate attack along the coating-substrate interface. The subcoating corrosion resulted in extensive spallation from the lower 60% of the container, such as is shown in Figure 2-28. The electrode melt infiltrated these areas and promoted continued corrosion. At the bottom of the cell, the zone between the remnant coating and the stainless-steel container was filled with iron disulfide (FeS<sub>2</sub>) and sodium-chromium sulfide. This zone accounted for 20% or more of the full electrode thickness.

The container corrosion altered the quantity and distribution of the electrode phases from what is normally found for cells terminated in the charged state. Only 35% of the active material was sulfur, whereas 80% to 90% is typical. Furthermore, the ratio of sulfur to sodium pentasulfide for a given region of the electrode was dependent on the severity of corrosion for the adjacent section of the container. As a result, this ratio declined from a maximum of about 9 near the top to a minimum of about 0.25 at the base of the electrolyte tube. This gradient was in sharp contrast to the normally uniform axial distribution observed for other electrodes in similar states of charge. The distribution of sulfur within the electrode was also unique in the lower section of the cell. Three bands of sulfur were present: one near the electrolyte, one near the spalled coating, and one within the corrosion zone. The low capacity of cell MKD01 was an understandable outcome of the altered electrode morphology. Stable corrosion products, such as FeS<sub>2</sub>, reduced the quantity of sulfur available for reaction with sodium, and normal electronic conduction within the electrode was impaired by the spalled molybdenum coating.



Figure 2-28. Corrosion Scale Between the Spalled Molybdenum Coating (upper) and the Container Substrate (bottom)

#### Cells VB023 and VB024

Cells VB023 and VB024 were part of a group of ETX cells that were inadvertently overdischarged. One characteristic of this group was reduced performance during subsequent recovery cycles. For both cells, the positive electrode was 90% sulfur. Sodium pentasulfide was restricted to isolated globules within the electrode, and a dark layer, ranging from 50  $\mu$ m to 200  $\mu$ m in thickness, at the electrolyte interface. The polysulfide layer contained high concentrations of iron (4% to 5%) and chromium (1.5% to 2%). Corrosion of the plated containers normally results in the transference of some chromium to the electrolyte, as was shown in Figure 2-27. The high iron concentrations, however, were surprising since no corrosion of the stainless-steel substrate was evident in either cell. It is postulated that the iron adversely affected the charging kinetics at the electrolyte interface during subsequent cycles aimed at regaining full capacity.

#### Cell AEC02

Cell AEC02, a prototypic cell designed to supply baseload power for intended satellite applications, developed an external short-circuit during heat-up at Wright Aeronautical Laboratories that caused the cell to selfdischarge. Prior to the attempted restart, the cell had been tested and passed inspection at FACC. The cell examination identified two possible causes, both involving assembly defects in the compression seals that could have been aggravated during shipment.

For the sodium seal, one section of the aluminum ring was partially melted, leaving a separation in the seal. If this condition existed prior to testing, it probably occurred during welding of the aluminum terminal for the sodium electrode.

For the sulfur seal, the gasket portion of the aluminum ring was dislodged when the seal was formed. Corrosion of this aluminum seal was extensive. One section of the sulfur seal, slightly offset from the damaged section of the sodium seal, was completely corroded. The degree of corrosion made it difficult to assess the initial effectiveness of the sulfur seal. The selfdischarge occurred when leakage through one of these seals formed a thin, conductive film that bridged the insulating alumina collar between the two compression seals. The positive-electrode composition was approximately sodium tetrasulfide, an indication that the self-discharge was extensive and required a highly conductive bridging film. This finding made leakage of molten sodium through the damaged sodium seal the more likely cause of the self-discharge.

### Chapter 3. Battery Technology Evaluation

### Introduction

Rechargeable cell and battery testing was performed within the Battery Technology Evaluation Element. Work was carried out at Argonne National Laboratory (ANL), Sandia National Laboratories (SNL), and at field experiment sites in Colorado and Hawaii. Evaluation tasks consisted of cell and battery laboratory testing at ANL, specialized cell and battery testing at SNL, and solar generator/battery system testing at the field sites.

The objective of these activities was to provide independent prototype testing. The majority of units tested were deliverable units from the DOE Office of Energy Storage and Distribution (OESD) battery development projects. During the year, cells and batteries from CSPL, ERC, FACC, Exxon, Lockheed, COMSAT, and JCI were evaluated. The results of these tests were used in part to verify developer claims and predictions. Additional tests were conducted to characterize each prototype fully. These tests assisted in identifying the strengths and weaknesses of each technology. In some cases, problem areas were identified for additional research and development tasks, either by the developer, or at a national laboratory. These evaluations provided essential information for critically judging the technical progress of each development project. In virtually all cases, the evaluation activities provided new performance and design information that was previously unknown by the developers.

A wide variety of test methods was utilized in these experiments. No two tests were the same. At ANL, tests were performed to determine peak power, specific power, selfdischarge rate, and lifetime. At SNL, evaluation techniques included capacity measurements, parametric and factorial tests to determine performance prediction equations, and special electrical, chemical, and mechanical studies. In all cases, collected data described cell or battery voltage, current, temperature, and other parameters determined by the technology under test. These data and results were distributed to DOE and national laboratory program managers for use in judging the progress of the development projects. The tests were conducted with the close cooperation of the respective developers, and the results were shared in a timely and open manner to provide the maximum benefit to each project.

In 1986, evaluation work at ANL was consolidated. Several different evaluation and analysis projects were brought together into one group. The National Battery Test Laboratory (NBTL) was replaced by the Analysis and Diagnostic Laboratory (ADL). Three activities were part of this project: Experimental Evaluations of Advanced Battery Technologies, Sodium/Sulfur Cell Posttest Examinations, and Modeling and Statistical Data Analysis. (Sodium/Sulfur Posttest Examinations are discussed in Chapter 2).

Under Experimental Evaluations of Advanced Battery Technologies, testing was completed on several FACC sodium/sulfur cells and one battery, an Energy Development Associates zinc/chloride battery, an Exxon zinc/bromine battery, and several Exide lead-acid batteries. New tests were started on a JCI flow-through lead-acid cell, and a CSPL sodium/sulfur cell. Evaluation continued on an Exxon 30-kWh zinc/bromine battery. Key results of these tests included the determination of the specific energies of FACC and CSPL cells between 100 and 200 Wh/kg. Cycle lives of the FACC loadleveling cells ranged from 659 to 1366 cycles. The 30-kWh zinc/bromine battery was found to be power-limited above 25 W/kg discharge rates. In addition, several design features of the zinc/bromine battery were identified as needing improvement. Tests of several other technologies were funded by other organizations at the ADL and are reported for completeness.

Work in Modeling and Statistical Analysis resulted in the development of a model of a sodium/sulfur cell with a conductive glass electrolyte. The model was used to characterize several cell designs and to predict cell performance. The model will be expanded next year to include cells with other electrolytes such as the beta"-alumina tubes used in CSPL cells.

At SNL, evaluation continued on FACC sodium/sulfur cells, and COMSAT and JCI nickel/hydrogen cells and batteries. Testing was concluded on several Exxon zinc/bromine batteries and a GEL zinc/bromine battery. New tests were started on CSPL sodium/sulfur cells and on an ERC zinc/bromine battery. Some key findings of these tests were that an Exxon 8-cell zinc/bromine battery was operated for over 2000 electrical cycles with good performance. The characteristics of this battery will be studied in detail next year to determine which factors contributed to its longevity. In the first test of a CSPL cell, abnormally high resistance was observed. The cell failed after 23 cycles. Other CSPL cells operated normally in initial tests. An ERC zinc/bromine battery failed after 8 cycles. The reasons for these unexpected failures were under study at the end of 1986. These results will likely impact the development projects as the causes of the failures are determined next vear.

A significant event occurred in the SNL field test work. A 20-kWh Exxon zinc/bromine battery was successfully charged by a photovoltaic array. This was the first advanced battery system operated in such a manner. Good battery performance was observed in these tests. The entire system operated well and the results indicated that large, advanced batteries such as this could routinely be charged with solar generators.

The remainder of this chapter presents these results in detail. The ANL work is described first, followed by the SNL laboratory evaluations, and finally by the SNL field test experiments.

### **Battery Evaluations at ANL**

The Analysis & Diagnostic Laboratories (ADL) at Argonne National Laboratory (ANL) was formed in April 1986 to carry out a battery technology-evaluation program under the direction of the Exploratory Battery Technology Development (ETD) Program at Sandia National Laboratories (SNL). The ADL project has identified deficiencies in advanced battery technologies and has defined the most promising R&D approaches for overcoming these deficiencies. The ADL effort encompasses

- Experimental evaluations of batterydevelopment technology. These evaluations include the parametric, performance, and life investigations required for the particular interim technologies.
- Analysis of experimental data. Experimental data were statistically analyzed to quantify the effects of key design and operational parameters on performance.
- **Post-experimental examinations.** Physical and chemical analyses of cell components were performed to determine degradation and failure mechanisms, and to identify areas requiring further R&D.
- **Research investigations.** These investigations provided basic modeling data and searched for solutions to technology limitations.
- Modeling of advanced batteries. Advanced batteries (sodium/sulfur, zinc/bromine, and so on) are being developed for loadleveling (LL) and electric vehicle (EV) applications. Electrochemical modeling permitted rapid, analytical prediction of battery performance and provided direction for experimental and postexperimental evaluations. In addition, the modeling effort quantitatively correlated post-experimental findings and experimental data.

### **ADL Highlights**

During 1986, the ADL performed technology evaluations for the DOE Office of Energy Storage and Distribution (OESD) and Office of Transportation Systems (OTS), the Electric Power Research Institute (EPRI), and others. The results of the OESD technology evaluations are primarily discussed here. However, selected results from the Electric Hybrid Propulsion Division of OTS (OTS/EHP) and "work-for-others" evaluations are presented to provide a more complete picture. The highlights of these technology evaluations are separated into three categories:

- experimental evaluations of advanced battery technologies,
- modeling and statistical analysis, and
- posttest examinations.

These three categories are introduced below.

**Experimental Evaluations of Advanced Battery Technologies.** 696 cells were tested in 1986. Tests were initiated on 261 cells, continued on 295 cells, and completed on 176 cells. Table 3-1 lists the batteries, modules, and cells tested; test results are summarized in Table 3-2.

### Table 3–1. ADL Experimental Evaluations of Advanced Battery Technologies

Number	Description	Supplier
a) Tests Initiated (	(261 Cells)	
1	89-Cell Sodium/Sulfur ETV-1 Sub-Battery	FACC
1	Sodium/Sulfur Single Cell	CSPL
1	Flow-Through Lead-Acid Single Cell (1986 Baseline)	JCI
1 2 2	140-Cell Nickel/Iron Battery Pack 5-Cell Nickel/Iron Module 5-Cell Advanced Nickel/Iron Module	Eaton/EPI/DSEP Eaton/EPI/DSEP EPI
2	5-Cell Advanced Nickel/Cadmium Module	ERC
b) Tests Continued	(295 Cells)	
1	124-Cell Zinc/Bromine Battery	Exxon
1	Sodium/Sulfur Single Cell	CSPL
2	5-Cell Nickel/Iron Module	EPI
1 2 2	140-Cell Nickel/Iron Battery 5-Cell Nickel/Iron Module 5-Cell Nickel/Cadmium Module	Eaton/EPI/DSEP Eaton/EPI/DSEP ERC

Modeling and Statistical Analysis. These evaluations were sponsored by four different programs:

- Under the ANL Advanced Battery Development Program, a mathematical model of a sodium/sulfur cell with conductive glass electrolyte was developed.
- Under the SNL/ADL program, the sodium/sulfur cell model for the glass

electrolyte is being modified to simulate the FACC and CSPL sodium/sulfur cells.

- Under EPRI support, a thermal model of the Jet Propulsion Laboratories (JPL) sealed lead-acid battery was developed and compared with a Gould GC2-EV200 battery model.
- A statistical analysis of test data on the JCI EV-2300 lead-acid battery was completed for EPRI.

## Table 3–1. ADL Experimental Evaluations of Advanced Battery Technologies (Continued)

Number	Description	Supplier	
c) Tests Completed	(176 Cells)		
4	Load-Leveling Sodium/Sulfur Single Cell	FACC	
4	Sodium/Sulfur EV Single Cell	FACC	
1	89-Cell Sodium/Sulfur ETX-1 Sub-Battery	FACC	
1	24-Cell Zinc/Chloride Load-Leveling Battery	EDA	
1	8-Cell Zinc/Bromine Module	Exxon	
1	6-Cell Lead-Acid Load-Leveling Module	Exide	
2	3-Cell Lead-Acid Load-Leveling Module	Exide	
1	Flow-Through Lead-Acid Single Cell	JCI	
4	5-Cell Nickel/Iron Module	SAFT	
2	5-Cell Nickel/Iron Module	EPI	
1	4-Cell Nickel/Zinc Module	Electro- chimica	

Table 3-2. Experimental Evaluations at ANL

## Sodium/Sulfur Technology (LL/EV) - FACC/CSPL

FACC

.

LL Cells	Cycle lives of 659 to over 1366 cycles (2.5 to 5.5 years).
	Special charge regime required to maintain full cell capacity.
EV Cells	Range exceeds 240 miles.
	High specific energy and peak power when compared to other technologies.
	Highest specific energy when cell discharge voltage is terminated at the knee of the discharge curve, but this incurs a risk of damaging the cell by over-discharge.
	Problems encountered with FACC charge/discharge algorithm.
CSPL	Initial evaluations indicate that specific energy of the naked CSPL cell is 18% greater than that of the naked FACC cell.
Zinc/Bromine Technology (EV) - Exxon	
	Up to discharge rates of 25 W/kg, specific energy is as great as that of the nickel/iron and nickel/cadmium technologies; zinc/bromine performance is power-limited above 25 W/kg.
	Driving profiles project a range of 58 to 94 miles (comparable to nickel/iron technology).
	Technology reliability and battery life are not yet adequate; additional R&D required.
Flow-Through Lead-Acid (EV) - JCI	
	Forced flow of electrolyte in this EV battery dramatically increased material utilization, but cut life down to 30 cycles.
Advanced Lead-Acid (LL) - Exide/C&D	
6-Cell Module	2300 cycles at 50 °C accrued (equivalent to 6400 25 °C cycles); still cycling.
3-Cell Module	1060 cycles at 60°C accrued (equivalent to over 3240 25°C cycles); still cycling.

### Table 3-2. Experimental Evaluations at ANL (Continued)

Advanced Lead-Acid (LL) - Exide/C&D (Continued)	
3-Cell Module	Terminated after 3950 equivalent cycles because of leaks in cell cases.
Advanced Nickel/Iron Technology - EPI	
1985 Technology	Nickel electrode 20% thicker than that of 1984 technology; 14% greater specific energy, but a loss in peak power.
1986 Technology	Nickel electrode 50% greater than that of 1984 technology; both specific energy and peak power greater than that of 1985 technology.
Advanced Nickel/Cadmium Technology (EV) - ERC	
	Specific energy comparable to the lower range of the nickel/iron technology.
	Electrolysis may jeopardize development of reduced-watering battery.
Changes in Testing Capability	
	67 computer-controlled test stations currently operating; test equipment ordered for 17 CSPL sodium/sulfur cells and modules.
Software Upgrades and Additions	Control tasks written to calculate cell discharge termination voltage for sodium/sulfur cells.
	Software written for testing FACC sodium/sulfur sub-battery.
	Software for the Exxon zinc/bromine battery extensively modified.
	Four FUDS-based driving profiles developed.
	Software developed for nonstandard charging algorithm in an Eaton battery pack.
	New FUDS profile based on data from Eaton generated; another Eaton FUDS profile implemented.
	Software developed that measures gas evolution from high float voltages.

Ξ

### Table 3-3. Modeling and Statistical Analysis at ANL

Electrochemical Model Development

Mathematical model of sodium/sulfur cells with glass and beta"-alumina electrolytes developed.

Thermal Model Application

This model showed that JPL sealed lead-acid module delivers more energy than Gould GC2-EV2000 battery with the same temperature rise.

Statistical Analysis of Test Data

Cell performance variations in JCI EV-2300 lead-acid battery found to depend primarily on peak-power demands and cell location.

Table 3-3 summarizes the progress in modeling and statistical analysis at ANL.

**Posttest Evaluation.** Posttest evaluation was performed on eight FACC sodium/sulfur cells. Five cells were for electric vehicle propulsion, two were for utility load leveling, and one was for satellite application.

Key posttest findings are presented in Chapter 2 of this report (Posttest Examinations of FACC Sodium/Sulfur Cells - ANL). Experimental evaluations of advanced battery technologies and modeling and statistical analysis are discussed below.

## Experimental Evaluations of Advanced Battery Technologies

#### **Test Description and Results**

Most of the data from these evaluations have been generated by test procedures developed at ANL and in cooperation with other battery testing organizations. These procedures, described in detail in previous reports, are summarized in Table 3-4. In addition, the ADL continues to explore improved test procedures, analyses, and methodologies.

Of the spectrum of tests performed, the Ragone plot is the most useful for comparing EV battery technologies. It maps the specific energy available from a battery as a function of the specific discharge power level. Ragone plots are provided in Figures 3-1, 3-2, and 3-3. They show the results of experimental evaluations performed at the ADL in 1985 and 1986 for the following technologies: sodium/sulfur, nickel/iron, nickel/cadmium, flow-through leadacid, and zinc/bromine.

Measurement of available peak power as a function of DOD is another useful test. These data can predict vehicle ranges (discussed in previous annual reports), in addition to providing a basis for technology comparison. The peakpower data obtained at ADL in 1985 and 1986 are shown in Figures 3-4 and 3-5.

Test results are distributed to DOE battery users as inserts to the National Battery Testing Laboratory (NBTL) Information Notebook. These results are also presented at conferences and published in the open literature. Battery users report that information in the NBTL inserts, which follows a standardized format, is most useful. This information is being considered for a computerized data base.

In 1986, information packets on the following subject areas were distributed to NBTL Information Notebook holders:

- performance characterization of the FACC sodium/sulfur EV cells, and
- the EDA zinc-chloride battery for LL applications.

Application	Procedure					
Load Leveling	Capacity Verification					
	Capacity and Energy versus Discharge Rate (Constant Power and Constant Current)					
	Capacity and Energy versus Temperature					
	Self-Discharge					
	Partial Discharge					
	Load Profiles					
	Life-Cycling					
Electric Vehicle	Capacity Verification					
	Capacity and Energy versus Discharge Rate (Constant Power and Constant Current)					
	Capacity and Energy versus Temperature					
	Self-Discharge					
	Partial Discharge					
	Load Profiles					
	Life-Cycling					
	Sustained Hill-Climbing					
	Peak Power versus DOD Driving Profiles (with and without regenerative braking): SAE J227aD/ETV-1, SFUDS79/IDSEP, and SFUDS/DSEP					

### Table 3-4. ADL Advanced Battery Technology Test Procedures

### Sodium/Sulfur Technology (LL/EV) – FACC/CSPL

For several years, DOE has conducted a program to develop sodium/sulfur batteries for LL and EV applications to meet cost and performance requirements. The key goal is to increase battery life while pursuing low initial costs. Recent contracts with FACC and CSPL have produced LL and EV cells and batteries for evaluation at ADL. Evaluations were recently completed on the following cells from FACC: four LL cells, five EV cells, and a sub-battery of 89 EV cells connected in series. CSPL evaluation has just been initiated.

FACC Technology. Two of the four LL cells were subjected to abbreviated performance characterization followed by life-cycle tests; the remaining two LL cells underwent life-cycle tests only. These evaluations indicate that the technology is improving, but long-term reliability is not yet adequate for utility applications. The cells exhibited cycle lives ranging from 659 to over 1366 cycles, equivalent to 2.5 to 5.5 years in utility use. It was found that full cell capacity could be maintained only by applying a special charge regime consisting of



- O (FACC) NAKED CELL CONSTANT POWER DISCHARGE TERMINATED AROUND VOLTAGE KNEE (RECEIVED IRREVERSIBLE DAMAGE AT LOWEST DISCHARGE RATE)
- △ (FACC) NAKED CELL CONSTANT POWER DISCHARGE TERMINATED WITH FORD ALGORITHM
- (CSPL) NAKED CELL TERMINATED WITH CSPL ALGORITHM
- (GACC) NAKED CELL + 30% BURDEN FOR PRO RATA SHARE OF BATTERY ENCLOSURE (Wt. = 0.98 kg) TERMINATED WITH

FORD ALGORITHM FORD DISCHARGE CUTOFF VOLTAGE ALGORITHM V = 1.760 - (0.008) I CSPL DISCHARGE CUTOFF VOLTAGE ALGORITHM V = 1.900 - (0.034) I I = CELL DISCHARGE CURRENT

Figure 3-1. Ragone Plots for Sodium/Sulfur Technologies

constant-current followed by constant-voltage charge.

Evaluations of the EV cells (SAE J227aD/IETV-1 driving profile with a 30% weight burden) indicate that the technology of these cells and the 89-cell EV sub-battery have the necessary power and capacity to drive an electric vehicle over 240 miles. The specific energy of the sodium/sulfur cells is very high in comparison to other technologies (compare Figures 3-1 and 3-2). Also, the peak power of sodium/sulfur cells available (as a function of DOD) exceeds that of nickel/iron cells (Figure 3-4).

The specific energy data for the Ford EV cells presented in Figure 3-1 were measured under three discharge-cutoff conditions. The highest values were obtained when the cell discharge voltage was allowed to terminate around the knee of the discharge voltage curve. However, the first cell discharged in this manner was severely damaged by a slight overdischarge. An algorithm that compensated for cell internal voltage losses by providing for a greater



Figure 3-2. Ragone Plots for Nickel/Iron and Nickel/Cadmium Technologies

discharge voltage margin (thus preventing overdischarge) was adopted for all subsequent tests. The lowest specific-energy values for Ford EV cells in Figure 3-1 reflect a 30% weight burden that accounts for a pro rata share of the insulated battery enclosure required for the high operating temperatures of the sodium/sulfur battery.

The evaluation of the 89-cell EV battery indicated there were problems with the charge/discharge algorithm provided by Ford. This complicated algorithm calculated the number of failed cells in a battery string. However, it was unable to satisfactorily account for a partial failure mode where an EV cell looked like a good cell on charge but acted like a shorted cell on discharge.

**CSPL Technology.** The CSPL technology evaluation has just been initiated at the ADL; however, from Figure 3-1 it is evident that the specific energy of the naked CSPL cell is about 18% greater than that of the naked Ford cell when both cell types use comparable discharge algorithms to prevent over-discharge.



Figure 3-3. Ragone Plot for 30-kWh Zinc/Bromine Battery with 208 Ahs of Charge



- O ERC (Ni/Cd) 1986 TECHNOLOGY
- SAFT (Ni/Fe) 1985 TECHNOLOGY
- EPI (Ni/Fe) 1986 TECHNOLOGY
- O ERC (Ni/Cd) 1985 TECHNOLOGY
- $\Delta$  EPI (Ni/Fe) 1985 TECHNOLOGY
- EATON/EPI/DSEP (Ni/Fe) TECHNOLOGY (SCALED TO 1/28 OF PACK WEIGHT)
- ✓ FACC (FORD) (Na/S) EV TECHNOLOGY (Wt. = 0.98 kg; NAKED CELL + 30% BURDEN)

Figure 3-4. Peak Power versus DOD for Nickel/Iron, Nickel/Cadmium, and Sodium/Sulfur Technologies

### Zinc/Bromine Technology (EV) - Exxon

SNL has been developing zinc/bromine battery technology for the DOE for a number of years through contracts with Exxon, ERC, and JCI. The objective is to advance zinc/bromine technology to meet the cost and performance requirements for EV and LL applications.

The ADL has been testing the performance of two EV battery systems from Exxon: one 1-kWh, 8-cell module and one 30-kWh, 124-cell battery. The evaluation results (compare Figures 3-2 and 3-3) indicate that, up to discharge rates of 25 W/kg, specific energy of the Exxon technology is comparable to that of the nickel/iron and nickel/cadmium technologies, but it is power-limited above discharge rates of 25 W/kg. Raising the temperature significantly affects the specific energy available for discharge (Figure 3-3). The ADL testing included performing charge/discharge driving profiles that simulate the operation of the battery in a van or

car. These driving profiles projected ranges of 58 to 94 miles, comparable to the present nickel/iron technology. The ADL evaluation also identifies component failures and electrolyte leakage as significant problems. Because technology reliability and life are not yet adequate, additional R&D in design, materials, components, and safety is necessary.



Figure 3-5. Peak Power Data for 30-kWh Zinc/Bromine Battery. Data were derived from SFUDS79 drive cycle.

#### Flow-Through Lead-Acid Technology (EV) - JCI

DOE/OTS/EHP has sponsored a cost-shared program with JCI to develop a flow-through lead-acid battery for electric vehicles to improve battery performance and life. The innovative design uses forced flow of the electrolyte through porous lead and lead dioxide electrodes, which dramatically increases the utilization of these materials.

JCI fabricated a proof-of-feasibility cell and a baseline cell for testing at ADL using DOE/OESD funds. Tests have demonstrated that material utilization is 85% greater than that obtained in commercial lead-acid batteries. This major increase in utilization (and resultant increase in specific energy) would extend vehicle range.

However, in addition to range, cycle life must be considered. The cycle life of each of these cells was less than 30, if cycle life is defined as the number of 80% or greater charge/discharge cycles before capacity drops below 75% of initial or rated value.

## Advanced Lead-Acid Technology (LL) - Exide/C&D

From 1979 to 1985, ANL, with funding from DOE/OESD and the cooperation of SNL, conducted a program on the development of lead-acid batteries to meet cost and performance requirements for load-leveling applications. The key goal was increasing battery life from 2000 to 4000 cycles while maintaining low initial cost. Until 1982, ANL directed cost-shared R&D contracts with Exide and C&D Batteries.

Exide developed a prototype design and three modules were delivered to the ADL in April 1982 for testing: one 6-cell module (3100-Ah rated capacity and 36-kWh at the 5-h discharge rate) and two 3-cell 18-kWh modules. ADL performed characterization (parametric performance evaluation and simulated application) tests and accelerated life-cycle (80% DOD) tests on these modules. These tests have been described in previous reports.

During 1986, life-cycle testing has continued on two of the three modules, and testing on the third module was terminated in late 1985. These tests are summarized below.

- Through November 1986, the 6-cell module accrued 2300 cycles at 50°C, equivalent to 6400 25°C cycles (one 50°C cycle is assumed equivalent to 2.8 25°C cycles).
- Through October 1986, one of the 3-cell modules accrued 1060 cycles at 60°C, equivalent to over 3240 25°C cycles (acceleration factor of 4.1 assumed).
- In December 1985, testing at 60°C was terminated on the other 3-cell module after it had accrued 3950 equivalent cycles. Leaks induced by the high temperatures caused leaks in two of the cell cases.

The capacity of all three of the above modules remained at over 100% of rated capacity.

Testing the above modules provided a measurement of cycle life at different temperatures, with which the feasibility and project economics for load-leveling applications could be assessed. These ADL tests show that the Exide lead-acid load-leveling modules have operated reliably, exceeding the design goal of 4000 cycles. Southern California Edison (SCE) has selected this technology for their 65-MWh, 10-MW, load-leveling facility in the Chino, California, area, which is planned for completion in 1987.

In addition, arsine and stibine emission investigations under EPRI's sponsorship were carried out under a cooperative effort during the DOE-sponsored life-cycle testing. It is planned that one cell from the 60°C test module terminated October 1986 and one additional cell that had accrued 2200 cycles at 40°C at Exide (terminated in 1985) will receive posttest analysis under EPRI sponsorship in support of the SCE project.

### Advanced Nickel/Iron Technology - EPI

Advanced nickel/iron battery technology has been under development by Eagle-Picher Industries, Inc. (EPI), since May 1978 under cost-shared DOE-OTS/EHP contracts. One of the latest contracts (initiated January 1986) seeks to improve the performance and reduce the cost of nickel/iron batteries. This R&D effort has focused on doubling the thickness of sintered nickel electrodes while maintaining the porosity and strength required for good performance and long life.

The results of ADL tests to evaluate performance and life characteristics of modules with plate thickness 20% greater than normal (1985 technology which was partially funded by DOE/OESD) and 50% greater than normal (1986 technology) are shown in Figures 3-2 and 3-4. The results indicate that the specific energy of the 1985 technology was 14% greater than that of the 1984 technology, but the 1985 technology exhibited a corresponding decrease in peak power (not shown in Figure 3-4). For the 1986 technology, both the specific energy and peak power have increased over that of the 1985 technology.

Figures 3-2 and 3-4 show results on other nickel/iron technologies evaluated in 1986.

Characterization test results of modules from the 1985 SAFT and 1986 Eaton/DSEP (EPI) technologies provide a spectrum of specific energies and peak powers. This shows that specific energies and peak powers of a given technology are highly dependent on design and construction.

## Advanced Nickel/Cadmium Technology (EV) - ERC

Since March 1985, an advanced nickel/cadmium battery has been under development by ERC under cost-shared contracts with DOE/OTS/EHP. Improved performance and reduced costs in this technology are sought. R&D is focused on low-cost polymer-bonded electrodes and design optimization for vehicle use. The ADL has conducted performance characterizations on the 1985 and 1986 technologies.

Results indicate that the nickel/cadmium specific energy is comparable to the lower range of the nickel/iron technology; however, in vehicular applications, available acceleration (peak power) at higher DODs may limit travel distance. In addition, lack of cell integrity (electrolyte weepage at the cell-top joints) early in cycle life of both 1985 and 1986 nickel/cadmium batteries indicates that hydrogen leakage may be a problem. Although not essential to the success of the program, escape of hydrogen and the resultant loss of electrolyzed water may jeopardize the project goal of developing a low-maintenance (reducedwatering) battery.

### Changes in Testing Capability

The ADL facilities were modified to meet the needs of the battery test program. Currently the ADL has 67 fully instrumented computercontrolled test stations, and equipment has been ordered to test 17 CSPL sodium/sulfur cells and modules. The additional equipment will satisfy the low current requirements for conditional start-up and operation of the CSPL cells.

Several major changes were made to the hardware and software components of the ADL automated data-acquisition and process-control system. The major hardware upgrade was the addition of two Digital Equipment LNO3-plus laser printers that replaced the difficult-tomaintain Versatec V80 printer/plotter. The laser printers offer improved performance and lower maintenance costs.

The major 1986 software upgrades and additions are listed below.

Supported by DOE-OESD:

- Control tasks were written to calculate cell discharge termination voltage dynamically for tests on sodium/sulfur cells (FACC and CSPL discharge algorithms).
- Software was provided for testing the Ford sodium/sulfur ETX-1 sub-battery, which consists of one-third of a battery pack. It accommodates separate charging and discharging supplies, monitors vacuum enclosure, controls the cooling fan, monitors the temperature probes (thirdorder polynomial calibration), amongst other features. The charge regime is a unique, three-step process that requires dynamic calculations of the termination criteria for each phase. The software can handle three strings of 29 cells. It can detect the failure of one or more cells per string and vary the charging conditions accordingly.
- Software for the Exxon zinc/bromine battery was extensively modified to allow manual control of battery pumps and valves and to support driving-profile discharges followed by the stripping phase.
- Four FUDS-based driving profiles were developed: 1) an improved light-van FUDS profile limited to 79 W/kg (360 s duration), 2) a version of the previous profile with much less structure (also 360 s in length), 3) a 1372-s FUDS-based profile for the IDSEP vehicle with power requirements as high as 112.6 W/kg, and 4) a variant of the IDSEP profile clamped to a maximum power of 79 W/kg.

### Supported by DOE-OTS/EHP:

• Software for an Eaton battery pack was developed featuring the following

nonstandard charging algorithm: 1) constant-current charge until temperaturecompensated battery terminal voltage reached, 2) constant-voltage charge until current tapers to a specified value, and 3) constant-current charge until a 120% or higher recharge factor is attained. To accomplish this, a charge permission signal from the Eaton equipment and an average power consumption signal from the accessory equipment (blowers, controllers, and heaters) have to be monitored.

- Major revisions were made to the drivingprofile software for the Eaton battery pack to support secondary profiles that can be executed at an arbitrary point within a standard driving profile. This software now supports a 20-s acceleration pulse 49.5 miles into a FUDS simulation, followed by termination or continuation of the FUDS discharge cycle.
- A new FUDS profile based on data from the Eaton Corporation was generated. This profile, which contained the definition of the secondary profile acceleration pulse mentioned above, requires a peak power of 63.6 W/kg and a minimum power load of 0.92 W/kg.
- The first FUDS profile based on data from Eaton Corporation was implemented. It modeled a DSEP van and had a peak power of 69.7 W/kg and a minimum load of 1.83 W/kg.

Supported by others:

• Software has been developed to support an ADL-designed system that measures the volume and rate of gas evolution resulting from high float voltages. It outputs instantaneous as well as average flow rates.

### Modeling and Statistical Analysis

### Electrochemical Model Development

A mathematical model was developed in 1986 for sodium/sulfur cells with conductive glass electrolyte. The model calculates distributions in current, potential, composition, and temperature based on cell geometry, sulfur polarization, and resistances (of the current collector, glass electrolyte, graphite matrix, and polysulfide melt). The model evaluated various cell designs and predicted the specific energy and specific power of the cell under different design and operating conditions.

Figure 3-6, an example of the model calculation, shows that the thickness of the glass electrolyte strongly affects the specific power of the cell. A cell with 0.1-mm thick glass can achieve a peak power of 900 W/kg at a 6.2-A discharge rate. This information helps select designs that meet the energy and power requirements for various applications. The model can also be used to study degradation mechanisms under various operation conditions. It has been extended to include other electrolyte materials in order to compare the performance of sodium/sulfur batteries from different developers (such as FACC and CSPL). Calculations from the modified model will be validated with the sodium/sulfur test data to identify advantages of different design features. Other electrochemical models will be developed for advanced systems such as tubular lithium/iron disulfide cells.



Figure 3-6. Modeling of Power in Glass Electrolyte Sodium/Sulfur Cells

#### **Thermal Model Application**

The ANL generic three-dimensional thermal model was published and transferred to several

industrial users in 1986. It was used to evaluate the thermal behavior of the advanced JPL sealed lead-acid battery for EPRI. This model showed that the JPL sealed module can deliver more energy than the Gould GC2-EV200 battery with about the same degree of temperature rise. Under a SAE J227aC profile, the maximum temperature rise for this battery was 15.5°C for a VW van, and 9.5°C for a Bedford van. Therefore, no excessive heating problems for this battery are anticipated in Bedford van applications. A report was prepared for EPRI on the thermal behavior of the JPL battery.

#### Statistical Analysis of Test Data

Data on capacity and peak power of JCI EV-2300 lead-acid batteries tested at ANL under EPRI support underwent multiple regression analysis to

- verify the statistical significance of the test results and
- quantify effects of operating parameters on battery performance variation and degradation.

The results show the primary factors causing performance variation were peak-power demands by the vehicle and cell location within the sixcell module. As the level of peak-power demand increased, degradation of capacity and specific peak power accelerated. For example, when the peak power (SAE J227aC profile for a VW van) increased from 35 W/kg to 57 W/kg, the capacity-degradation rate increased from 0.230 to 0.317 Ah/cycle. When power demand was increased by the same amount, the degradation rate in specific peak power increased from 0.112 to 0.191 W/kg/cycle.

Analysis of test data on the 54 cells indicated that the two end cells in each six-cell module had a consistently higher rate of capacity degradation. On the average, the difference in capacity degradation rates between middle cells and end cells was about 0.11 Ah/cycle. In most cases, the end cells eventually limited the capacity of the module. The causes of poorer performance by the end cells are being investigated.

### Battery Evaluations at SNL

SNL battery evaluation activities were divided into two categories:

- Prototype Battery Evaluations. Flowing electrolyte cells and batteries, sodium/sulfur cells, and nickel/hydrogen cells and batteries were tested under specialized parametric evaluation regimes. Computer-controlled test facilities completed in 1982 were used to perform these activities.
- Battery Field Tests for Solar Applications. Two battery/solar energy system experiments were in progress at remote sites, while another was in progress at SNL's Photovoltaic Advanced Systems Test Facility (PASTF). Sandia-designed, computer-controlled data acquisition systems were used in these experiments.

Several significant events occurred in the prototype evaluation effort. An Exxon zinc/bromine battery completed 2025 electrical cycles this year. It was removed from test prior to failure for posttest examination. This unit is the longest-lived prototype tested to date, and has provided valuable data concerning the longevity of zinc/bromine batteries. Evaluation was completed on two other Exxon zinc/bromine batteries, one ERC zinc/bromine battery, one GEL zinc/bromine battery, and one Lockheed zinc/redox cell. The ERC battery failed after eight cycles. It will be disassembled early next year to determine the cause of failure. The Lockheed cell performed better than units tested at SNL in 1985, but fundamental problems were identified during these tests. In other areas, evaluation of six FACC sodium/sulfur cells continued. By year's end, one cell had completed 680 cycles with stable performance. Other FACC cells demonstrated unexpected charge acceptance limitations. One CSPL cell was placed on test and failed after 23 cycles. The cause of this failure, which resulted in electrolyte fracture, is under investigation. Three other CSPL cells were placed on test, and initial performance was good. Several nickel/hydrogen cells and batteries were evaluated during the year. Experiments were performed to characterize several charging methods.

Battery field tests with solar electric generators provided valuable data for the sealed lead-acid and zinc/bromine technologies. A 20-kWh Exxon zinc/bromine battery was successfully operated with a photovoltaic array in 1986. The sealed lead-acid/wind turbine generator experiment in Colorado was concluded after 18 months of successful operation.

To support the evaluation activities, the battery laboratory was maintained and improved during the year. Equipment was assembled and software modified for testing CSPL cells. One test bench was completed for electrical evaluations of sodium/sulfur cells or strings, and plans were made to modify another existing bench for this same purpose. Another test bench was completed that provided stations with fumehood and environmental-chamber access. These stations will be used primarily for flowingelectrolyte battery evaluations. Plans were made and fabrication started on a portable test station for running peak-power and simple power profile tests on small cells. In addition, the laboratory equipment was calibrated on schedule and maintained as necessary.

### **Prototype Battery Evaluations**

### Flowing Electrolyte Batteries Test Results

Six flowing-electrolyte cell or battery units were tested electrically, chemically, and mechanically during 1986. These units represented two technologies and four developers. Two zinc/bromine batteries completed electrical evaluation and were disassembled during the year. Table 3-5 describes these cells and batteries. A data summary is presented in Table 3-6, and the status of these cells and batteries is summarized in Table 3-7.

**Evaluation Procedures.** The evaluation procedures used on these units consisted of electrical charge and discharge using various rates and charge levels. In addition, chemical analyses of several battery electrolytes were conducted. These were considered necessary for system maintenance and for evaluation of system problems. Data were collected on pump and plumbing longevity and maintenance

	Table 3-5.	Flowing	Electrolyte	Cells	and	<b>Batteries</b>	Tested	at SNL	in	1986
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SNL ID No.	Type	Developer (ID No.)	Start Test Date	No. of Cells	Capacity (Ah)	Wt. (kg)
300	Zinc/Bromine	Exxon (PAM-18)	10/82	20	40 @ C/3	65
301	Zinc/Bromine	Exxon (S8-2)	10/82	8	40 @ C/3	46
419	Zinc/Bromine	Exxon (11140-76)	4/86	8	80 @ C/3	49
430	Zinc/Bromine	ERC (SNL-5-1)	10/86	5	125 @ C/3	
394	Zinc/Bromine	GEL (DP-71)	12/84	17	130 @ C/4	118
424	Zinc/Redox	Lockheed	9/86	1	3.5 @ C/2	

### Table 3-6. Flowing Electrolyte Battery Data Summary as of December 1986

SNL* ID No.	Mean Coulombic Efficiency**	Mean Voltaic Eff.**	Mean Energy Eff.	Total No. of Cycles	No. of Cycles in 1986	Status
300	68.7 ± 0.4	$67.6 \pm 0.3$	46.5 ± 0.4	727	0	Failed
301	86.9 ± 0.2	$77.3 \pm 0.1$	$67.2 \pm 0.2$	2025	505	Off Test
419	68 ± 2	$73.8 \pm 0.5$	50 ± 2	123	123	Failed
430	37 ± 14	76 ± 2	$28 \pm 10$	8	8	Failed
394	74 ± 1	79.7 ± 0.5	59 ± 1	260	68	Failed
424	88 ± 1	$83.0 \pm 0.3$	73 ± 1	79	7 <del>9</del>	Off Test

See Table 3-5 for battery identification. Uncertainties are expressed at 95% confidence limits.

# Table 3-7. Status of Flowing-Electrolyte Cells and Batteries Tested at SNL in 1986

Exxon 1.2-kWh Zinc/Bromine	No successful cycles in 1986; 727 cycles completed.			
Battery (SNL ID No. 300)	Excessive hydrogen evolution at the zinc electrode caused increase in electrolyte pH.			
	Failure attributed to electrolyte warpage and electrolyte cross-mixing through burn holes and flow frame; but these factors do not completely explain elevated pH of electrolyte.			
	Electrolyte contamination by metals suspected; battery components being investigated as possible sources of iron, nickel, and chromium.			
	Results to be shared with JCI for use in battery development.			
Exxon 500-Wh Zinc/Bromine Battery (SNL ID No. 301)	Voluntarily terminated after 2025 cycles (4 years), demonstrating this technology is capable of long life.			
	Efficiency prediction equation developed from test data on this battery.			
	Battery to be disassembled in 1987 to characterize its longevity.			
Exxon 1-kWh Zinc/Bromine Battery (SNL ID No. 419)	Initial performance inconsistent because of lack of specifications on electrolyte pump flow rate.			
	Terminated at cycle 123; failure attributed to blockage of electrolyte flow (from degraded adhesive materials) and electrode warpage.			
ERC Zinc/Bromine Battery (SNL ID No. 430)	Cell stack clamping bolts had to be tightened to maximum recom- mended torque to reduce electrolyte leakage to a manageable rate.			
	Almost uncontrollable electrolyte transfer through the separators made evaluation difficult and caused battery failure after only eight cycles.			
	Causes of failure to be determined when ERC delivers a replacement cell stack.			
GEL Zinc/Bromine Battery	Initial performance comparable to Exxon and ERC units.			
(SNL ID No. 394)	After 130 cycles, significant decline in performance until terminated at 260 cycles.			
	Poor performance attributed to electrolyte flow system that may have caused zinc to break off from zinc electrode.			
Lockheed Zinc/Redox Cell (SNL ID No. 424)	Performance superior to previous zinc/redox cells, but fundamental problems encountered:			
	<ul> <li>poor zinc-deposition quality,</li> </ul>			
	• irreversible transport of active materials across the membrane,			
	• transfer of water through the membrane, and			
	• increasing resistance of the ferricyanide electrode.			

requirements. Failure analyses were conducted on the two batteries that failed during the year.

A typical electrical cycle for these systems consisted of a timed, constant-current charge related to a theoretical zinc loading. After a 1-to-5-min open-circuit wait following charge, a constant-current discharge was imposed until the cell or battery voltage fell below a predetermined cutoff level, typically 1.0 V per cell. Periodically, it was necessary to discharge these units to the completely discharged condition (0 V). This is a maintenance requirement of the zinc flow technology. The frequency of this deep discharge, a variable in the operation of these systems, depends on the cell design and varies from every one to every forty cycles.

The measured parameters of these tests included cell or battery voltages, currents, temperatures, and electrolyte pressures or flow rates. Several items were calculated from these data: amp-hours and watt-hours in and out of the battery, and coulombic, voltaic, and energy efficiencies for each charge/discharge cycle.

The efficiency values reported in Table 3-6 represent averages over the life of each unit while at SNL. One of the goals of these investigations was to evaluate the cells and batteries using meaningful and comparable test regimes. Individual design limitations were considered during test planning; test regimes for each cell or battery were different and involved various charge and discharge rates, zinc loading, and temperatures. Thus, individual test conditions must be considered when interpreting these data.

Baseline cycles were defined for each of the units tested. The cycles were based on developer guidelines and design information. These regimes and corresponding battery electrolyte characteristics are specified in Tables 3-8 and 3-9, respectively.

Other electrical tests were conducted in addition to baseline cycles. Self-discharge rate and internal resistance were determined. Once stable operation of a system was confirmed with baseline cycles, a factorial test regime was imposed on the Exxon and GEL batteries. This plan systematically varied charge and discharge rates, zinc loading, and in some cases temperature. The effect of such variations on efficiency and performance was determined.

Typically, after this plan was completed, a qualified life-cycle test was begun. While not

strictly a life test because of the previous treatment, these tests aged the units and provided additional information about the system's longevity. The failure criteria for these tests was battery performance of less than 40% average energy efficiency for five consecutive cycles using the baseline test. Failure was also declared if the cell or battery became unserviceable because of leakage or component failures.

The Exxon batteries were tested using a standard electrolyte consisting of 3M zinc bromide (discharged state) and 1M quarternary ammonium compounds (bromine complexing agents). Two ammonium compounds were used, in equal ratios: N-ethyl, N-methyl morpholinium bromide and N-ethyl, and N-methyl pyrollidinium bromide. The ERC zinc/bromine battery used a similar electrolyte composition. Only one bromine complexing agent was used and potassium chloride was added to the electrolyte to improve its conductivity. The discharged electrolyte in the GEL zinc/bromine battery was composed of 1.6M zinc bromide and 2M ammonium chloride.

In the zinc/redox system, each electrode required a specified electrolyte. The discharged zinc electrolyte consisted of a saturated solution of zinc oxide in 2N sodium hydroxide. The discharged ferricyanide electrolyte was a saturated solution of sodium ferrocyanide in 2N sodium hydroxide.

Battery electrolytes were chemically analyzed using traditional wet methods and instrumental techniques. Bromine, ferricyanide, and trace metal concentrations were determined. Electrolyte pH was monitored and adjusted with hydrobromic acid to maintain a pH of less than 3.0 in the Exxon and ERC batteries. Specific gravity and viscosity were measured for the GEL battery. These analyses were used to evaluate chemical changes during electrical tests.

Required and preventive maintenance was carried out on each unit. Problems with plumbing components, electrolyte pumps, thermal management systems, and cell case leaks were encountered, documented, and resolved.

Exxon 1.2-kWh Zinc/Bromine Battery (SNL ID No. 300). Electrical evaluation of the Exxon controller battery was completed in 1986. The controller designation refers to the microprocessor control unit supplied with the battery. There were no successful cycles run by this battery in 1986; the test data reported in last

_	SNL* ID No.	Electrode Area (cm <sup>2</sup> )	<u>Current Density</u> Charge Discharge (mA/cm <sup>2</sup> ) (mA/cm <sup>2</sup> )		Zinc Loading (mA/cm <sup>2</sup> )	Electrolyte Temperature (°C)
_	300	600	20	20	60	20
	301	600	20	20	60	20
	419	1160	20	20	90	20
	430	872	34	34	138	30
	394	1936	10	10	62	25-42
	424	60	35	35	70	40

### Table 3-8. Baseline Cycle Regimes for Flowing-Electrolyte Batteries

\* See Table 3-5 for battery identification.

### Table 3-9. Electrolyte Characteristics of Baseline Cycles for Flowing-Electrolyte **Batteries**

 SNL* ID No.	Anolyte ( Pressure (psi)	Catholyte Pressure (psi)	Total Volume (1)	Electrolyte Utilization (%)
300	3	3	10	50
301	3	3	4	50
419	7	6	8	65
430	13	10	15	37
394	2.5**	2.5**	44	54
424	3	6	3	20

\*\*

See Table 3-5 for battery identification. This battery utilized only one electrolyte stream. The electrolyte pump operated for 12 s every 3 min. The other systems described in this report utilized at least two electrolyte flow systems, and the pumps were operated continuously.

year's report are the final results. Several cycles were attempted in 1986, but all were unsuccessful and resulted in very low energy efficiencies (less than 10%). These data indicated that the battery had reached the failure condition.

Figure 3-7 illustrates representative efficiency data over the life of this battery at SNL. The drop in efficiency that occurred early in life was caused by a 9-month stand during which there was no testing because of the failure of the Exxon battery controller. SNL built and installed a new controller for this battery, but when testing was resumed, the battery performance immediately declined and then stabilized. Parametric tests were performed subsequent to this drop in performance, and the remainder of the evaluation was a qualified life test. Baseline cycles were run in sets of five cycles with intervening complete discharges. The brief drop in performance that occurred after cycle 500 was caused by a pump motor failure and a subsequent one-month stand while a new pump was obtained. Efficiency then declined gradually until falling off sharply after cycle number 727.



Figure 3-7. Efficiencies versus Cycle Number for Exxon Zinc/Bromine Battery 300

As the battery aged, increasing quantities of hydrobromic acid were added to the electrolyte to maintain its pH below 3.0. Early in life between cycles 74 and 117), the battery required 0.3 ml hydrobromic acid per cycle to maintain the specified pH. Electrolyte pH gradually increased during cycle testing and more hydrobromic acid were added as necessary. Between cycles 687 and 717, 7.7 ml hydrobromic acid per cycle was added to the battery electrolyte for pH maintenance. If the pH was allowed to rise above 3.0, a gray floating precipitate formed in the electrolyte. This material blocked flow channels and caused very poor battery performance. However, the large quantities of bromine added as hydrobromic acid resulted in high bromine concentrations in the anolyte, and a significant amount of brominated complexing agent was present at all times in both electrolytes. Bromine in large quantities in contact with the zinc deposit resulted in high self-discharge rates and poor coulombic efficiency.

Hydrogen evolution at the zinc electrode contributed to the increase in electrolyte pH. This was confirmed in a special test in which the gases in the electrolyte reservoirs were sampled and analyzed by mass spectrometry. In the catholyte reservoir at the end of charge, hydrogen was 0.6% by volume, while in the anolyte reservoir, it was 7%. There was about 19% oxygen in the reservoirs. The balance of the gas was primarily nitrogen.

In another test, the battery was operated in a glove bag with an argon atmosphere and electrically charged and discharged twice. No change in efficiencies or the rate of pH increase was observed for the cycles run in the glove bag. These results indicated that oxygen intrusion into the battery was not the cause of elevated electrolyte pH.

The battery was disassembled on 5 March 1986, after being partially charged. A video tape was made of the procedure and later edited into a brief summary tape. During the disassembly, several observations were made. The current collector screens on the end electrodes were corroded but intact. The resistance through the screens was not measured. All of the electrodes except the end electrodes were severely warped. Near one end of the stack, holes had been burned through the separator and flow frame. These holes allowed catholyte and anolyte to mix, which contributed to reduced coulombic efficiency. Many separators had burned areas and showed evidence of localized hot spots. Figure 3-8 shows a zinc electrode from this battery. Warpage, poor zinc deposition, and burned holes in the flow frame are visible.



Figure 3-8. Zinc Electrode from Exxon Zinc/Bromine Battery 300 after 727 Cycles. Note warpage, poor zinc deposit, and burned hole in flow frame (lower right).

Based on these results, electrode warpage and electrolyte cross-mixing through burn holes in the separator and flow frame were identified as the primary causes of failure. These conditions explain the poor performance observed in this battery, but they do not completely explain the elevated electrolyte pH. Samples of electrolyte, electrodes, and separators were submitted for chemical and physical analysis following the disassembly. Not all of these tests were complete by the end of the year. The preliminary results indicate that the battery may have been contaminated by metals such as iron, nickel, and chromium. The possible sources of these materials in the battery are the four-way valve, bromine-complex valve, and temperature and electrolyte sensors. The results will be finalized during 1987.

Exxon 500-Wh Zinc/Bromine Battery (SNL ID No. 301). Evaluation of an Exxon eight-cell battery continued in 1986. A qualified life-cycle test, begun in 1984, continued using primarily baseline cycles. Battery performance declined gradually until cycling was voluntarily terminated in November 1986 after 2025 cycles had been completed. An additional 20 cycles were run on this battery at Exxon prior to its delivery to Sandia in 1982. Representative efficiency data are plotted in Figure 3-9 over the life of the battery. A weak cell caused the sharp temporary drop in efficiency around cycle 1500. When this was observed, the frequency of complete discharges was increased from every 5 to every 3 cycles. The more frequent complete discharges allowed the weak cell to recover, although overall battery efficiency continued to decline.



Figure 3-9. Representative Efficiencies Over the Life of Exxon Zinc/Bromine Battery 301

Normal battery maintenance was conducted during the year. Both the anolyte and catholyte pump motors had to be replaced because they wore out. Hydrobromic acid was added to maintain electrolyte pH below 3.0. During the last 175 cycles, the battery required 0.2 ml/cycle of hydrobromic acid for pH maintenance. Battery resistance as measured by polarization methods was stable at about 110 m $\Omega$  prior to the last measurement at cycle 2021. It jumped to 130 m $\Omega$  at that point. No other maintenance was performed on the battery.

Further parametric tests were run during the year to develop an efficiency prediction equation. The equation was based on test data that were obtained in 1983 and 1986. These data were treated with statistical techniques and the resulting equation was found to predict accurately battery performance within 95% confidence limits. The data from the tests run this year were corrected for battery aging to correlate the results to the 1983 parametric data. The equation was used to predict battery efficiency at several levels of charge rate, discharge rate, zinc charge loading, and temperature. Figure 3-10 shows predicted battery efficiencies as a function of temperature at specified charge and discharge rates and zinc charge loading. This model shows that voltaic efficiency is proportional to temperature, while coulombic efficiency is inversely proportional. The net effect on energy efficiency is minimal, however. Other plots of predicted battery performance as a function of any of these variables can now be generated.

Once 2025 cycles had been completed, the battery was removed from testing. It had not reached the performance failure criteria, but had begun to decline noticeably. The battery will be disassembled in early 1987 and fully analyzed to characterize its longevity. Exxon 1-kWh Zinc/Bromine Battery (SNL ID No. 419). At the conclusion of the Exxon zinc/bromine development contract, an 8-cell battery was delivered to SNL. It was the only laboratory unit evaluated at SNL that contained 1200-cm<sup>2</sup> electrodes. The battery had been tested at Exxon, but the details of its history were not available. It was assembled by Exxon personnel and placed on test in April 1986.

Figure 3-11 presents the cycle history of this battery at SNL. Early in life, the battery performed inconsistently. This was probably because of insufficient electrolyte flow. Both electrolyte pump motors were controlled by a power supply and their outputs were independently adjustable. Lacking any definitive guidance from Exxon, the motors were adjusted to pump electrolyte at pressures comparable to other Exxon batteries tested at SNL. Inconsistent performance was then observed, and the pump motors were adjusted several times until a setting was found that caused battery efficiency to stabilize. This occurred at about cycle 41.

Performance was stable after that point until the battery failed. Cycles during the stable period were run in sets of five, with a complete discharge after the fifth cycle. Contrary to the other Exxon batteries evaluated at SNL, this battery showed no difference in efficiency between cycles immediately following a complete discharge and cycles not preceded by a complete



Figure 3-10. Predicted Performance of an Exxon 8-Cell Zinc/Bromine Battery Based on Parametric Data



Figure 3-11. Battery Efficiency versus Cycle Number for Exxon Zinc/Bromine Battery 419
discharge. No explanation has been proposed for this behavior. A self-discharge test was run using baseline cycles during a period of stable performance. The battery was charged and then allowed to stand with the electrolyte pumps running for 13 hours. Coulombic efficiency declined an average of 2.5% per hour, voltaic efficiency declined 0.4% per hour, and energy efficiency declined 2% per hour.

Battery maintenance was routine during the first 110 cycles of life. Both pump motors were replaced after the first cycle because they had worn out. Apparently, the motors had been used at Exxon extensively before being assembled with this battery and sent to SNL. The battery required 0.5 ml of hydrobromic acid per cycle to maintain the proper pH. Battery internal resistance was measured using polarization methods and was found to be about half of that determined in other Exxon batteries. The resistance of the battery at the end of a baseline charge was approximately 50 m $\Omega$ .

At cycle 112, battery performance changed significantly. Efficiency became inconsistent and low, and dropped below the failure criteria. One and sometimes two cells dropped out early in discharge, indicating nonuniform electrolyte flow distribution inside the cell stack. No abnormal operating conditions, such as elevated electrolyte temperature, were found that correlated with the sudden change in performance.

Battery evaluation was terminated after cycle 123. Performance was below the failure level and the battery refused to accept charge at normal currents and voltages. The cell stack was disassembled on 9 December 1986. The condition and electrical continuity of the end currentcollector electrodes was excellent. The cause of battery failure was blockage of electrolyte flow channels inside the cell stack and electrode warpage. Figures 3-12 and 3-13 illustrate these two conditions, respectively.

Large quantities of black, sticky particles coated and obstructed the narrow flow paths on each electrode. Based on similar conditions in comparable Exxon batteries, these particles were assumed to be degraded adhesive materials.

Adhesives were used to seal the cell stack during construction. Exxon found that the adhesive degraded after prolonged exposure to the electrolyte. Adhesive particles would circulate inside the battery, picking up loose carbon particles. These particles eventually became lodged in the narrow flow channels on the electrodes. Once these channels were blocked, electrolyte flow became nonuniform and some electrodes became starved of active materials. The battery rapidly failed after this occurred. Electrode warpage contributed to the nonuniform electrolyte flow. While the warpage was significant, this was not the worst case of warpage compared to other Exxon batteries.

The disassembly concluded the evaluation of this battery. The components were retained at SNL for possible future analyses.

ERC Zinc/Bromine Battery (SNL ID No. 430). The first ERC prototype zinc/bromine battery was delivered to SNL in late June 1986. It consisted of a five-cell stack, three electrolyte pumps, and associated plumbing. It differed from the Gould zinc/bromine battery tested at SNL in 1982 in three ways. The ERC bromine electrodes used an improved electrolyte flow system. An improved technique was used to bond the electrodes to the flow frames. Also, the reservoirs utilized an improved cover design to reduce the likelihood of leakage and air intrusion.

The unit was assembled at SNL by ERC personnel in July, but the catholyte reservoir was found to leak and had to be returned to ERC for repair. It was shipped back to SNL in August. SNL received the instruction manual from ERC in September, and the first flow system tests were run in early October. The cell stack leaked at an unacceptable rate during these tests. To reduce this leakage, the cell-stack clamping bolts were tightened to the maximum recommended torque of 30 ft-lbs. This action reduced the leakage to a manageable rate.

Electrical tests were begun in late October. Very inconsistent and lower-than-expected efficiencies were observed, as is seen in Figure 3-14. This performance was accompanied by rapid and almost uncontrollable electrolyte transfer through the separators.

Electrolyte transfer resulted from unequal pressures across the separators. In any flowingelectrolyte battery, each separator in the stack can be exposed to a different pressure differential, depending on the state of the electrolyte flow path on either side. These pressure gradients are different for each cell and are difficult to measure. The only control over



Figure 3-12. Separator/Flow-Frame Assembly from Exxon Zinc/Bromine Battery 419 after 123 Cycles. Note the small black particles blocking the inlet flow channels at the top of the separator.

the pressure gradients is to change the electrolyte pump output.

The transfer of electrolyte through the separators caused volume changes in the reservoirs. When transfer was rapid and not monitored closely, the receiving reservoir overflowed and spilled electrolyte. Bromine was ultimately carried into the zinc electrolyte and chemically discharged the zinc deposit, yielding lower coulombic efficiency.

During these tests, electrolyte transfer rates of approximately 200 ml/h were observed. This rate was estimated by measuring the change in the level of the electrolyte in the reservoirs. To control the transfer, it was necessary to monitor the battery and adjust the output of the pumps every 15 minutes. On two occasions when the battery was not monitored for 30 minutes, the battery reservoirs overflowed.

Because of the unexpected performance of the battery and the intensive effort required to operate it, battery evaluation was terminated in December 1986 after eight electrical cycles. ERC plans to deliver a replacement cell stack to SNL in early 1987. At that time, the first stack will be disassembled and the causes of failure determined.

GEL Zinc/Bromine Battery (SNL ID No. 394). Evaluation of the GEL zinc/bromine battery was completed in 1986. The battery was



Figure 3-13. Warped Electrode from Exxon Zinc/Bromine Battery 419 after 123 Cycles. A significant amount of warpage is perpendicular to the electrolyte flow path and probably obstructed flow.

purchased from GEL in 1984 with the intent of comparing its performance with that of Exxon and ERC units. This battery was designated by GEL as a Duke Power design. After stable baseline performance was established, a factorial test regime was imposed. The results of these tests were described in last year's report. In 1986, a qualified life test using baseline cycles was run on the battery. Its performance steadily declined during the year, and it reached the failure criteria in October 1986. Testing was terminated at that time after 260 cycles.

Coulombic efficiency declined steadily after cycle 130 until the test was terminated. Data for

cycles 190 through 260 are plotted in Figure 3-15. The large swings in coulombic and energy efficiency values prior to cycle 230 were due to lower coulombic efficiencies for cycles not preceded by a complete discharge. Early in life, the battery had routinely run for 20 cycles between complete discharges with no effect on performance. Between cycles 190 and 230, the battery was operated with 2 or 3 consecutive cycles between complete discharge. The first cycle after a complete discharge demonstrated higher coulombic efficiency compared to subsequent cycles. A complete discharge allowed the efficiency to recover somewhat. The other



Figure 3-14. Efficiency versus Cycle Number for ERC Zinc/Bromine Battery 430

result of this lower efficiency was excessive heat build-up in the battery and consequent test shutdown. After cycle 230, a complete discharge was performed after each cycle.

GEL was consulted concerning the performance problems. GEL personnel suggested that a design problem in the electrolyte flow system might have allowed zinc to break off the zinc electrode and fall into a part of the plumbing that did not receive proper electrolyte circulation. Thus, zinc might be effectively lost from the battery by this process. On several occasions, zinc bromide was added to the electrolyte to ensure that adequate zinc was present. Subsequent analysis of the electrolyte indicated that the additional zinc was lost somewhere inside the battery.

The battery will be disassembled in 1987, as time permits. Because the epoxy case that surrounds the battery will have to be sawed apart, tear-down will be difficult. The nature of any problems inside the battery may be hard to determine because of the required disassembly procedure.

Lockheed Zinc/Redox Cell (SNL ID No. 424). Two 60-cm<sup>2</sup> cells, with necessary auxiliary equipment, were shipped to SNL in mid 1986 as development-contract deliverables. A test system was designed and built by SNL personnel and one cell was operated for about one month. This cell test used a Nafion membrane. Baseline cycles only were used to characterize the performance of this unit. The cell differed from zinc/redox



Figure 3-15. Efficiency versus Cycle Number for GEL Zinc/Bromine Battery 394

cells tested previously at SNL in that an improved zinc electrode was used. The SNL test system was also improved to make cell maintenance easier. The only operational difference compared to the earlier tests was that a brief reverse charge was applied to the cell at the end of each discharge. This procedure, required by Lockheed, attempted to maintain a balanced state-of-charge in the two electrolytes.

Efficiency data are plotted in Figure 3-16. Performance of this cell was superior to that observed in the prior cell tests conducted in 1985. The large drop in coulombic efficiency at cycle 44 occurred after a two-week stand on open circuit. The decrease was attributed to a change in the zinc electrode. Reference electrode data indicated that the zinc electrode became capacity-limiting subsequent to cycle 43.

The test was terminated after 79 cycles. Several problems were identified during this test, all of which had been observed in the earlier tests. The loss of capacity in the zinc electrode and poor zinc-deposition quality were the key limitations. Poor zinc deposits ultimately broke off the electrode surface and then blocked the flow channels. The situation required that the cell be opened and the restrictions manually removed. Once the zinc electrode began to exhibit this behavior, there was no known way to recover it.

Another performance limitation was a slow decrease in the voltaic efficiency. Based on reference electrode data, the efficiency change was related to an increase in the contact resistance of the ferricyanide felt electrode with its current collector. Over time, a high-resistance layer composed of an iron hydroxide species built up on the felt and current collector. It could be removed by a hydrochloric acid wash in order to reduce the resistance to original levels.

Other problems included a gradual transfer of electrolyte from the ferricyanide system to the zinc system. The process of reverse-charging the cell each cycle reduced the loss of ferricyanide species resulting from electrode inefficiencies. This loss was not observed during this test, although it may have been evident during a longer test. There were minimal leaks from the plumbing and cell case during the test. Again, the duration of the test probably eliminated materials degradation and leaks as a problem area.

No further tests were planned for these cells due to the change in emphasis of this project. (See Zinc/Redox Battery - Lockheed, Chapter 2.)



Figure 3-16. Efficiency versus Cycle Number for Lockheed Zinc/Redox Cell 424

#### Sodium/Sulfur Cell Testing at SNL

During 1986, SNL tested sodium/sulfur cells developed by FACC and CSPL. Test results are shown in Table 3-10. The status of the sodium/sulfur cells is summarized in Table 3-11 and is discussed in detail below.

FACC Cells. At the beginning of 1986, six Ford Aerospace (FACC) sodium sulfur cells were on test at Sandia. This testing dealt with three 155-Ah Mark IID load-leveling cells and three 55-Ah ETX electric vehicle cells. Two of the three load-leveling cells were tested in a lifecycle capacity test regime that consisted of a 30-A discharge rate and an 18-A charge rate. Both cells experienced a charge-acceptance problem. For cell 391, the problem started after 222 cycles had been completed; for cell 389, the problem occurred early in cycle life. In both cells, if the charging current was reduced or a taper charge was used, the capacity of the cells would be normal (155 Ah). These cells were removed for test late in the year. A posttest analysis will be performed on the cells to try and determine the cause of their problems.

Cell 390, the third load-leveling cell, continued to be tested on an 80% depth-ofdischarge cycle test and is still performing with over 680 cycles completed; however, this cell is starting to experience charging problems similar to the other two load-leveling cells. Without taper charging or running a two-step charge, the cell's capacity has been reduced to 130 Ah.

Two of the three Ford ETX electric vehicle cells were tested during most of 1986. Cell 411, the third cell, failed after 60 cycles when it experienced a freeze/thaw cycle. Figure 3-17 is a photograph of this cell and shows that upon failure, the metal exterior can ruptured. Plots of voltage and temperature versus time are shown on Figure 3-18. The cell cooled from 350°C to 130°C, and when the electrolyte ruptured, an increase in temperature was observed. A posttest analysis will be conducted on this cell.

A parametric test was run on the other two ETX cells (407 and 410). The purpose of this evaluation was to develop a cell capacityprediction equation based on statistical data analysis. A Box-Behnken test regime was used to evaluate the effect of three parameters on cell capacity. The three parameters were charge rate, discharge rate, and operating temperature. A similar but simpler regime had been run on an FACC load-leveling cell in 1985, the results of which were reported last year. The regime used in 1985 did not allow the calculation of an accurate prediction equation. Thus, the more sophisticated Box-Behnken regime was adopted for the 1986 tests.

The three parameters resulted in 13 different combinations for these tests. Each combination was run for five consecutive cycles. Baseline cycles were run between each parametric combination. Thus, the test regime required over

atika dit _k trođe	SNL ID#	No. of Cells	Nominal Capacity (Ah)	No. of Cycles	Test Regime	Capacity % of Rated
	FACC Na	/S				
	389(LL) 390(LL) 391(LL)	1 1 1	155 155 155	320** 681 296**	Capacity 80% DOD Parametric/	81 @ C/5 84 @ C/5 81 @ C/5
	407(EV) 410(EV)	1 1	55 55	247 278	Capacity Capacity Capacity	106 @ C/3 106 @ C/3
	411(EV)	1	55	60*	Capacity	duration of the 183 wilds dependent of
	CSPL Na,	/S				
	427(PB) 434(PB) 435(PB) 436(PB) 437(PB) 438(PB)	1 1 1 1 1 1	10 10 10 10 10 10	22 32 32 19 5 2	Break-in/Capacity Break-in/Capacity Break-in/Capacity Break-in/Capacity Break-in Break-in	93 @ C/3 93 @ C/3 93 @ C/3
Fai Rei	led noved from 1	testing	ntes a man tagit of this , fire mout of and compen are 2-18 Th	anaqaa golodiq golodiq golidiq golidiq golidiq golidiq		

### Table 3–10. Sandia Sodium/Sulfur Technology Test Summary

130 cycles and several months to complete. Table 3-12 summarizes the test regime and presents the discharge capacities for one of the cells in each parameter combination.

In order to calculate prediction equations from these data, a new software package was ordered in 1986. It was installed on the battery laboratory's HP1000 computer late in the year. The statistical data evaluations will be conducted in 1987.

Life-cycle capacity tests were also run on ETX cells 407 and 410, and they have completed 247 and 278 cycles, respectively. The capacity of these cells have only dropped slightly from 60 Ah to 58 Ah. This value is still above the nominal capacity of 55 Ah for these ETX cells.

CSPL Cells. A contract with Chloride Silent Power, Limited, (CSPL) was initiated in 1986 and six of their small (PB) electric vehicle cells were placed on test at Sandia. The cells were placed on test as test stations became available. The first CSPL cell tests at Sandia began in September 1986. The cells were placed in individual furnaces and heated to 350°C at a 6°C/h rate. Open-circuit voltage readings were taken at 150°C, 250°C, and 350°C. A break-in test plan consisting of 10 cycles was provided by CSPL and followed very closely by Sandia. The plan suggested that the cells first be discharged for five minutes at a 0.050-A rate. The opencircuit voltage of the cell after this discharge was 2.075 V. The remaining cycles in the break-in plan required that the discharge and charge currents be slowly increased from 1 A to 3 A and the amp-hours removed be increased from 3 Ah to 9 Ah. At the end of these cycles, the endof-discharge cell resistance for most of the cells was below 45 m $\Omega$ .

Sandia cell 427 was the first cell tested, and after experiencing a freeze/thaw cycle caused by an unscheduled power outage, the break-in plan was followed. The cell appeared to function

### Table 3-11. Status of Sodium/Sulfur Cells Tested at SNL in 1986

FACC Cells	
389(LL)	Charge acceptance problems early in cycle life.
	Removed from test; posttest analysis to be performed.
390(LL)	Still performing after 680 cycles, but starting to experience charge acceptance problems.
391(LL)	Charge acceptance problems after 222 cycles.
	Removed from test; posttest analysis to be performed.
407(EV)	Undergoing parametric testing (Box-Behnken test regime) to model the effect of charge/discharge rate and operating temperature on performance.
	Capacity still above nominal level at 247 cycles.
410(EV)	Undergoing parametric testing (Box-Behnken test regime) to model effect of charge/discharge rate and operating temperature on performance.
	Capacity still above nominal level at 278 cycles.
411(EV)	Metal can ruptured after 60 cycles when it underwent freeze/thaw cycle.
	Posttest analysis to be conducted.
CSPL Cells	
427	Underwent unplanned freeze/thaw cycle.
	High end-of-discharge cell resistance (150m $\Omega$ ); cell failed after 23 cycles.
	Shattered electrolyte being reconstructed to determine initial point of fracture.
434,435,436	Undergoing break-in/capacity cycles.
437,438	Undergoing break-in cycles.

normally after this problem; however, after the 10 break-in cycles were completed, the end-ofdischarge cell resistance remained high, (150 m $\Omega$ ). Ten baseline capacity cycles were then run in an attempt to reduce the cell resistance (a baseline capacity cycle consisted of a 3-A discharge and charge). Finally, after completing 23 cycles, the cell failed. The cell was cooled at the 6°C/h rate and removed from the furnace. Photographs and X-rays were taken of the cell, and then the cell was opened. The electrolyte had shattered and is presently being reconstructed in an attempt to determine the fracture point.

Three other CSPL cells completed the breakin test cycles and were placed on baseline capacity tests while an additional two cells have just started their break-in tests. Table 3-13 shows the open-circuit voltage values of all six cells as the cells were being heated. The table also shows the open-circuit voltage of each cell after a 50-mA current was placed on the cell. It appeared that cell 435 had a higher than normal



Figure 3-17. Sodium/Sulfur Cell 411 with Ruptured Exterior Can



Parameter Combination	Charge Rate (A)	Discharge Rate (A)	Temperature (°C)	Capacity (Ah)*	
1	9	27	300	47 ± 3	
2	9	27	375	$62.7 \pm 0.2$	
3	18	27	300	49 ± 3	
4	18	27	375	$62.6 \pm 0.1$	
5	13	9	300	53 ± 2	
6	13	9	375	57.9 ± 0.3	
7	13	45	300	45 ± 3	
8	13	45	375	$61.6 \pm 0.2$	
9	9	9	337	58.3 ± 0.1	
10	18	9	337	$58.3 \pm 0.3$	
11	9	45	337	55.8 ± 0.3	
12	18	45	337	56.4 ± 0.3	
13	13	27	337	59.0 ± 0.2	

# Table 3-12. Parametric Test Regime for FACC Sodium/Sulfur Cell 410

\* Uncertainties are 95% confidence limits.

### Table 3–13. Open Circuit Voltage Values for CSPL Sodium/Sulfur Cells

_	Cell No.	150°C	250°C	359°C	OCV After Load	_
	427	2.470	2.406	2.485/2.416*	2.075	
	434	2.096	2.373	2.498	2.075	
	435	2.862	2.711	2.520	2.075	
	436	2.311	2.411	2.564	2.074	
	437	2.092	2.155	2.316	2.075	
	438	2.102	2.090	2.269	2.076	

\* OCV after freeze/thaw.

voltage value at 150°C; however, the opencircuit voltage after seeing a load appeared to be normal. The values for the failed cell 427 also appeared to be normal after experiencing a freeze/thaw.

Tests including life-cycle, parametric, and simplified FUDS will be conducted on these cells in the coming months. In addition, SNL plans to test several four-cell strings.

### Nickel/Hydrogen Testing at SNL

A nickel/hydrogen battery with prismatic cells in a common pressure vessel is being developed initially for remote solar applications. The battery development, under cost-sharing contracts at COMSAT Laboratories and Johnson Controls, Inc., is described in a previous section of this report (see Nickel/Hydrogen Battery -COMSAT/JCI, Chapter 1). These contracts provide for cells and batteries to be delivered periodically to Sandia for evaluation. There were seven nickel/hydrogen cells and three batteries on test during calendar year 1986. Nickel/hydrogen testing at Sandia, discussed in detail below, is summarized in Table 3-14.

Test Procedure. SNL has conducted both characterization and cycle-life tests on these units. The standard cycle-life test procedure for the latter starts with an initial charge that is terminated when the increase in pressure per amp-hour input decreases to 50% of the linear value. The pressure slope is calculated every minute; the units are psi/Ah. The cycle test itself consists of a discharge at 20-A constant current to 1.0 V/cell, followed by a 20-A charge until the pressure slope again drops to 50% of the linear value. There are usually 50 cycles per set.

Following a set of cycles, two capacity tests are run. The charge and discharge currents are the same as for the cycle test. The first discharge is to 1.0 V/cell, followed by a charge terminated when the pressure slope reached 25% of the linear value. The second discharge is to 0.5 V/cell, with the capacity to 1.0 V/cell being interpolated. The cell or battery is left discharged until the start of the next set of cycles. The capacity values for the second discharge are tabulated in Table 3-15. The principal design variations, coolant temperature, and cycles each unit has accumulated to date are also included in Table 3-15. Battery and Cell Tests. Battery 2 was put on test in June 1984. It has now accumulated 1159 cycles, including many under different charge and discharge regimes to characterize performance. Capacity had been declining, and cycle testing was suspended in September 1986 until a decision can be reached about adding more electrolyte (see discussion on cell 12 below). In the meantime, it has been connected to a small solar array and a constant current load to investigate this system operating in parallel without an intermediate controller. The hardware and software are now being checked.

Battery 3 capacity to 1.0 V/cell was also declining but remained fairly constant to 0.5 V/cell. This indicated a softening of the knee of the discharge curve. The catalyst lot used in this battery was suspect, as were some of the tab welds; both were noted in the posttest examination of cells 15, 16, and 17, which were assembled about the same time. This battery was removed from test in September to make room for Battery 4 and returned to JCI for posttest analysis.

Battery 4, the final deliverable on the COMSAT contract, was received at Sandia in October 1986 and put on test. It has five individual cells constructed the same as cell 23, connected in series to form a nominal 6-V battery. It is described in more detail in a previous section of this report (see Nickel/Hydrogen Battery - COMSAT/JCI, Chapter 1). Voltage and temperature versus time are plotted in Figure 3-19 for the first pair of capacity tests. The second charge to 25% of the linear pressure slope did not increase the capacity over that of the first to 50%; both were about 128 Ah. However, the additional charging resulted in higher cell temperatures, as did discharging below 1.0 V/cell. Modifying the standard test sequence to eliminate these characteristics is under consideration. The battery has now accumulated 57 cycles, with the latest capacity at 135 Ah.

Cell 10 was the first cell with the thicker (0.070-inch) positive electrodes. While it performed well, the capacity was less than had been predicted based on the additional active material. Backscattered electron image analysis by COMSAT showed that, although the sintered nickel substrate was uniform, the distribution of active material was not. JCI improved the

# Table 3-14. Nickel/Hydrogen Testing at SNL

Test Procedure	
Cycle Life	Charge until increase in pressure decreases to $50\%$ of linear slope, followed by discharge to $1.0 \text{ V/cell}$ .
Characterization	Two capacity tests: 1) discharge to 1.0 V/cell, 2) recharge until pressure slope 25% of linear value, followed by discharge to 0.5 V/cell.
Battery/Cell Status	
Battery 2	Capacity declining.
	Cycle testing suspended, but will be resumed if cell 12 tests show that adding more electrolyte rejuvenates performance.
	Connected to solar array until testing can be resumed.
Battery 3	Capacity to 1.0 V/cell dropped off, but fairly constant to 0.5 V/cell; problems with catalyst suspected.
Battery 4	Modification of standard test sequence being considered to address changes in charging and thermal behavior.
Cell 10	Uniformity problems encountered in distribution of active material in positive electrode, which prompted JCI to improve impregnation process.
Cell 12	Capacity declining; to be returned to JCI to determine if adding electrolyte will improve performance.
Cell 18	Capacity lower than that of cell 23; 38 wt % KOH.
Cell 19	Poorer performance without lithium oxide added to the electrolyte, indicating LiOH beneficial.
Cells 20 and 22	Some capacity decline; removal of Gore-Tex backing needs more evaluation.
Cell 23	Capacity higher than cell 18; 33 wt % KOH.
Prismatic, Common Pressure Vessel Battery	
	1.67%/day capacity loss (open circuit, stand at room temperature).
	No improved performance with constant-voltage charging.
	Open-circuit stand decreases voltage on discharge below 1.0 V/cell; reducing overcharge does not.
	High coulombic efficiencies when battery cycled without full recharge.

S/N	Positive Thick (in)	Li Add.	Gore-Tex on Negative	Coolant Temp (°C)	Cycles	Capacity (A 1.0 V/c	$\frac{h}{0.5 \text{ V/c}}$
•========				······			
Battery 02 03 04	.032 .032 .070	No No Yes	Yes Yes Yes	10 10 10	1159 762 57	75.0 82.7 135.1	93.3 109.1
Cell 10 12 18 19 20 22 23	.070 .032 .070 .070 .070 .070 .070	No No Yes Yes Yes Yes	Yes Yes Yes No No Yes	10 10 10 10 10 10	631 1312 521 461 463 279 226	114.8 82.0 146.0 135.0 146.5 137.5 151.3	152.9 112.4 174.4 170.6 172.1 170.1 175.6

# Table 3-15. Nickel/Hydrogen Test Results (December 1986)



Figure 3-19. Voltage and Temperature versus Time for Battery 4

impregnation process, which resulted in much more uniform distribution of positive active material and a corresponding increase in capacity, as demonstrated by cell 18 and subsequent cells. Cell 10 was removed from test in June to make room for cell 23.

Cell 12 components are similar to those used in battery 2. This is the only cell now on test with the 0.032-inch thick positive electrodes. Testing began in November 1984 and 1312 cycles have been accumulated to date. The first 563 cycles were conducted at room temperature, after which 10°C coolant was circulated through the external cooling coil. Capacity has been declining, and it will be returned to JCI in January 1987 to determine if additional electrolyte will rejuvenate performance. Depending on the results, a decision will then be made whether to add electrolyte to battery 2.

Cells 18 and 23 are the same construction, having the thicker positive electrodes (0.070-inch) and lithium additive in the electrolyte, but the KOH concentration was reduced from 38 wt % to 33 wt % in cell 23. They are both performing very well with capacities of 146 Ah and 151 Ah for cells 18 and 23, respectively. The capacity of cell 18 has declined somewhat from a peak of about 150 Ah near 400 cycles.

Cells 20 and 22 are the same construction as cell 18 except that they do not have the hydrophobic backing on the negative electrode. This was an effort to reduce cost. To date, they are performing almost as well as cell 18. There has, however, been some capacity decline lately, and additional testing will be required to determine whether removal of the Gore-Tex backing is a viable option.

Cell 19 is constructed the same as cell 18, but there was no lithium oxide added to the electrolyte. Performance is somewhat poorer, further indicating that the lithium hydroxide has a beneficial effect.

**Prismatic, Common-Pressure-Vessel Battery.** A number of tests designed to characterize the prismatic, common-pressure-vessel nickel/hydrogen battery were conducted during the year. These can be summarized by the observations:

- Capacity loss during a 24-day open circuit, stand-at-room temperature averaged 1.67%/day.
- Constant-voltage, current-taper charging, as opposed to constant-current charging, did not improve performance.
- Open-circuit stand decreases the voltage plateau on discharge below 1.0 V/cell, but reducing the amount of overcharge does not.
- High coulombic efficiencies (96%) are obtained when the battery is cycled without full recharge.

### **Battery Field Tests at SNL**

Three battery field test programs were conducted by SNL during 1986. Two of these programs were contracts, one with Solar Energy Research Institute (SERI) and another with Hawaii Natural Energy Institute (HNEI). Both contracts dealt with battery systems interfaced to wind turbine generators (WTGs). The battery under test at SERI was a GNB 27.5-kWh (at the 24-h rate) sealed lead-acid system, while the battery at HNEI was a gel-cell lead-acid system manufactured by JCI. The third field test was conducted at Sandia's Photovoltaic Advanced System Test Facility (PASTF) and involved an Exxon 20-kWh zinc/bromine battery. The goals of these tests were to determine battery performance, life, and maintenance requirements under field conditions. The entire system, including the wind turbine or photovoltaic array, was also evaluated. Load satisfaction and energy utilization were key performance measures. The battery field tests conducted by SNL are discussed in detail below. A summary of this SNL work is found in Table 3-16.

### SERI Tests

The SERI project, located at Rocky Flats, Colorado, has been in existence for over four years. The first battery tested was a conventional lead-acid battery. This battery was replaced with a sealed lead-acid battery in May 1985. The results of the conventional lead-acid battery tests

# Table 3-16. Battery Field Tests at SNL

SERI Tests	
	GNB 22.5-kWh sealed lead-acid battery interfaced to wind turbine performed well, but problems encountered with wind turbine.
	60% to 80% of load satisfied by battery, and 20% to 40% by wind turbine; load demand nearly always met.
	SOLSTOR II computer model verified by 31 80% DOD cycles.
HNEI Tests	
	Plan to interface gel-cell lead-acid battery to wind turbine to provide power to utility grid and cattle ranch delayed:
	• Problems with three-phase electrical connections to utility grid.
	• Software development required.
	Test results to be compared with a computer model previously developed by HNEI.
PASTF Tests	
	Exxon PV-20 zinc/bromine battery interfaced to photovoltaic array cycled 67 times during the year.
Baseline Capacity Cycling	70-A charge/discharge rate cycled by Firing Circuits battery cycler.
Solar Cycling	35-A charge from PV array (through Abacus controller); 70-A discharge through Firing Circuits battery cycler.
	Results indicate zinc/bromine battery compatible with photovoltaic array.
	More tests required with Abacus controller removed.
Stand-Loss Tests	Only a slight decrease in efficiency observed.
Parasitic Energy- Consumption Tests	Energy consumption at +20°C almost double that of -20°C.
Maintenance Problems	Electrolyte pump motor failure.
	Leaks in electrolyte reservoir.
	Reliability problems with data acquisition system.
	Increased HBr usage.

-

were documented in previous ETD annual reports. The sealed lead-acid battery continued to be tested during 1986, and an additional \$10,000 was placed in the contract to allow testing to continue through the 1986 calendar year. During the 18 months that the battery was on test, it required absolutely no maintenance and performed exceptionally well. The 2-kW wind turbine, on the other hand, required frequent periods of maintenance and had several failures. These problems included slip rings wearing out and blades cracking. Finally, in December 1986, strong winds damaged the wind turbine, and the tests on the battery were terminated.

The following data represent all the months the sealed lead-acid battery was on test starting with June 1985. This testing continued through May 1986, at which time the battery was capacity tested. Also at that time, the equipment was calibrated and preventative maintenance was performed on the wind turbine. Testing resumed in August 1986 and continued until the turbine failed. This experiment was operated in a standalone mode and had an hourly load profile that yielded 2.8 kWh per day.

Figure 3-20 is a plot of the monthly load satisfaction for this testing period. Between 60% and 80% of the load was satisfied by the battery while the wind turbine provided only 20% to 40% of the load. The wind turbine contributed more to load satisfaction in the winter than in the summer, since winds were stronger and more constant in the winter. One of the original design criteria was to have the load satisfied 99% of the time. Only once in the testing period was the load not met, and this occurred in the summer when the WTG output was at a minimum. Figure 3-21 is a chart showing the total WTG energy distribution for this testing period. Of the 2.5 MWh of energy produced by the WTG, only 10.9% went to the load while 32.9% went to charge the battery. The remainder, 56.2%, was excess and was lost to a dummy load. It is important to note that this site was chosen because of WTG availability and testing experience and not because of a desirable wind regime.

Evaluation of battery performance was a key objective in this program. Capacity tests were performed on the battery upon delivery to Rocky Flats, and these values were lower than those claimed by the manufacturer ( $\approx 21.8$  kWh at the 24-hour rate). As previously mentioned, in June 1986, the capacity tests were repeated. A decline of 1.5 kWh in battery capacity was observed.

A computer simulation model called SOLSTOR II developed at Sandia was used to determine an optimized system configuration for this experiment. The model optimized the battery size and energy flows based on achieving a minimum system life-cycle cost. During this testing period, a total of 31 equivalent 80% depth of discharge (DOD) cycles was produced, and these values compared favorably to the design





WTG ENERGY IN kWh

Figure 3-21. WTG Energy Flow from June 1985 to October 1986 (SERI/Rocky Flats Experiment)

Figure 3-20. Load Satisfaction for June 1985 to October 1986 (SERI/Rocky Flats Experiment)

values generated by the model. By verifying the SOLSTOR II predictions, the model now can be used with confidence for sizing future systems.

### HNEI Tests

The contract for the second wind/battery program was placed in October 1986 with HNEI. This project, carried out on the island of Hawaii, is a cooperative effort between private industry, the State of Hawaii, the University of Hawaii, and SNL.

The plan was to interface a 10-kW wind turbine to a 120-kWh gel-cell battery and tie the output to the utility grid. In addition, the energy produced could also be used to provide back-up power for a cattle ranch. The start of the project, however, was delayed because of problems with the three-phase electrical connections to the utility grid. In addition, software needed to be written to control the inverter operation.

The tests to be conducted include load leveling, back-up power, and grid stability (source leveling). Results from these tests will then be compared with the computer model results to verify the model. This model was developed in a previous contract that Sandia had with HNEI. From this work, Sandia hopes to gain "hands-on" experience with this type of system.

### **PASTF Tests**

The third field test project to be conducted by SNL involves the Exxon PV-20 zinc/bromine battery. This battery was tested at Sandia's Photovoltaic Advanced Systems Test Facility (PASTF). Seventy-six cycles were run on the battery during the year at a maximum of one cycle per day. Tests were run only during working hours because of safety problems at this location. Table 3-17 is a summary of the types of tests conducted during 1986, the number of cycles run for each test, and the average energy efficiencies for each set of tests. The average energy efficiency for the baseline tests was 58%. This average value was lower than the maximum value of 67% when the battery was first tested. The average energy efficiency of the battery when connected to the PV array was higher than the baseline value. This was due to a lower charge rate (40 A versus 70 A for baseline tests). The average energy efficiency for the stand-loss tests was lower than the baseline value; however, these tests were performed late in battery life.

The types of tests consisted of baseline capacity, stand-loss, parasitic energy consumption, and solar. Figure 3-22 is a set of plots that represent the efficiencies and energy output versus cycle number of all the cycles run on this battery to date. The first 35 cycles were performed at Exxon, and the remainder were run at Sandia. The coulombic, voltaic, and energy

Type of Test	No. of Cycles	Average Energy Efficiency (%)
Pagalina	40	50 ± 1 6
Stand Loss with Pumps on	49	28 ± 1.0 51 ± 2.5
Parasitic Epergy	3	$31 \pm 2.3$
Consumption	4	$56 \pm 0.9$
PV/Battery Cycles with	-	$30 \pm 0.9$
Abacus Interface	19	60 + 2 6
PV/Battery Cycle without		00
Abacus Interface	1	60

efficiencies have decreased only two or three percent from the values obtained when Sandia first started testing the battery.



Figure 3-22. Exxon's PV-20 Experiment at Sandia: Efficiencies and Energy Output versus Cycle Number

During the first three months of 1986, baseline capacity cycles were run using a Firing Circuits unit to cycle the battery. The charge and discharge rate for a baseline capacity cycle was 70 A. Starting in April 1986, the battery was interfaced through an Abacus controller to a portion of a Hughes 30-kW flat plate photovoltaic (PV) array. The battery was charged from the array at a rate of approximately 35 A (limited by the maximum current capability of the Abacus unit) and then discharged through the Firing Circuits battery cycler into the utility grid at a 70-A rate.

Figure 3-23 is a plot that represents one of the solar tests; it shows the battery voltage and temperature during charge and discharge. The voltage fluctuations on charge represent cloudy periods during the day. These fluctuations had little if any effect on the charging efficiency. The coulombic and voltaic efficiencies were both 77.1%. A total of 18.39 kWh was removed from the battery. The temperature of the electrolyte never exceeded 35°C, and the maximum temperature occurred during the discharge portion of the cycle. This was the first advanced battery system to be interfaced to a photovoltaic array, and the results indicate that a zinc/bromine battery and photovoltaic array are compatible. In the next testing phase the Abacus controller will be removed and the battery will be interfaced directly to the PV array. So far, only one test has been run and no conclusive data were collected. If the battery can function without the Abacus interface, a large-cost item would be removed from the system.

Three stand-loss tests were performed on PV-20, and the results are shown on Figure 3-24. After the battery was fully charged, the electrolyte pumps were left on, and the battery was allowed to stand for periods of one, three and one-half, and five hours. The graph shows a decrease in coulombic, voltaic, and energy efficiency with time.



Figure 3-23. Exxon's PV-20 Voltage and Temperature Behavior



Figure 3-24. Exxon's PV-20 Stand-Loss Results (Electrolyte Pumps On)

Four parasitic energy-consumption tests were conducted, to show the amount of energy required by the electrolyte pump motors. controller, and the electrolyte chiller during a 7-h cycle. The chiller was the biggest energy user, so the tests included changing the temperature set point. On two of the tests, the on-off operation of the chiller was software controlled, and the temperature was changed from -20°C to +20°C. On the other tests, the chiller was on continuously, and the temperature was set at +20°C. All four tests were started with the battery at +25°C. The chiller used nearly double the energy when the temperature of the chiller was set at +20°C instead of -20°C. The reason for this was that to maintain +20°C, the heater and compressor in the chiller cycled on and off continuously, while at -20°C the compressor was on continuously and there were no surge currents.

Maintenance definitely was an issue on this battery. Two electrolyte pump motors were replaced during the 18 months of testing. Corrosion of the brushes in the motors appeared to be the problem. This would have been a bigger issue if the battery had not been kept extremely clean. Small leaks developed in the electrolyte reservoir and around the bolts that held the stack together; however, the electrolyte that did leak was cleaned up weekly. The data acquisition system experienced numerous problems, and the flow meter circuitry also needed repair. Finally, the frequency in which hydrobromic acid had to be added to the electrolyte substantially increased as the battery aged. A posttest analysis of this battery will be conducted in the near future.

# **Chapter 4. Battery Technology Improvement**

### Introduction

The objective of the Technology Improvement element is to investigate and solve specific problems encountered during the development of advanced secondary batteries. The following three criteria are used to select and continue tasks associated with this element:

- the prime contractor does not have the resources to address the problem adequately;
- the solution to the problem must be important to the continued development of the technology and, therefore, useful to the prime contractor;
- adequate resources must be available to allow a timely contribution to be made.

The intent of this element is to conduct the majority of the tasks at SNL. As such, secondary benefits provided by this element to the ETD program include a better and more active understanding of the obstacles facing each technology, which allows, in turn, more effective program leadership, plus a means to utilize the wide range of excellent capabilities and resources at SNL directly in the technology development process. The number and size of these tasks are limited to ensure that proper perspective is maintained with respect to the primary technology-development goal of the ETD program. Finally, nonessential overlap with Technology Base Research (TBR) activities is minimized because of the close working relationship with the industrial partner and the individual tasks.

When the Technology Improvement element was established as part of the ETD program in 1985, it had seven tasks. In 1986, three of these tasks were terminated and four were continued. No new tasks were initiated during 1986 in order to focus limited resources on the remaining tasks to ensure that the Technology Improvement objectives can be satisfied in the near future. The three terminated tasks included

- The development of new beta"-alumina electrolytes. This task, carried out at Oak Ridge National Laboratory (ORNL), was stopped because it more properly fits into the TBR program.
- The identification of techniques for improving chromium platings on sodium/sulfur containers. This task was postponed until container-corrosion objectives specific to the CSPL program can be defined.
- The study of the effect of contaminants on the behavior of the sodium/sulfur positive electrode. This task was suspended until the full effect of contaminants on cell performance has been characterized. Posttest analysis will provide needed contamination-related performance information.

Two of the four tasks active in 1986 support aqueous battery development; the other two support sodium/sulfur technology. These tasks are

- membrane development for zinc/redox batteries,
- durability of zinc/bromine materials,
- failure analysis of beta"-alumina electrolyte degradation, and
- modeling electrolyte stress during freeze/thaw cycling of Na/S cells.

This chapter summarizes the progress made on the four active 1986 tasks.

# Membrane Development for Zinc/Redox Batteries

Many electrochemical devices utilize ionic exchange materials as their separator. Examples include secondary flow batteries, chlor-alkali cells, and fuel cells. In these applications, high ionic conductivity, good ionic selectivity, and good chemical durability are required. One of the largest problems impeding the advancement of the zinc/redox battery technology is the availability of a low-cost membrane material (Chapter 1, Zinc/Redox Battery - Lockheed). The purpose of this task is to identify and/or develop acceptable, low-cost ionic exchange materials for the zinc/redox environment and to evaluate their electrochemical performance and stability.

This task has been active since 1984, with a close link maintained with Lockheed Missiles and Space Corp. (LMSC), the principal developers of the zinc/redox technology. Based on the results obtained in 1985, activity during 1986 focused on two classes of membranes: radiatively grafted styrenes and sulfonated polysulfones. Progress on

this task is discussed below and is summarized in Table 4-1.

### **Radiatively Grafted Membranes**

Homogeneous membranes will often fail quickly when tested in a redox flow battery. Their failure appears to be due to relatively minor reductions in the membranes' mechanical properties that lead to physical cracking. This failure mode can be substantially reduced by radiatively grafting the active site onto a stable fluorinated film. In this way, the mechanical properties of the membrane are governed by the stable substrate material. In previous years, such membranes have been prepared by radiatively grafting styrene onto polytetrafluoroethylene (PTFE) film with subsequent sulfonation of the styrene. The membranes performed well under simulated zinc/redox conditions for extended periods of time before the active site eventually degraded.

The degradation of the active site has tentatively been attributed to the presence of tertiary hydrogens, which are known to be particularly susceptible to oxidative attack. To test this theory, model compounds similar to the grafts of radiatively grafted membranes were synthesized. One of the compounds contained a

Radiatively Grafted Membranes	
	Tests with PTFE membranes grafted with styrene and alpha- methylstyrene confirm theory that tertiary hydrogens adversely affect oxidative stability.
	Alpha-methylstyrene grafted membranes satisfy the permeability, conductivity, stability, and cost requirements for use in the zinc/redox battery.
Sulfonated Polysulfone Membranes (SPS)	
	SPS membranes cast from hot solutions are pinhole-free and satisfy the nominal requirements of the zinc/redox battery.
	Membranes made from the acid form of SPS resins found to have 70% less resistivity than the sodium salt form

### Table 4–1. Membrane Development for Zinc/Redox Batteries

tertiary hydrogen while a methyl group replaced the tertiary hydrogen in the other compound. Both compounds were aged in an oxidatively aggressive aging solution and then analyzed chemically. The solution of the compound with a tertiary hydrogen contained several times more degradation products than did the solution of a compound without a tertiary hydrogen.

On the basis of the model compound results, several membranes were prepared by RAI Research Corp. (Hauppauge, NY). Styrene or alpha-methylstyrene was radiatively grafted onto a 0.012-cm PTFE film followed by sulfonation. Stability was determined by exposing these membranes to a saturated solution of potassium ferricyanide in 5N sodium hydroxide at 50°C for various times. This solution is a strong oxidizing agent and is similar to the electrolyte of the zinc/redox battery. Figure 4-1 shows the weight loss experienced by various membranes as a function of exposure time. Previous life-cycle testing of single cells at LMSC has shown that weight loss caused by a strong oxidizing agent is an accurate indicator of the useful life of a membrane. Each data point represents the average of four trials.

In each instance, the membrane containing the styrene graft experienced substantially more degradation than the membrane containing the alpha-methylstyrene graft. These membranes were sent to LMSC for in-cell evaluation. As shown in Chapter 1, the results from the testing of these improved membranes were very encouraging; both types of RAI membranes are yielding very acceptable cell performance. Additionally, their results confirm that the elimination of the tertiary hydrogen provides a more stable membrane.

### Sulfonated Polysulfone Membranes

Samples of sulfonated polysulfone (SPS) membranes prepared on a laboratory bench at SNL often contained pinholes or other small defects that caused catastrophic failure during testing. A test fixture was fabricated that allows the iron permeation rate over the entire operating area of the membrane to be measured quickly. This procedure was used to pretest all membranes for leaks and thus easily screen out undesirable membranes prior to in-cell testing. The effective area of this fixture was similar to that of LMSC's single cell. In the course of performing these screening tests, it was discovered that membranes cast from hot solutions were less liable to leak than those cast from cold solutions. New membranes were then cast from hot solutions, using previously optimized SPS resins, to produce pinhole-free membranes. These membranes provided acceptable energy efficiencies (>80%) in LMSC's test cell over 84 cycles.



#### 1 - 35 WT% α-METHYLSTYRENE GRAFT

Figure 4-1. Weight Loss of Radiatively Grafted Membranes Prepared from Styrene (a,b) and  $\alpha$ -Methylstyrene (c,d) as a Function of Time in a Saturated Potassium Ferricyanide Solution

A small contract was placed with Springborn Laboratories (Enfield, Conn.) to scale up the laboratory casting procedures to fabricate relatively large samples of two types of SPS materials: nonporous, solvent-cast membranes, and asymmetrically porous membranes. The latter material features a gradient of porosity: there are large pores on one side tapering to practically no pores on the other side. This type of material potentially has the advantage of having low resistance, but still maintains good selectivity.

In this contract, Springborn was requested to prepare 300 g of two SPS resins, one with an ion exchange capacity (IEC) of 0.91 milliequivalents per dry gram (meq/dg) and one with an IEC of 1.41 meq/dg. The high-IEC resin was to be used to solvent-cast 5  $ft^2$  of a thin membrane (1.5 mil) and 5 ft<sup>2</sup> of a thick membrane (3.5 mil). The low-IEC resin was to be used to fabricate 2 ft<sup>2</sup> of the asymmetrically porous membrane by known phase-inversion techniques. Only partial delivery of these membranes was made during 1986: 2 ft<sup>2</sup> each of the thin and thick solvent cast membranes. The area resistivities and iron transport rates of these membranes are given in Table 4-2. These properties satisfied the nominal requirements for the zinc/redox battery and the membranes were sent to LMSC for cycle testing.

All SPS membranes evaluated to date were made from the sodium salt form of starting resin. Recently, it was found that at the same ion exchange capacities, membranes made from the acid form of SPS resins had 70% lower area resistivities than their sodium salt counterparts  $(0.7 \ \Omega \cdot cm^2 \text{ versus } 2.3 \ \Omega \cdot cm^2)$ . Furthermore, this decrease in area resistivity was achieved without any apparent sacrifice of selectivity. Membranes in acid form showed no signs of ferricyanide transport at room temperature for a period of three weeks. These membranes were easy to cast. and pinhole problems were not encountered. It is possible that crosslinking of SPS may have occurred during the drying step of the casting procedure, which may account for the higher selectivity observed with these membranes.

In response to a recent SNL news release on SPS membranes, requests have been received from fifteen different companies to evaluate these SPS membranes, including International Fuel Cell Corp., Ray-O-Vac, and Jet Propulsion Laboratories. All the requests have been fulfilled, and feedback has been requested.

# Durability of Zinc/Bromine Materials

The flow frames, carbon-plastic electrodes, and storage tanks for the Exxon (JCI) zinc/bromine batteries are fabricated from polypropylene and copolymers of ethylene and propylene because of their low cost and ease of fabrication. One disadvantage of polypropylenebased thermoplastics is their demonstrated susceptibility to attack by bromine-containing electrolytes. The characterization of this degradation process has been studied at SNL for several years. During 1986, these studies have been extended to the lifetime of the two key materials: the propylene copolymer flow frames and the carbon-plastic electrode. Additional activities included study of the effect of stabilizers and the determination of the distribution of bromine across the thickness of polypropylene.

The current status of the activities associated with this task is summarized in Table 4-3. A description of the results obtained during 1986 is given below.

### Aging Studies

In previous durability studies, the mechanical properties of materials that were aged at 70°C were unmeasurable because of extreme degradation. While analysis of these samples

# Table 4–2. Physical Properties of Sulfonated PolysulfoneMembranes Produced by Springborn Labs

Thickness (mils)	Area Resistivity (Ω•cm <sup>2</sup> )	Iron Transport Rate (moles/cm <sup>2</sup> /hr)
1.5	1.19	< 10 <sup>-5</sup>
3.5	4.86	< 10 <sup>-5</sup>

### Table 4-3. Durability of Zinc/Bromine Materials

**Aging Studies** 

Lifetime estimates of the polyolefin construction materials were made based on tensile elongation of aged samples.

Antioxidant Stabilizer

Incorporation of a phenolic-type antioxidant achieves limited improvement in polyolefin stability.

Bromine Profile Experiments

> Bromination of polypropylene by bromine found to be a diffusioncontrolled process with more degradation near the surface.

**Gaseous Bromine Tests** 

26% decrease in molecular weight caused by exposure to gaseous bromine at ambient temperatures; mechanism not understood.

provided insight into the chemistry and mechanism of the degradation processes, estimates of lifetimes could not be made. Therefore, some of these accelerated aging experiments were repeated under milder conditions. In this new study, aging was carried out in the catholyte (70% state of charge) at 35°C, 45°C, and 55°C for time periods of two, four, and six months. These conditions proved to be sufficiently mild to ensure sample survivability but not so mild that property changes did not occur. To distinguish between thermally induced oxidation and degradation caused by the electrolyte, a parallel series of experiments was carried out in air. Percent elongation at tensile failure was chosen as the mechanical property to monitor because this parameter is sensitive to degradation-induced changes in chemical and physical structure.

Changes in tensile elongation of the polypropylene copolymer in air after six months at 35°C, 45°C, and 55°C were significantly less than those from samples exposed to the electrolyte at the same temperatures. The elongation of the air-aged samples decreased by less than 7% at all three temperatures, whereas decreases in elongation of the cathode-aged samples ranged from 11% to 94%. As expected, the catholyte is far more chemically aggressive toward polyolefins than air is.

In contrast, the difference in the percent decreases in elongation between air and the catholyte were less pronounced with the carbonplastic electrode. Decreases in elongation of the air-aged samples ranged from 24% to 30% compared to 22% to 55% for the catholyte-aged samples. These results suggest that carbon may function as a stabilizer against bromine attack.

Arrhenius time-to-failure plots for the polypropylene copolymer (HPO) and the carbonplastic electrode (CPE) are shown in Figure 4-2. Ambient temperature lifetimes of 7 and 66 months were estimated for HPO and CPE, respectively. In these lifetime estimates, it was assumed that the Arrhenius model is valid and that functional failure will occur when the tensile elongation decreases by 80%.

### **Antioxidant Stabilizers**

Limited improvement in the stability of polyolefins was realized from the incorporation of antioxidants. A decrease in elongation of 50% was found for polypropylene stabilized with Irganox 1010 compared to a 90% decrease for



Figure 4-2. Time-to-Failure Plots of Two Polyolefinic Materials

unstabilized polypropylene after three months exposure to the catholyte at room temperature (Figure 4-3). After six months of exposure under the same conditions, decreases in elongation were 64% and 97%, respectively, for stabilized and unstabilized polypropylene. Similar results were obtained with Agerite and Irganox-synergist combinations. Possible loss of stabilizers by leaching may account for this rather lackluster performance. It is also conceivable that better stabilization could have been realized at higher concentration levels.



Figure 4-3. Effect of a Hindered Phenolic Stabilizer on the Stability of Polypropylene Exposed to a Bromine-Containing Electrolyte

### **Bromine Profile Experiments**

Physical processes such as diffusion and chemical attack are involved when aggressive chemical agents such as bromine degrade polymeric materials in bulk form. If diffusion into the bulk is a rapid process relative to the reaction rate, degradation occurs uniformly throughout the sample at a rate controlled by the reaction itself. If, on the other hand, diffusion is slow relative to the rate of chemical reaction, degradation occurs primarily near the surface of the sample. In this case, the active agent simply reacts before it has a chance to diffuse into the interior of the sample. This latter degradation reaction is classified as heterogeneous.

To distinguish between these two possible modes of degradation, polypropylene tensile bars were exposed to gaseous bromine at room temperature for a period of two weeks. The samples were then extracted with chloroform, dried in a vacuum oven at 50°C, and analyzed by electron-microprobe analysis for bromine content as a function of depth across the  $3200-\mu$ m thickness dimension of the sample. A U-shaped profile of bromine content (wt %) was observed. The bromine concentration at the surface of the sample was 4% and rapidly decreased to about 0.5% at a distance of only 160  $\mu$ m. These data suggest that the degradation is predominantly heterogeneous.

### **Gaseous Bromine Tests**

The number-average molecular weight of polypropylene that was exposed to gaseous bromine for two weeks at room temperature decreased from 32000 daltons to 23500 daltons, a decrease of 26%. The mechanism of this chain cleavage is not currently known.

# Failure Analysis of the Beta"-Alumina Electrolyte

The objective of this task is to identify mechanisms that cause electrolyte failure in sodium/sulfur cells. Two activities are included: 1) fractographic analysis of electrolytes from actual cells and 2) experimental evaluation of the electrochemical degradation of beta"-alumina. The latter study, performed by A. Virkar at the University of Utah, supplies fundamental information for determining potential mechanisms of electrolyte degradation. Fracture analysis of electrolytes from CSPL cells was initiated in late 1986 and its results will be included in the 1987 ETD report. The remainder of this section briefly summarizes the progress made during 1986 on the electromechanical subtask.

At high localized current densities, degradation of the beta"-alumina electrolyte can occur in the form of cracking. The cracks grow under the pressure generated as sodium flows into the crack through the walls. The magnitude of that pressure is determined by the resistance to the flow of sodium out of the crack opening.

The objective of the current study is to determine how mechanical stresses in the electrolyte might affect the degradation process through change in the resistance to the flow of sodium. For example, compressive stress might restrict the flow by reducing the size of the crack opening. Also, compressive stress could reduce the stress intensity at the crack tip so that crack growth would be impeded. It is clear from analyses of failed sodium/sulfur cells that there are many possible sources for mechanical stresses in electrolyte tubes during charging and discharging. In addition, the inclusion of partially stabilized zirconia as a toughening additive to beta"-alumina can produce high local compressive stresses.

Table 4-4 provides a summary of the experimental findings. These findings are discussed in more detail below.

### **Room-Temperature Experiments**

The first series of experiments in this study was conducted at room temperature, using a sodium nitrate solution for the electrolysis. Barshaped specimens were fabricated from powder consisting of 8.85 wt % sodium oxide, 0.75 wt %

### Table 4-4. Failure Analysis of the Beta"-Alumina Electrolyte

Room-Temperature Experiments

Mechanical degradation of unnotched electrolyte bars suppressed by compressive loading, enhanced by tensile stress.

Mechanical degradation of notched electrolyte bars not suppressed by compressive loading.

High-Temperature Experiments

> Initial experiments show no mechanical degradation in notched electrolyte bars under a slight compressive load, but profuse dendritic growth observed when temperature lowered below the melting point of sodium.

Additional testing at higher compressive loads underway.

lithium oxide and 90.4 wt % aluminum oxide by sintering die-pressed and isostatically pressed compacts at 1585°C for five minutes in sealed platinum containers. Subsequently, the samples were annealed at 1450°C for two hours in packed beta"-alumina powder. Density of the ceramics was typically greater than 98% of theoretical.

Some of the bar-shaped specimens were notched on one side with a diamond blade of 0.006-inch thickness. Notched and unnotched samples were partially silver painted as shown in Figure 4-4. With the exception of the side directly opposite the silver-painted region, the rest of the bar was coated with a water-resistant electrically insulating paint. Strips of aluminum foil were attached to the silver-painted regions as electrical leads. Specimens were then placed into the loading apparatus shown in Figure 4-5. All of the notched samples (except those that received no electrolytic treatment) and some of the unnotched samples were electrolyzed without mechanical load for 3 s at 5 to 7 mA. This treatment generated a starter dendrite that would be extended during subsequent electrolysis under various mechanical loading conditions. In addition, some of the unnotched bars were electrolyzed under load without starter dendrites. The residual strength of the bar in bending after electrolysis was used as the measure of the extent of degradation of the material.



Figure 4-4. Notched and Unnotched Specimens

Tables 4-5 and 4-6 show the results of strength testing after electrolysis under pressure. Clearly, from Table 4-5, the degradation of unnotched bars was suppressed by compressively loading the region in which the dendrites were growing, and tensile stress enhanced the degradation. For notched bars, compressive stress did not mitigate the degradation and may even have enhanced it, in accordance with the analysis by Virkar (Virkar, A. V., J. Mat. Sci. 21, 859 (1986)) and previous experimental results of Kuribayashi and Nicholson (Kuribayashi, K., and P. S. Nicholson, J. Mat. Sci. 18, 1590 (1983)).

### **High-Temperature Experiments**

Although the room-temperature experiments have provided conclusive evidence that local stress affects the degradation of beta"-alumina undergoing electrolysis, they may not truly reflect what happens when the temperature is above the melting point for sodium. To address the question of high-temperature degradation, the study is being extended to the temperature range 300-350°C. Because of the difficulties of providing a sodium source at high temperature, the initial experiments are being conducted with the electrolyte bars in a temperature gradient. Sodium enters the bar from an aqueous solution of sodium nitrate at room temperature and exits through a notch in the high-temperature end of the bar. The bar geometry and heating arrangement have been chosen so that thermal stresses are minimal.

The first experiments with a small compressive load on the notched sample produced no dendrite growth, and no degradation occurred at current densities of  $10 \text{ A/cm}^2$ , provided the notch temperature was above the melting point of sodium. However, as soon as the notch temperature dropped below the melting point, profuse dendrite growth occurred at modest current densities. Additional experiments to determine the effect of larger compressive loads and tensile load tests are underway.



Figure 4-5. Experimental Arrangement for Electrolysis Under Stress

### Table 4–5. Degradation by Electrolysis of Unnotched Bars

Electrolysis Treatment	Pressure During Electrolysis	Failure Stress (After Electrolysis) (MPa)
	a) Without Starter Dendrites	
None	None	220
4.9 mA, 10	None	86
4.8 mA, 10	30 MPa compression	165
≈5 mA, 10	15 MPa tension	55
	b) With Starter Dendrites	
6.9 mA, 10	None	36
7.6 mA, 10	50 MPa compression	53
5.3 mA, 10	25 to 30 MPa tension	37

Electrolysis Treatment	Pressure During Electrolysis	Failure Load (After Electrolysis) (kg)	
None	None	34.6	
≈5 ma, ≈15	None	18.2	
≈5 ma, ≈15	15 MPa compression	16.0	

### Table 4–6. Degradation by Electrolysis of Notched Bars

### Modeling Electrolyte Stress During Freeze/Thaw Cycling Of Na/S Cells

Freeze/thaw cycling of sodium/sulfur cells will occur during the normal operation of most installed battery systems. Many of the cell failures observed during this severe type of thermal cycling are because of electrolyte fracture (Gross, F., et al., "Present Tasks of Research in Sodium/Sulfur Battery Development," Extended Abstracts: Volume 84-2, the Electromechanical Society, October 1984, pp. 151 and 152, and Beauchamp, E.K., B-Alumina Electrolyte Failure in Sodium/Sulfur Batteries, SAND86-0019, Sandia National Laboratories, July 1986, pp. 7-11). The ultimate objective of this task is to develop and validate an analytical methodology that predicts stress within sodium/sulfur cell components during freeze/thaw cycling. In order to accomplish this goal, a more immediate objective was recognized: an understanding of the important thermomechanical processes that can cause deleterious stress conditions. The final analytical methodology, along with the information gained during its formulation, will be very useful to battery designers in their efforts to minimize thermal effects and thus improve lifetime performance.

Three integrated activities are being performed in this task. The first involves the development of the calculational model itself. Significant aspects include identifying materialsbehavior models, incorporating these models into a structural-analysis code, performing calculations, and modifying the models based on information from the calculations and the other two activities. The primary difficulty in modeling the thermomechanical response of a sodium/sulfur cell is being able to provide accurate materials models for the positive electrode as it undergoes thermal cycling. The required information, data, and insight for the calculations, the materials model development, and final validation will be supplied by two supporting activities: the measurement of the physical and mechanical properties of the primary positive-electrode materials and the direct measurement of thermal and stress distributions generated within the cell during freeze/thaw cycling.

This task was initiated in 1985 with efforts focusing on the two experimental activities. Progress during 1986 consisted of formulating a detailed program plan, performing initial thermomechanical calculations, and refining experimental apparatus and techniques. With the successful completion of this preliminary phase, the first significant results from this task will be produced during 1987. A summary of the specific progress made during 1986 is given in the remainder of this section, and the highlights of this summary are presented in Table 4-7. This information also formed the basis for a paper presented at the 170th Electrochemical Society Meeting held in October 1986.

### **Modeling Study**

During 1986, the first attempt was made to model the thermomechanical response of this complex system. This effort consisted of selecting

### Table 4–7. Modeling Electrolyte Stress During Freeze/Thaw of Sodium/Sulfur Cells

Modeling Study

Simplified simulation of freeze/thaw behavior of an FACC sodium/sulfur cell confirms that gap between the two C-shaped segments of the positive electrode caused tensile failure of electrolyte.

Physical Property Measurements

> Much work required on acquiring thermo-physical properties of positiveelectrode materials (sulfur, sodium, and graphite felt).

> Characterization studies planned to establish relationship between crystallization and thermal history of sodium polysulfides.

**Cell Behavior** 

Laboratory cell redesigned; several cells built and one safety test completed.

Electrolyte stress determined by monitoring strain on the container.

Adiabatic thermal measurements will determine solidification/crystallization behavior of sodium polysulfides.

Acoustic emission measurements planned to pinpoint when electrolyte first fractures.

an appropriate structural code, identifying and incorporating materials models that utilize existing data, and finally using these models in the code to predict stress distributions for a relatively simple freeze/thaw problem. The prime objectives of the calculation were to gain familiarity with the operation and some of the capabilities of the selected structural code, identify critical physical properties and cell characteristics, and determine where significant improvements are needed in the materials model.

The simple problem that was chosen for this initial modeling effort involved the simulation of an in-service failure of a sodium/sulfur cell produced by the Ford Aerospace and Communications Corporation (FACC). A fractographic examination of the surface of the failed electrolyte from this cell was performed at SNL (Beauchamp, E. K.,  $\beta$ -Alumina Electrolyte Failure in Sodium/Sulfur Batteries, SAND86-0019, Sandia National Laboratories, July 1986, pp. 7-11). This cell utilized a positive electrode consisting of two C-shaped segments. A gap existed in the contact zone with the electrolyte between the two segments. Based on the fractographic results, a mechanism was postulated that tensile stresses on the outside of the electrolyte caused fracturing along the periphery of the contact zone.

To confirm that the presence of a gap could indeed cause the electrolyte to fracture during freezing, cell configurations with and without a gap in the positive electrode were modeled. The following simplifying assumptions were used in the formulation of this problem, the most significant of which were related to the properties and behavior of the positive-electrode materials:

- The cell failed in the fully discharged state with the positive electrode composed entirely of eutectic mixture denoted as  $Na_2S_3$ .
- Solidification (and crystallization) of the  $Na_2S_3$  occurred at the equilibrium

temperature predicted by the phase diagram, 235°C (no supercooling).

- The positive electrode was modeled as a linear-elastic material with temperature dependent elastic modulus and Poisson's ratio. These two parameters were varied linearly. The electrode material was assumed to undergo a linear transition from a melt or a "soft" material at 235°C to a brittle material as it cooled to 25°C.
- Both the beta"-alumina electrolyte and the metal container were treated as linearly elastic materials.
- At any given time, isothermal conditions existed within the entire cell.

The simulation consisted of cooling the cell from a stress-free state at the melting point of positive electrode  $(235 \,^{\circ}C)$  to an ambient temperature of  $25 \,^{\circ}C$ . The positive electrode has the highest coefficient of thermal expansion; the electrolyte the lowest. As the cell cools, the different materials contract at different rates thereby inducing stresses within the cell.

Using problem symmetry, finite-element meshes were constructed on the plane section of the FACC cell being studied. A schematic diagram of the plane section and the finiteelement representation is shown in Figure 4-6 for the configuration with the electrode gap. The numerical simulation of the freezing cell in both configurations was performed on the CRAY-1S computer using the nonlinear, finite-element structural code JAC (Biffle, J. H., JAC-A Two Dimensional Finite Element Computer Program for the Non-Linear Quasistatic Response of Solids with the Conjugate Gradient Method, SAND81-0998, Sandia National Laboratories, April 1984).

Selected results from the two numerical simulations are shown in Figure 4-7. The general conclusions drawn from the results of this simulation are discussed below. Stress in the electrolyte for a cell configuration without a gap in the positive electrode is compressive, uniformly distributed, and increases as the temperature decreases. Under such conditions, electrolyte fracture is unlikely. However, the presence of a gap produces a stress distribution through the electrolyte that resembles beam flexure. A tensile stress is concentrated on the surface at the periphery of the gap and its magnitude increases as the temperature decreases. The location of high tensile stress in the electrolyte is found to be consistent with that identified by Beauchamp as being the location of the primary fracture (see reference at beginning of discussion on modeling electrolyte stress during freeze/thaw cycling).

For comparison, strength tests of Ceramatec beta"-alumina specimens indicate that unindented rings have a tensile strength of approximately 20,000 psi. Thus, the magnitudes of the stresses calculated in this analysis are indeed sufficient to produce a fracture. Additionally, these results show that volumetric changes because of thermal expansion may be the key process that influences electrolyte stress.









Figure 4-7. Contours of Constant Stress Superimposed on a Schematic Diagram of the Two Cell Configurations

### **Physical Property Measurement**

Only a few of the needed thermo-physical properties are known for the electrically active positive-electrode materials (sulfur and sodium polysulfides), and almost none are known for the composite electrode that includes the graphite felt. For the initial modeling effort discussed above, only the coefficients of thermal expansion, elastic modulus, and Poisson's ratio were required. For the more sophisticated predictive capabilities required in the future, the values of these properties must be accurately known. In addition knowledge of some other properties may be necessary (for example, thermal transport properties, heats of fusion, degree of supercooling). Because of the tendency for the sulfur and sodium polysulfides to supercool, possibly to a metastable configuration at room temperature, the crystalline nature and subsequent mechanical response of the electrode cannot be considered "fixed" at a given composition and temperature. Thus, these properties are dependent on thermal history.

In order to characterize the behavior and measure the needed properties of the electrode materials, techniques involving differential scanning calorimetry (DSC), dilatometry, and dynamic mechanical analysis (DMA) will be used. The characterization studies will attempt to establish, at least qualitatively, a relationship between crystallization and thermal history (that is, how rapidly a metastable amorphous sodium polysulfide will crystallize at room temperature, when crystallization will occur on reheating, the volume change associated with such phase changes, and so on).

The mechanical properties (elastic modulus, shear modulus, and Poisson's ratio) of the positive-electrode compositions are basically unknown. The thermo-analytical technique of dynamic mechanical analysis (DMA) will be used at SNL to measure these mechanical properties. The characteristics of DMA that make it attractive for this application include the following: it can be done inside an inert atmosphere glove box, measurements can be performed on a single sample as temperature is varied, and a wide range of moduli (1 MPa to 200 GPa) can be determined. The elastic or shear modulus can be measured directly, and Poisson's ratio can then be inferred by making measurements on samples with different geometries. Finally, thermal expansion measurements on the electrode materials will be made using dilatometry.

### **Cell Behavior**

The primary objective of this activity is to provide the necessary data for eventually validating the analytical methodology being developed. In the near term, however, this activity will be a critical component of the effort to develop an understanding of the important thermomechanical processes that can be responsible for deleterious stress conditions.

To accomplish these goals, a laboratory cell that can be properly instrumented and altered is needed. The initial design of this cell was described in the 1985 ETD annual report. Because of persistent cantilever-type failures of the electrolyte during assembly and heating, this cell was redesigned and assembly tolerances were tightened. The main design change was the addition of a flange and plate on the bottom of the cell to replace the plug. This allows the sulfur electrode to be placed into the cell following assembly of the main seal and filling of the cell with sodium. The new design and assembly procedures were shown in early 1987 to be successful. Several cells have been built. electrically cycled at temperature, and subjected to freeze/thaw cycling.

Because of the ease of instrumenting and controlling conditions, the laboratory cell will be used in the majority of the initial measurements. The behavior of PB cells from CSPL will also be determined once experimental procedures become established. Two basic types of measurements will be made during freeze/thaw cycling of these cells: stress and thermal.

The stress measurement is based on the observation that electrolyte stress is produced by processes occurring in the positive electrode (Gross, R., et al., "Present Tasks of Research in Sodium/Sulfur Battery Development," *Extended Abstracts: Volume 84-2, The Electrochemical Society,* October 1984, pp. 151-152 and Beauchamp, E. K.,  $\beta$ -Alumina Electrolyte Failure in Sodium/Sulfur Batteries, SAND86-0019 Sandia National Laboratories, July 1986, pp. 7-11). This situation allows indirect determination of electrolyte stress by monitoring the state of stress in the container. For this purpose, strain gauges are welded to the container in a variety of positions.

Adiabatic thermal measurements are useful to determine solidification and possibly crystallization behavior of the sodium polysulfides. Additionally, acoustic-emission measurements might be performed on the CSPL cells. The objective of these measurements will be to determine at what time and temperature during the freeze/thaw cycle the electrolyte first fractures. This currently undocumented information will be very valuable when screening the types of mechanisms that may be responsible for the stress (for example, entrapment of a supercooled sodium polysulfide phase).

Because of the cantilever failure problem with the laboratory cell, only one significant stress measurement experiment was completed during 1986. A safety test was performed in which the cell was overdischarged to form sodium disulfide. Based on the observed expansion of the container after cooling, a uniform tensile stress of approximately 40,000 psi was calculated to be present in the container. The corresponding uniform compressive stress that was probably imposed on the electrolyte would not be expected to and did not lead to electrolyte fracture. This result is qualitatively useful because it shows that the undesired formation of sodium disulfide can produce significant stress in the cell. Beauchamp proposed that a localized overdischarge produced sodium disulfide that resulted in a point loading and electrolyte failure of an actual cell (see reference at beginning of discussion on modeling electrolyte stress during freeze/thaw cycling).

### Future Activity

The preliminary results obtained during 1986 are qualitatively encouraging. Most useful is probably the observation that volumetric changes in the positive electrode may be the key process that affects component stress. However, because of the unexpected nature of the failures, we know that more detailed cell-failure information along with a relatively sophisticated model must be eventually developed to be useful to the designers of sodium/sulfur cells. The current lack of detailed knowledge about cell characteristics and materials behavior is a recognized factor that has led us to divide the program into four "successive" phases. The basic objective of each of these phases is as follows (with approximate completion dates given in parentheses):

I. Predict the stress levels in the electrolyte assuming relatively simple cell operating characteristics and material properties and compare the results with those observed in actual cell failures (February 1987).

II. Perform sensitivity calculations and stressmeasurement experiments to quantify the important parameters affecting component stress and determine specifically if sodium polysulfide distributions, thermal gradients, and/or freeze/thaw conditions are critical factors (October 1987). III. Improve materials-behavior models and begin validating the methodology using the information gained from the experimental subtasks and posttest analysis of actual cells (March 1988).

IV. Modify the calculational method as needed for alternate cell designs, validate the final formulations of this method with the results from the on-going stress-measurement experiments, and transfer the methodology to interested developers (December 1989). \*1 р. -

# **APPENDIX**

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