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DEVELOPMENT OF ADVANCED BATTERIES AT ARGONNE NATIONAL LABORATORY:

SUMMARY REPORT FOR 1979

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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DEVELOPMENT OF ADVANCED BATTERIES AT ARGONNE NATIONAL LABORATORY: SUMMARY REPORT FOR 1979

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Previous reports in this series

ANL-76-45 Rev.	May 1976
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PREFACE

This work is a summary of the accomplishments during 1979 in Argonne National Laboratory's program on advanced batteries. This work is carried out at Argonne, primarily in the Chemical Engineering Division, and at the laboratories of various contractors. Some of the efforts of the many scientists, engineers, and technicians who have contributed to this program during the year are reflected in the list of publications at the end of this report, and in other publications planned for the near future. Although acknowledgement of the contributions of individuals is beyond the scope of this brief report, their efforts are essential to the success of the program.

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ABSTRACT

This report presents a summary for 1979 of Argonne National Laboratory's program on the development of advanced batteries. These batteries are being developed for electric-vehicle propulsion and stationary energy-storage applications. The principal cells under investigation at present are of a vertically oriented, prismatic design with one or more inner positive electrodes of FeS or FeS_2, facing negative electrodes of Li-Al alloy, and molten LiCl-KCl electrolyte; the cell operating temperature is 400-500°C. A small effort on the development of a calcium/metal sulfide cell is also being conducted.

During 1979, cell and battery development work has continued at ANL and contractors' laboratories. A 40 kW-hr electric-vehicle battery (designated Mark IA) was fabricated and delivered by Eagle-Picher Industries, Inc. to ANL for testing. During heat-up, one of the modules failed due to a short circuit. A failure analysis was conducted and the Mark IA program completed. Development work on the next electric-vehicle battery (Mark II) was initiated at Eagle-Picher and Gould Inc. Work on stationary energy-storage batteries has consisted primarily of conceptual design studies.

I. OVERVIEW OF BATTERY PROGRAM

The advanced battery project at ANL is aimed at the development of high-performance, electrically rechargeable batteries for electric-vehicle propulsion and for stationary energy storage. The widespread use of electric vehicles would conserve petroleum fuels, since the energy for charging the batteries could be provided by coal, nuclear, hydroelectric, or other energy sources; a side-benefit would be realized in decreased air pollution in congested urban areas. The use of stationary energy-storage batteries for load leveling on electric-utility systems could save petroleum by reducing the need for gas turbines to meet peak power demands. The stationary storage batteries may also find application in systems utilizing solar, wind, or other cyclic or intermittent energy sources.

The battery cells that are currently under development consist of a lithium-aluminum or lithium-silicon negative electrode, an FeS or FeS_2 positive electrode, a separator to provide electrical isolation of the electrodes, and molten LiCl-KCl electrolyte. The melting point of the electrolyte (352°C at the eutectic composition of 58.2 mol % LiCl) requires a battery operating temperature in the range of about 400-500°C. The overall electrochemical reaction for the Li-Al/FeS cell can be written as follows:

$$2LiAl + FeS \overset{2e^-}{\rightleftharpoons} Li_2S + Fe + 2Al \qquad (1)$$

The theoretical specific energy for reaction 1 is about 460 W-h/kg, and the voltage vs. capacity curve has a single voltage plateau at about 1.3 V. The reaction is actually much more complex than shown; for example, an intermediate compound, $LiK_6Fe_{24}S_{26}Cl$ (J phase), is formed through a reaction with the KCl in the electrolyte. The overall reaction for the Li-Al/FeS_2 cell can be written in two steps:

$$2LiAl + FeS_2 \overset{2e^-}{\rightleftharpoons} Li_2S + FeS + 2Al \tag{2}$$

$$2LiAl + FeS \overset{2e^-}{\rightleftharpoons} Li_2S + Fe + 2Al \tag{3}$$

The total theoretical specific energy for reactions 2 and 3 is approximately 650 W-h/kg. The voltage vs. capacity curve has two voltage plateaus, one at about 1.7 V (reaction 2) and the other at 1.3 V (reaction 3). The Li-Al/FeS_2 cells are often designed to operate only on the upper voltage plateau; these are referred to as "upper plateau" cells. Reaction 2 and 3 also involve several complex intermediate phases (generally ternary compounds of lithium, iron, and sulfur).

Most of the cells that have been fabricated during the past year have been of a prismatic, multiplate design with two or more positive electrodes and facing negative electrodes (see Fig. 1). Porous separator sheets between the electrodes serve as electronic insulators, while at the same time providing a path for the migration of lithium ions through the electrolyte absorbed in the separator material. Since the negative and positive electrodes are both porous structures of the active material filled with electrolyte, screens or cloths are often used on the electrode faces to prevent the escape of active materials from the electrodes into the separator. To enhance the electronic conductivity of the electrodes, metallic current collectors are used to provide a low-resistance current path from all areas of the electrode to the terminal. In nearly all of the present cell designs, the negative electrodes are grounded to a steel can or housing, and the terminal of the positive electrode extends through the top of the cell can via an electrically insulating feedthrough. The top of the cell can is also provided with a tube, which is closed off later by a weld, to permit the addition of electrolyte to the cell after assembly.

The lithium/iron sulfide cell can be assembled in a charged, uncharged, or partially charged state. To assemble a Li-Al/FeS or Li-Al/FeS_2 cell in the charged state, the negative electrodes are normally cold- or hot-pressed from Li-Al powder (usually 46-50 at. % lithium), which may or may not be mixed with some of the LiCl-KCl electrolyte powder. The positive electrodes are formed similarly by cold- or hot-pressing FeS or FeS_2 powder with or without added electrolyte powder. In the case of the uncharged cells, the positive electrode is pressed from a mixture of Li_2S and iron powder in the appropriate proportions; the negative electrode in this case is an aluminum structure (e.g., pressed wire, porous metal, solid plate) which is converted to the Li-Al alloy electrochemically when the cell is charged. Partially charged cells can be fabricated from mixtures of the above materials in intermediate ratios.

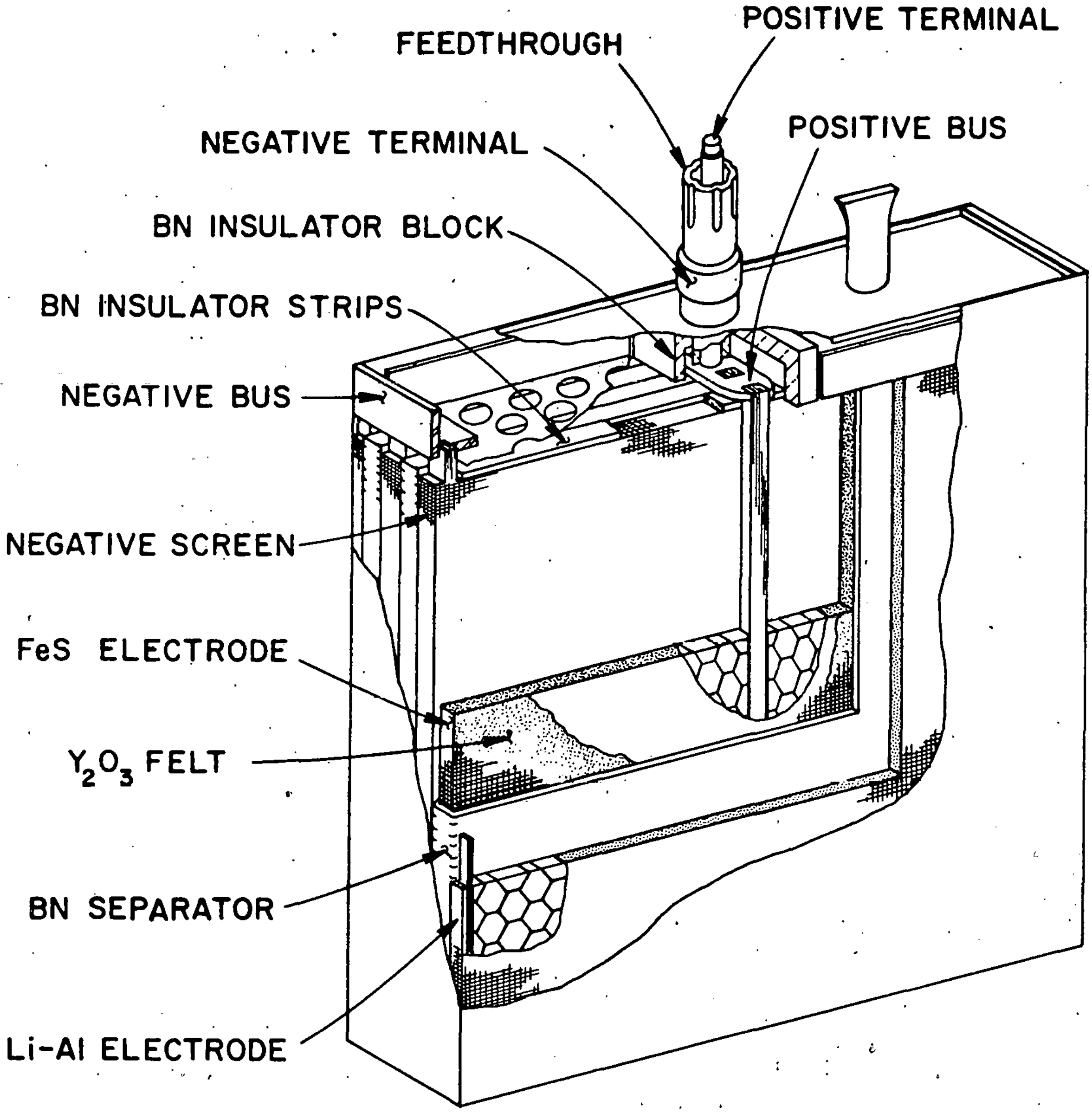

Fig. 1. Lithium/Iron Sulfide Cell

The major requirements for an electric-vehicle battery are high specific energy (W-h/kg), high volumetric energy density (W-h/L), and high specific power (W/kg). Economic considerations require a minimum battery lifetime of about 3 yr (about 500 deep discharge cycles or equivalent) and a cost of about \$50-60/kW-h.* Stationary energy-storage batteries have somewhat less stringent specific-energy and specific-power requirements, but this application demands a longer lifetime (about 10 years and 2000 cycles) and a cost of \$45-55/kW-h. As a result of these requirements, considerably different approaches are being taken in the designs of cells and batteries for these two applications.

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*Costs in 1979 dollars.

The program on the electric-vehicle battery involves the development, design, and fabrication of a series of full-scale lithium/iron sulfide batteries, designated Mark IA*, II, and III. The performance and lifetime goals for the Mark IA, II, and III batteries are presented in Table 1. The main

Table 1. Program Goals for the Lithium/Iron Sulfide Electric-Vehicle Battery

Goal	Mark IA 1979	Mark II 1982	Mark II 1984	Mark III 1986
Battery Capacity, kW-h				
Automobile	--	20-40	20-40	20-60
Van	40	40-60	40-60	--
Specific Energy,[a] W-h/kg				
Cell (average)	80	125	125	160
Battery	60	100	100	130
Energy Density, W-h/liter				
Cell (average)	240	400	400	525
Battery	100	145	200	300
Peak Power,[b] W/kg				
Cell (average)	80	125	125	200
Battery	60	100	100	160
Battery Heat Loss,[c] W	400	200	150	125
Lifetime				
Deep Discharges[d]	200	300	500	800
Equivalent Miles[e]				
Automobile	--	30,000	50,000	80,000
Van	--	25,000	42,000	--

[a] Calculated at the 4-h discharge rate.

[b] Peak power sustainable for 15 s at 0 to 50% state of discharge; at 80% discharge, the peak power is 70% of the values shown.

[c] The values shown represent the heat loss of the battery through the insulated case; under some operating conditions, additional heat removal may be required.

[d] Delivery of 80% of the initial battery capacity at the 4-h rate.

[e] Based upon battery energy consumption at 232 W-h/ton mile.

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* The original plan was to develop a series of Mark I batteries (IA, IB, and IC); however, a decision was made to proceed directly from Mark IA to Mark II in the development program.

purpose of the Mark IA battery, which was fabricated during 1979, was to evaluate the overall technical feasibility of the Li-Al/FeS system for the electric-vehicle application and to identify potential problem areas. The Mark II battery, which also will consist of Li-Al/FeS cells, has somewhat higher performance goals than Mark IA; but the major objective is to develop designs and materials that will have a potential for low-cost manufacture in mass production. The Mark III battery, expected to demonstrate even higher performance and longer lifetime than those of Mark II, will probably consist of Li-Al/FeS_2 cells.

Most of the effort during the past year on the stationary energy-storage battery has involved conceptual design studies of a 100-MW-h energy-storage plant. The goals for this plant are listed in the right-hand column of Table 2. As shown in Table 2, testing of a 5-MW-h battery module in the Battery Energy Storage Test (BEST) facility is expected to follow successful demonstration of lithium/iron sulfide electric-vehicle batteries. This facility, which is being constructed under joint sponsorship by the U.S. Department of Energy, the Electric Power Research Institute, and the Public Service Co. of New Jersey, will be used to test various types of batteries as load-leveling devices on an electric utility system.

Table 2. Program Goals for Lithium/Iron Sulfide Stationary Energy-Storage Batteries

Goal	BEST[a]	Demonstration
Battery Performance		
Energy Output, kW-h	5,000	100,000
Sustained Power, kW	1,000	20,000
Cycle Life	500-1,000	2,000
Discharge Time, h	5	5
Charge Time, h	10	7
Cell Performance		
Specific Energy, W-h/kg	60-80	60-150
Specific Power, W/kg	12-20	12-30
Cell Cost, $/kW-h	--	25-40[b]

[a] Battery Energy Storage Test Facility.

[b] Projected cost for a production rate of 2000 MW-h/yr in 1979 dollars.

A major objective of the program at ANL is to transfer the technology to interested commercial organizations as it is developed, with the ultimate goal being a competitive, self-sustaining industry for the production of lithium/iron sulfide batteries. Technology transfer is implemented by various means, including the assignment of engineers or scientists from industrial companies to ANL on a cost-sharing basis, and the subcontracting of development work on cells, batteries, and auxiliary items to industrial firms. Cost, design, and marketing studies are also conducted with the assistance of subcontractors and consultants. Various academic institutions are also involved in the program through temporary student and faculty assignments, subcontracts, and consultants, mainly in the area of electrode modeling. At the present time, approximately sixty percent of the funding in this program is used for subcontracted work.

The research and development work at ANL includes cell and battery testing, post-test examinations of cells, cell and battery engineering development, materials development and testing, cell-chemistry studies, and commercialization studies. As improvements are made in the ANL cell materials and designs, they are incorporated into the cells fabricated by the subcontractors.

In addition to the research and development program on lithium/iron sulfide batteries, a small effort on alternative cell systems has been maintained under a separate budget activity. The objective of this work is to develop a new battery system that uses abundant, low-cost materials while maintaining the performance levels required for electric vehicles or stationary energy storage. During the past year, this program has been focused on the use of calcium alloys as the negative electrode material.

II. COMMERCIALIZATION STUDIES

The objective of the commercialization studies at ANL is to provide data on the manufacturing cost and market requirements for the lithium/iron sulfide battery. The commercialization studies are conducted at ANL with assistance from industrial subcontractors and consultants. These studies involve the identification of potential markets, manufacturing cost analyses, financial plans, and evaluations of competing technologies.

In 1976, an estimate[1] was made of the cost, in dollars per kilowatt-hour, to mass-manufacture an Li-Al/FeS cell for stationary energy-storage (SES) applications. During 1979, the cost for this type of cell was updated and used as the basis for estimating the cost to mass-manufacture Li-Al/FeS and Li-Al/FeS_2 cells for electric-vehicle (EV) applications. For both applications, the cost was estimated for cells assembled in the uncharged and charged states. As shown in Fig. 2, the cost is about \$31 to 33/kW-h for uncharged EV cells, \$53 to 55/kW-h for charged EV cells, \$24/kW-h for uncharged SES cells, and \$41/kW-h for charged SES cells. The total materials cost for each cell, also shown in Fig. 2, represents about 52 to 65% of the total cell cost. The most expensive materials were the following: lithium (metal and compounds), \$4.61 to 14.26/kW-h; BN felt separator, \$4.00 to 8.50/kW-h; feedthrough components, \$2.40/kW-h; positive current collector, \$1.45 to 2.20/kW-h; and aluminum, \$1.43 to 1.66/kW-h.

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[1] W. L. Towle, J. E. A. Graae, A. A. Chilenskas, and R. O. Ivins, Cost Estimate for the Commercial Manufacture of Lithium/Iron Sulfide Cells for Load Leveling, Argonne National Laboratory Report ANL-76-12 (March 1976).

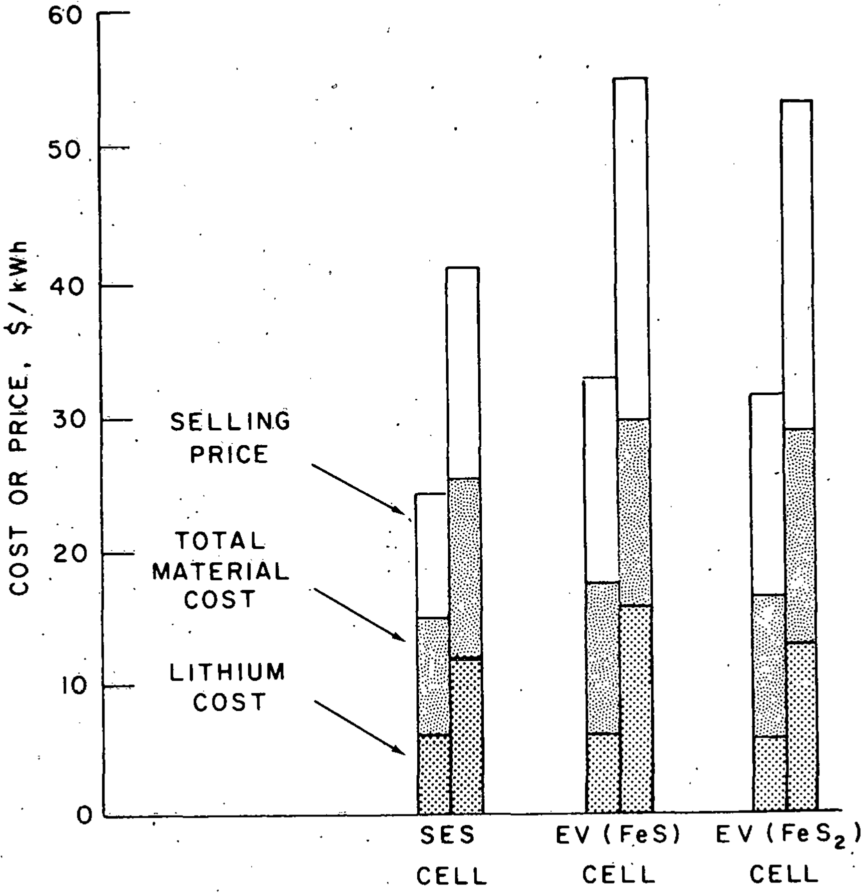


Fig. 2. Cost Estimated for Stationary Energy-Storage and Electric-Vehicle Cells. (For each cell type, the column on the left represents the uncharged cell and that on the right represents the charged cell.)

III. INDUSTRIAL CONTRACTORS

The two major subcontractors--Eagle-Picher Industries, Inc. and Gould Inc.--are developing manufacturing procedures as well as fabricating and testing cells and batteries for electric-vehicle applications. In addition, some of the industrially fabricated cells and batteries are being tested at CEN's testing facilities. Other subcontractors include Rockwell International, General Motors Corp., and the Institute of Gas Technology.

A. Major Subcontractors

Over the past year, Gould has fabricated about forty-five Li-Al/FeS bicells (one positive plate) and five multiplate cells (two positive plates). All of these cells had LiCl-KCl electrolyte and BN felt separators (see discussion of this material in Section VI.B). Testing of these cells was conducted at the Gould and CEN facilities.

Initially, Gould cells were fabricated in the uncharged state. However, uncharged cells cycled during the past year have shown poor negative-electrode utilization and electrode swelling. Recently, therefore, Gould cells have been assembled from electrodes in the half-charged state. One such cell showed little or no performance decline over an extended period of cycling (>300 cycles). Testing of half-charged cells will be continued in the next year. Another improvement in the cell fabrication procedure was initiated at Gould in 1979. In the past, electrodes were formed by a hot-pressing operation in a glove box, which is time-consuming and expensive. A much simpler technique, cold pressing in a dry room, has recently been employed to fabricate half-charged positive and negative electrodes. Preliminary results indicate that this fabrication technique has great promise.

In general, the Gould cells have shown very good performance characteristics, but relatively short lifetimes. Post-test examinations indicated two main reasons for cell failure: extrusion of active material from the positive-electrode edges, and failure of the electrical feedthrough. A "picture frame" assembly, shown in Fig. 3, has been reasonably successful in preventing extrusion of active material from the positive electrode. In the electrical

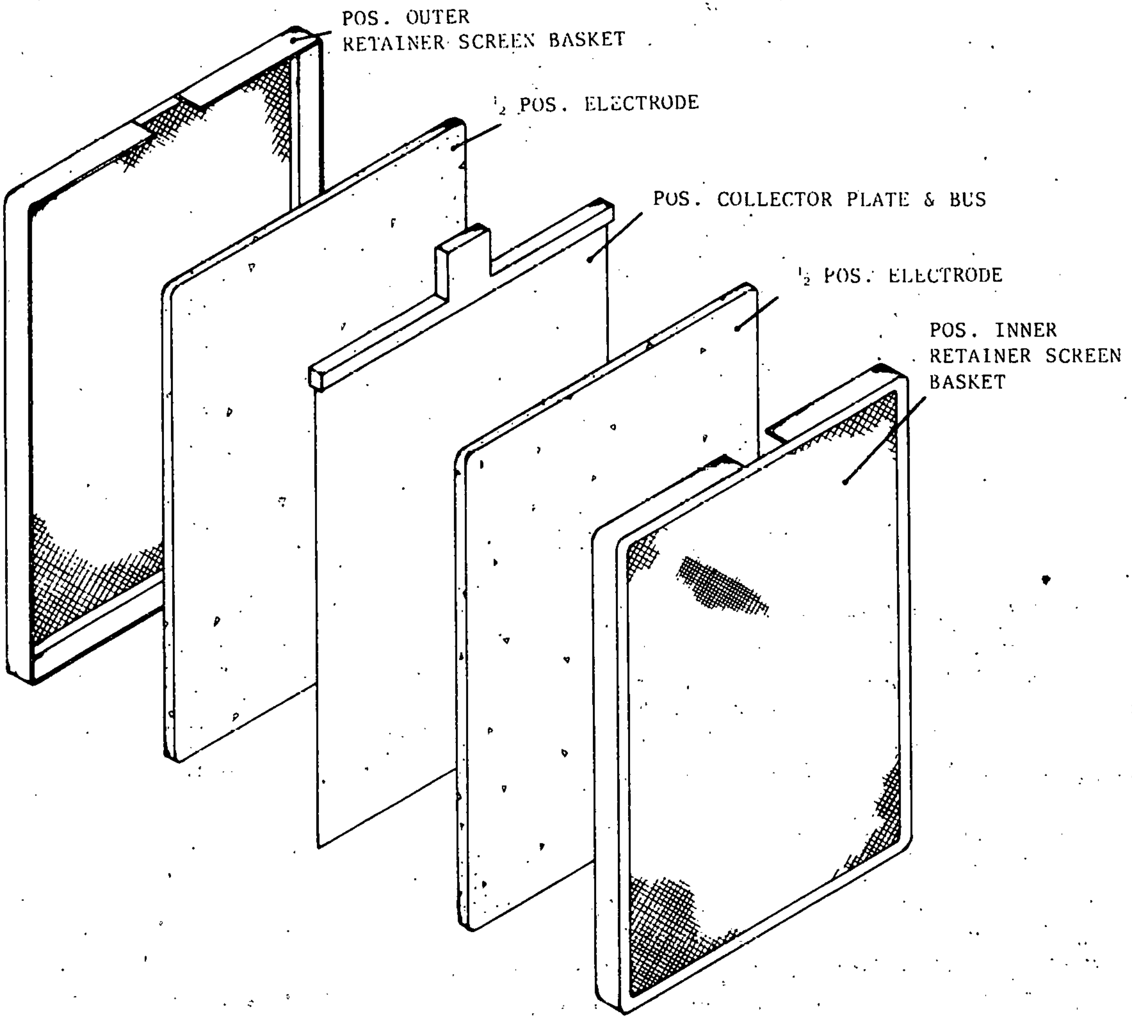


Fig. II-3. Containment Assembly for the Positive Electrode feedthroughs of earlier cells, the reliability of the seal was poor, and frequent cell failure occurred as a result of cracks forming in the lower (Y_2O_3) and upper (Al_2O_3) insulators. Consequently, the feedthrough design was changed by the following modifications: replacement of the lower and upper insulator materials with BeO, replacement of the previous nickel terminal rod with a copper-filled stainless steel rod, and improved welding procedures. The recent feedthrough design appears to have resulted in the elimination of the feedthrough as a failure mechanism.

The Gould cell with the longest lifetime in 1979 was a Li-Al/FeS bicell (theoretical capacity, 72.5 A-h). This cell was operated for about 350 cycles (six months) and, as shown in Fig. 4, maintained very stable coulombic efficiency, capacity, and specific energy. In addition, the voltage vs. cell capacity curves on charge and discharge were nearly identical at cycles 50 and 284, thereby indicating that the Gould bicell has the potential for attaining long lifetimes. Figure 5 shows the coulombic efficiency, capacity, and specific energy attained during the first twenty cycles by a Gould multiplate cell (theoretical capacity, 210 A-h); the resistance for this cell was a fairly low value of 2.5 mΩ. These performance data represent the state of the art for the Gould multiplate cell. Efforts during the next year at Gould will be concentrated on improving the lifetimes of their cells.

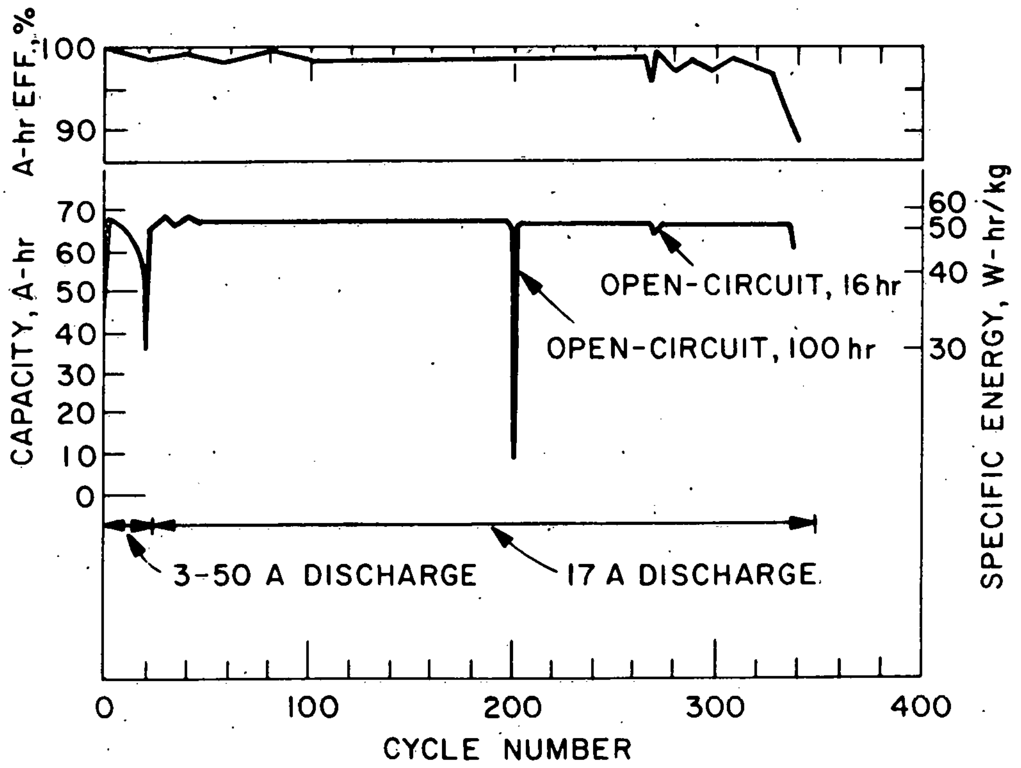


Fig. 4. Performance Data on the Longest Operating Gould Cell

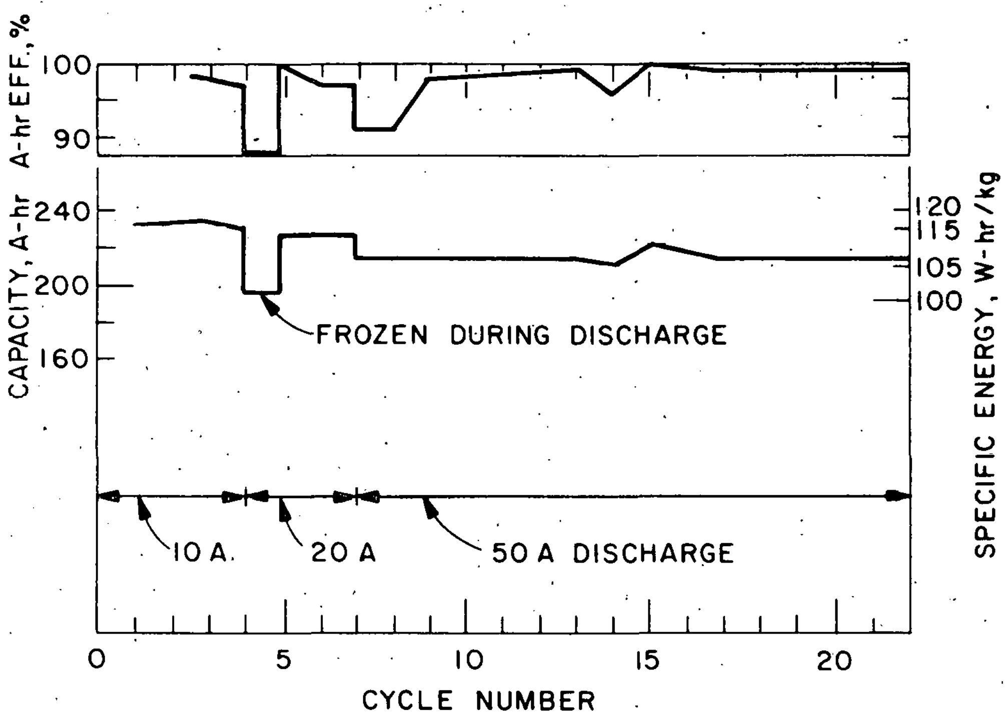


Fig. 5. Performance Data on Gould Multiplate Cell

In February 1978, Eagle-Picher was awarded a contract for the development, design, and fabrication of the 40-kW-h Mark IA battery. On the basis of previous test results, Eagle-Picher selected a Li-Al/FeS multiplate cell design (three positive and four negative electrodes) for this battery. These cells normally had the following design characteristics: dimensions of 19 × 18 × 4 cm, weight of 4 kg, and theoretical capacities of 410 A-h for the positive electrodes and 440 A-h for the negative electrodes. The separator was BN fabric and the electrolyte was molten LiCl-KCl.

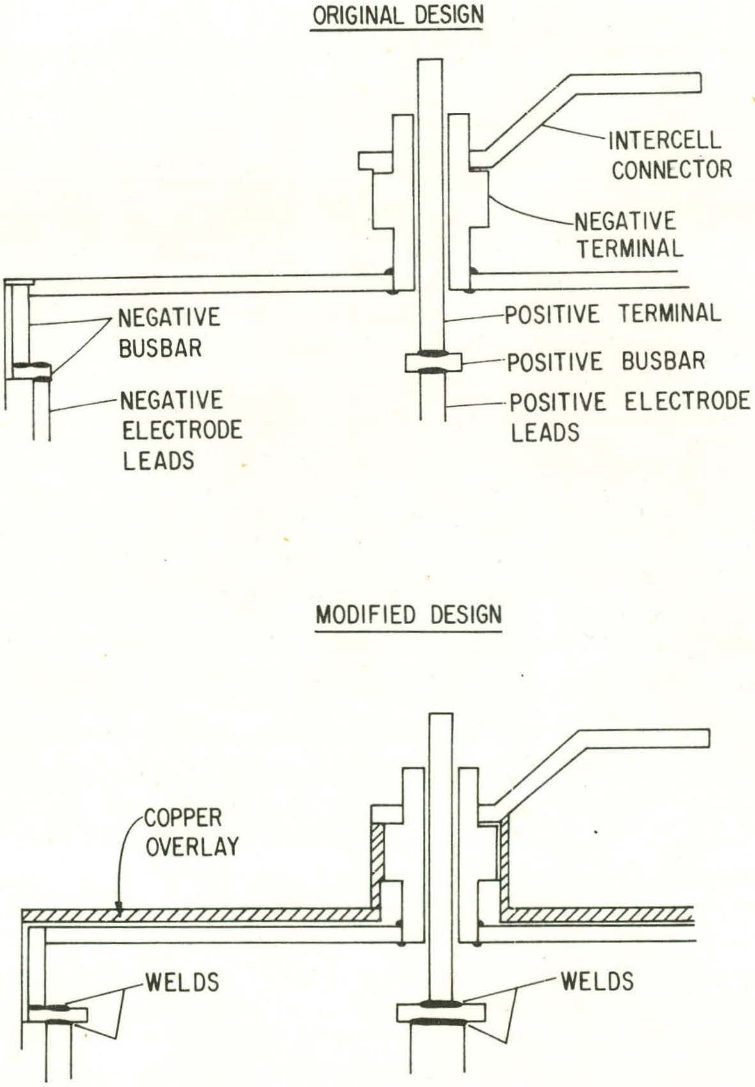
During the development phase of the Mark IA program, about 130 multiplate cells were fabricated by Eagle-Picher and then tested either at their own laboratories or ANL to determine the effect on performance of the following design variables: method of particle retention, current-collector material and design, additives to the positive electrode, and LiCl content of the electrolyte. Table 3 presents the average performance and cycle life of the six multiplate cells that operated for the highest number of cycles before failure. As shown in this table, the initial specific energy was above, and the specific power below, the goals set for the Mark IA cell in Table 1. Intensive efforts at ANL and Eagle-Picher showed that the specific power could be improved by various design modifications, primarily by improving the connection between the electrode leads and bus bars and by adding a copper layer to the cell top to reduce the resistance between the negative bus bar and the intercell connector (see Fig. 6). These design modifications, when incorporated into the final design for the Mark IA cell, resulted in a specific power of 95 W/kg at 50% depth of discharge, well above the Mark IA goal. In

Table 3. Average Performance Data of Six Eagle-Picher Multiplate Li-Al/FeS Cells

	Six-Cell Average
Initial Specific Energy,[a] W-h/kg	101.3
Specific Power,[b] W/kg	54.4
Cycle Life	258
% Decline in Energy per Cycle	0.12

[a] Measured before cycle 24 at a 4-h rate.

[b] Measured at 50% state of charge.


ORIGINAL DESIGN

MODIFIED DESIGN

Fig. 6. Modifications Made to Mark IA Cell to Improve Specific Power

safety tests, Budd Co. ruptured charged Mark IA cells at operating temperature, exposing the contents to room-temperature air, by two methods: pressing the cell until and beyond rupture and dropping a 50 kg weight onto the cell at 48 km/h (30 mph). No signs of fire or other chemical reactions were observed after rupture of these cells.

After completion of the cell development phase, Eagle-Picher initiated fabrication of the cells and other hardware for the Mark IA battery, which was delivered to ANL for testing in May 1979. The battery consisted of two 20-kW-h modules, each having 60 multiplate cells (assembled charged) arranged in two rows of 30 cells and connected in series. These cells were restrained by a stainless-steel tray and housed in a thermally insulated case to limit heat losses at the cell operating temperature. The insulated case consisted of double-walled metal (Inconel 718) with multilayered foil in the evacuated space. In addition, each module had provisions for thermal management (heating and cooling) and mica insulation to electrically isolate the cells from one another and other battery hardware. A photograph of the Mark IA module is presented in Fig. 7.

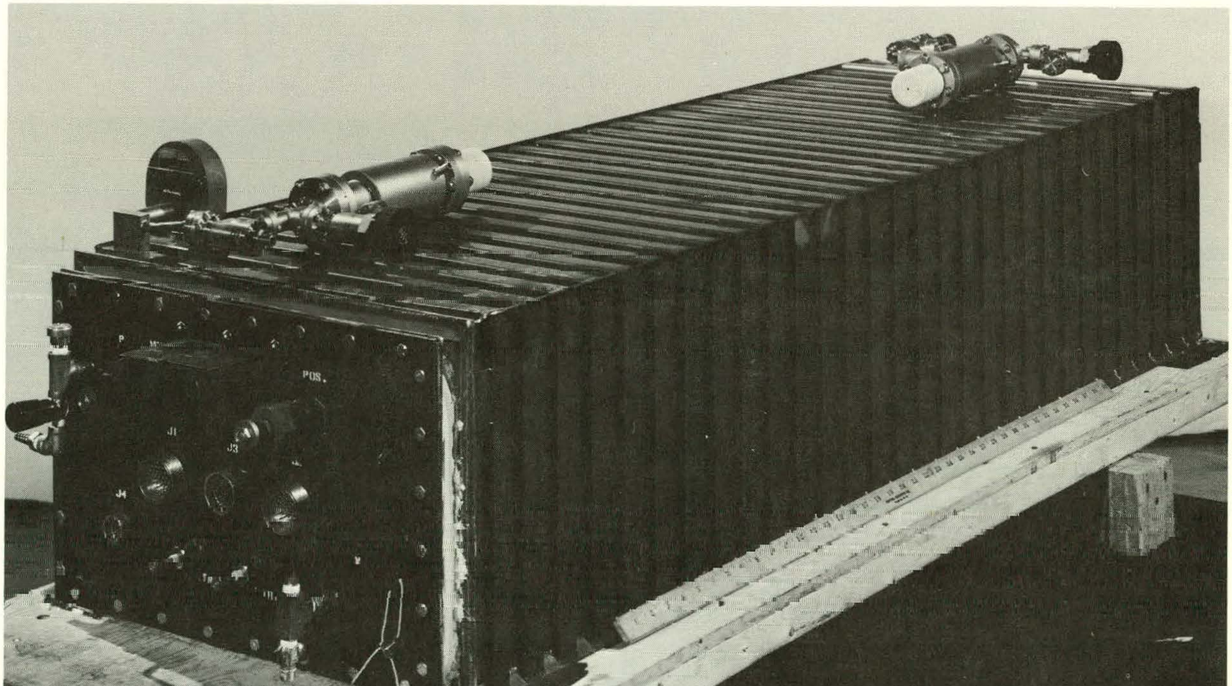


Fig. 7. Photograph of Mark IA Module.
ANL Neg. No. 301-79-411

During startup heating prior to electrical testing, one of the modules developed a short circuit external to the cells. The initial indication of difficulty was a small drop in the voltage of several cells, followed by short circuits in the balance of the cells and localized temperatures above 1000°C. The other module, which was alongside and connected in series, was unaffected by the failure. A team consisting of ANL and Eagle-Picher personnel conducted a detailed failure analysis as the failed module was disassembled, and the other module was examined for purposes of comparison. The general conclusion was that the short circuit was initiated (1) by electrolyte leakage and the resulting corrosion in the nearby region which formed metallic bridges between cells and the cell tray, or (2) by arcing between cells and the cell tray through butt joints in the electrical insulation. The above two mechanisms were also believed to have been responsible for failure propagation. On July 30 and 31, detailed findings of the failure analysis team were presented to a committee of battery experts appointed by DOE. The major topics presented in this review included the Mark IA battery design and design philosophy, a description of the failure, possible mechanisms for failure initiation and propagation, the most probable sequence of events involved in the failure, and design recommendations resulting from the analysis. Members of the DOE committee were in agreement with the conclusions of the failure analysis team. The remaining cells from this program are being used for cell testing, failure analysis experiments, and assembly of a ten-cell module. No further development work will be done on the Mark IA battery.

Concurrent with the fabrication of the Mark IA battery, Eagle-Picher constructed a small (6 V, 2 kW-h) module consisting of five Mark IA cells connected in series and housed in a steel (Inconel 718) case insulated with vacuum-foil insulation. At Eagle-Picher, this module was operated for 10 cycles and exhibited acceptable performance. During cycles 3 and 5, the module was subjected to vibrations equivalent to 2.3 years of vehicle operation; the performance did not appear to be affected by the vibrations. Upon completion of these preliminary tests, the module was sent to ANL where it was used to test a charger/equalizer unit developed at ANL (described in ANL-79-64, p. 21); this unit successfully charged and equalized the cells in this module, which operated for 70 cycles before failure. Post-test examinations revealed that two of the five cells had developed short circuits in the feedthroughs. Another small (6 V, 4 kW-h) module was fabricated by Eagle-Picher for testing at ANL. This module, which was fabricated for the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) to determine the viability of this system for fork-lift applications, consisted of five parallel-connected pairs of Mark IA cells. These five cell pairs were connected in series and thermally insulated by a stainless steel case with Min K insulation (a siliceous material).* The performance of this module was about as anticipated (e.g., a specific energy of 52 W-h/kg at the 6-h discharge rate). After 24 cycles of operation, the MERADCOM module developed a short circuit in the feedthrough of one of the cells, which was replaced. After 11 more cycles, another feedthrough in a cell developed a short circuit, and operation of the module was terminated.

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*A product of Johns Manville Corp.

Experience with these two 6-V modules has shown that the development of short circuits in the feedthroughs of cells is a problem during battery operation; such failures seldom occurred in Eagle-Picher cells that were individually cycled. In these modules, the intercell connectors, which are not flexible, place a stress on the positive terminal rods of the feedthroughs. This stress, which is probably somewhat variable during cycling, eventually results in electrolyte penetration through the feedthrough insulators and a subsequent short circuit ensues.

Early in 1979, three preliminary cost and design studies on the Mark II battery were completed by Eagle-Picher Industries, Inc., Gould Inc. and the Energy Systems Group of Rockwell International. Later in 1979, subcontracts were awarded to Eagle-Picher and Gould to proceed with development of the Mark II battery.

As a result of the Mark IA experience, the original strategy for the development of the Mark II battery has been revised into two phases. For the first phase of the Mark II program, the subcontractors will develop 10-cell modules that will be required to pass qualification tests (yet to be defined). Emphasis is being placed on cell reliability, with special attention given to the design recommendations from the Mark IA failure analysis. The subcontractors have been given the option of selecting the cell size (capacity, plate size, number of plates) with ANL approval. No specific energy density, volumetric energy density, or power density requirements will be placed on these modules. The cells have the goals given in Table 1; however, the emphasis on cell reliability and the subcontractors' choice of cell size may result in cells of the 10-cell modules falling somewhat short of the specific-energy goal of 125 W-h/kg. Development of a light-weight, thermally efficient battery case is not a part of phase I of the Mark II program, but is being pursued in a parallel, independent effort by the Linde Division of the Union Carbide Corp.

Early in 1980, each Mark II subcontractor will fabricate at least three of the same size modules, which will then be tested to assess cell reliability and module performance. Based upon the results from these tests, a decision will be made by ANL to have the subcontractors produce three or more 10-cell modules for qualification tests at ANL in October 1980, or to extend the module development effort. This decision will be made independently for each subcontractor. Phase II of the Mark II program will involve the fabrication of a full-size electric-vehicle battery, which will be tested in a vehicle at ANL in 1982.

B. Other Subcontractors

During the past year, the Energy Systems Group of Rockwell International fabricated and tested fourteen Li-Si/FeS electric-vehicle bicells. All of the cells had AlN or Li_3PO_4-Li_4SiO_4 powder separators and LiCl-KCl electrolyte. Several of the cells were operated for well over 200 cycles at discharge current densities of 30 to 90 mA/cm^2 and achieved utilizations for the positive active material of 40 to 50%. However, at the present time, no further testing of this type of cell is planned at Rockwell.

In other studies at Rockwell, Li_3PO_4-Li_4SiO_4 and MgO powder separators were tested in experimental cells to determine whether the ion-conductive properties of the Li_3PO_4-Li_4SiO_4 would cause a significant decrease in the cell resistance. No significant differences in the ohmic or polarization resistances were evident.

The Research Laboratories of the General Motors Corp. is investigating the discharge behavior of the positive electrode in Li-Al/FeS_2 test cells. These investigations are concerned with the performance of the FeS_2 electrode as a function of the electrode thickness, porosity, current collector material, and the composition of the electrolyte. The results of these studies will be used in the development of a comprehensive mathematical model for the FeS_2 electrode.

The only current-collector material that has been used successfully in FeS_2 electrodes to date is molybdenum, which is expensive and difficult to fabricate. The Institute of Gas Technology has conducted studies on pack boronization methods using B_4C, KBF_4, and graphite to form protective coatings of FeB and FeB_2 on low-carbon steel (ASTM 1008 or 1018) current collectors for FeS_2 electrodes. A boronized steel sample exhibited corrosion protection in LiCl-KCl eutectic electrolyte at 425°C up to a potential of 2.13 V vs. lithium metal. Initial experiments with boronized steel samples in LiCl-KCl eutectic saturated with Li_2S have also indicated adequate corrosion protection; however, further work is needed to provide more conclusive results. It is possible that the inclusion of a boronizing agent in the positive electrode material would produce a self-healing effect on microcracks or other imperfections in the iron-boride protective coatings. Ion-microprobe analysis showed that boron is incorporated into steel when it is exposed to iron borides, but not when exposed to elemental boron.

IV. CELL DEVELOPMENT

Over the past year, ANL has fabricated about 50 engineering-scale Li-Al/FeS cells. These cells were assembled in the charged, uncharged, or semi-charged state. For most of the cells, the electrodes are pressed mixtures of active materials and electrolyte, the separator material is BN felt or MgO powder, and the electrolyte is LiCl-KCl. The objective of these tests is to identify and test cell and electrode designs that provide improved performance and lifetime or reduced cost in mass manufacture. In addition, reference electrodes and cell models are being used to determine design modifications that should result in improved cell performance.

A. Advanced Cell Development

In previous ANL cells, low-carbon steel was routinely used as the current collector material for the FeS electrode; however, for long-term application (>5 yr), this material is not satisfactory. Corrosion studies by the materials group indicated that nickel and an iron-based alloy developed at ANL (Fe-5 wt % Mo) have the potential to provide current collection for longer periods. Subsequently, three Li-Al/FeS bicells, designated R-47, -48, and

-53, were fabricated in the uncharged state with similar designs except for the collector material--low-carbon steel for R-47, nickel for R-48, and Fe-Mo for R-53. The theoretical capacities for all three cells were 210 A-h for the negative electrode and 144 A-h for the positive electrode. To date, Cells R-47 and -48 have been operated for over 500 cycles and have shown nearly identical performances: the cell resistance is about 3.8 mΩ at full charge; the utilization of the positive electrode is 60% at a current density of 72 mA/cm^2; and the capacity decline rate is about 0.01% per cycle. After operation of these cells is terminated, post-test examinations should reveal the reason for their similar performance. The third cell, R-53, has been operated for more than 250 cycles and has shown similar positive-electrode utilization and capacity retention to those of the other two cells. However, the resistance for this cell is higher than that of the other two (4.4 mΩ). The higher resistance is believed to be due, in part, to the higher specific resistivity at 450°C of the Fe-Mo alloy, which is 64 μΩ-cm as compared with 52 μΩ-cm for low-carbon steel.

Earlier work (see ANL-79-64, p. 17) had indicated that the utilization of the FeS electrode is improved when the LiCl-KCl electrolyte is 66.7 mol % LiCl (liquidus, 425°C) rather than the eutectic (liquidus, 352°C). This departure from the eutectic, however, raises the liquidus temperature close to the operating temperature of the cell, which may result in solidification of part of the electrolyte. Therefore, addition of a third compound to the LiCl-KCl electrolyte was investigated as a means of increasing the lithium ion concentration without significantly raising the liquidus temperature. Testing of small-scale cells (15-cm^2 electrode area) identified 62.7 mol % LiCl-28.2 mol % KCl-9.1 mol % LiF, which has a melting point of 397°C, as a potential electrolyte for the Li-Al/FeS cell. Subsequently, an engineering-scale Li-Al/FeS bicell having the LiCl-KCl-LiF electrolyte was operated at 430°C, which is 20°C lower than the normal operating temperature. To date, this cell has been operated for 56 cycles and has attained a performance about equal to that of a similar cell with the 66.7 mol % LiCl electrolyte. Although still preliminary, these results indicate that LiCl-KCl-LiF has promise as an alternative electrolyte to LiCl-KCl.

For the past several years, Cu_2S has been added to the positive electrode of Li-Al/FeS cells to improve performance. Post-test examinations of cells of this type at ANL have indicated, however, that cell failure is sometimes caused by deposition of copper in the separator. In recent studies, TiS_2 was investigated as a possible additive because the product Li_xTiS_2 is an intercalation compound that is ionically and electronically conductive.[2] In tests of small-scale Li-Al/FeS cells (15-cm^2 electrode area), the addition of 10 wt % TiS_2 to the positive electrode was found to significantly improve the cell resistance. Subsequently, an engineering-scale bicell with an FeS-10 wt % TiS positive electrode was fabricated and tested. The resistance of this cell, 2.5 mΩ at 90% discharge, was more than 50% lower than that of a similar cell with no additive (5.8 mΩ at 90% discharge). Further testing of this additive in engineering-scale cells is planned.

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[2] M. S. Whittingham, J. Electrochem. Soc. 123, 315 (1976).

Testing of Mark IA cells has shown that they exhibited a large loss in capacity during cycling (about 1.0 A-h/cycle), which has not been a problem with ANL and Gould Li-Al/FeS cells. It was thought that the negative-to-positive electrode capacity ratio, about 1.0 for the Mark IA cells and 1.3 for the ANL and Gould cells, might be responsible for the different rates of capacity loss for these cells. Therefore, two cells, designated M-8NP and SM8F08, were fabricated with the same design except for the capacity ratios, which were 1.0 and 1.4, respectively. As shown in Table 4, the capacity decline rate of SM8F08 was about 50% lower than that of the other cell. In addition, the specific energy and specific power for Cell SM8F08 were about 10-20% higher than those of Cell M-8NP. These results indicate that cell performance and lifetime can be improved by having capacity ratios greater than one.

Table 4. Tests of Two Cells to Assess the Effect of Capacity Ratio on Performance

	M-8NP	SM8F08
Pos. Elect. Thickness, cm	0.63	0.63
Neg. Elect. Theor. Capacity, A-h	120	174
Pos. Elect. Theor. Capacity, A-h	120	120
Specific Energy, W-h/kg		
37-mA/cm^2 Current Density	71	78
74-mA/cm^2 Current Density	63	72
110-mA/cm^2 Current Density	52	63
Specific Power, W/kg		
3% Discharge	90	103
50% Discharge	63	73
Cycle Life	185	>154[a]
% Capacity Decline Per Cycle	0.07	0.04

[a] This cell is still in operation.

A series of engineering-scale Li-Al/FeS bicells was tested to determine the optimum capacity loading (*i.e.*, the theoretical capacity divided by the electrode volume) for the positive electrode. For these tests, five Li-Al/FeS bicells were fabricated with positive-electrode loadings of 1.0 to 1.6 A-h/cm^3, as shown in Table 5. The performance data in this table indicate that the optimum loading is 1.4 A-h/cm^3. Higher or lower loadings resulted in a decrease of the specific energy; the loading did not have much effect on the specific power.

Table 5. Tests of Five Cells to Assess the Effect of Capacity Loading on Performance

	M-15	M-13	SM8F08	M-14	M-11
Pos. Elect. Loading, A-h/cm^3	1.0	1.2	1.4	1.5	1.6
Specific Energy,[a] W-h/kg	60	63	72	63	55
Specific Power, W/kg					
3% Discharge	96	100	103	102	102
50% Discharge	73	71	73	74	71
Cycle Life	57	27	>154[b]	28	365

[a] Measured at a current density of 74 mA/cm^2 (4-h rate).

[b] Cell still in operation.

B. Cell Modeling Studies

Engineering modeling studies are being conducted at ANL with the objective of developing empirical equations that relate cell performance and lifetime to the physical and chemical characteristics of the cell and the mode of cell operation. Very general equations have been developed to fit FeS and FeS_2 bicells and multiplate cells; the coefficients in the equations were determined by multiple regression analysis of performance and lifetime data from previously operated cells. Good agreement has been obtained between predicted and actual cell performance and lifetime. This model will be very useful in the optimization of the electric-vehicle cell design.

The performance of any electrochemical cell system critically depends upon the current collector transmitting the current from the location where it is electrochemically generated to the electrode terminals. A computer program has been developed by Globe-Union Inc.[3] which mathematically models the competing effects of electrochemical and electronic voltage losses within an electrochemical cell. Newman and Pollard* have used this model to predict the effect of the weight for a positive current collector (low-carbon steel) in an Li-Al/FeS cell on the specific power and specific energy. This model should be useful in determining the optimum weight for the positive current collector of the Mark II cell. In the future, this model will be used to predict the optimum distribution of conductor material across the collector grid.

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[3] William H. Tiedmann and John Newman, Current and Potential Distribution in Lead-Acid Battery Plates, Proc. Symp. on Battery Design and Optimization, pp. 39-49 (1979).

*Consultants to ANL from the University of California at Berkeley.

C. Reference Electrode Systems

Micro-reference electrodes are being developed to investigate the polarization characteristics of electrodes in Li/FeS engineering-scale cells and to carry out other electrochemical studies of this cell system.

A reference electrode must have a well-defined potential and be electrochemically stable for long periods (months). These two potential characteristics were evaluated for five reference-electrode couples: Ag/AgCl/Cl^-, $Ag/Ag_2S/S^{2-}$, $Ni/Ni_3S_2/S^{2-}$, Fe/LiAl/Li^+, and Al/LiAl/Li^+. These couples had a BeO tubing as a housing and a Y_2O_3 plug on top of a short section of Al_2O_3 to form a diffusion barrier.

Of the five couples tested, the $Ni/Ni_3S_2/S^{2-}$ couple had the most reproducible potential (1.361 ± 0.0015 V*) and the best long-term stability (±0.0005 V/dy*). Since the Al/LiAl/Li^+ couple also had a very reproducible potential and good short-term stability, it was selected as an in-situ calibration standard for the $Ni/Ni_3S_2/S^{2-}$ reference electrode.

Six of these reference electrodes were implanted in an ANL-type Li-Al/FeS bicell, and measurements of the working electrodes' potentials were made during constant-current discharge and current interruption. The results indicated that large potential gradients develop on the electrode surface during discharge, which cause a nonuniform current distribution on the electrode surface; this nonuniform distribution produces excessive electrode polarization, thereby limiting the specific energy of the cell. In a subsequent experiment, a single reference electrode was positioned in a Li-Al/FeS bicell with Mark IA-type electrodes; measurements of electrode potential vs. utilization indicated that the cell capacity was limited by the negative electrode during discharge and the positive electrode during charge. In the future, polarization measurements will continue to be made with engineering-size cells as well as smaller cells.

V. PERFORMANCE AND LIFETIME SUMMARY

A. Status Cell Program

The objective of this program is to establish the status of the development of various cell designs. To this end, the performance and lifetime attained by at least six cells of identical design and operating mode will be used to establish the status of a particular design.

During the past year, nine Li-Al/FeS bicells were cycled on the same operating mode: temperature, 460°C; charge and discharge cutoff voltages, 0.90 V and 1.62 V, respectively; and discharge current density, 74 mA/cm^2. The design for this cell is the same as that of a previously tested ANL cell

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*Measured vs. a 3 to 5 A-h electrode of Li-Al alloy.

which had shown excellent performance characteristics for more than 300 cycles. For this cell design, the positive electrode has no additives and a capacity loading of 1.4 A-h/cm^3; the electrolyte is 66.7 mol % LiCl-33.3 mol % KCl; and the separator is BN felt treated with $LiAlCl_4$ to improve wettability. At present, these cells have been operated for 100 to 230 cycles and have exhibited specific energies of 63 to 68 W-h/kg. The results from these tests should be useful in selecting the optimal cell design for the Mark II battery.

B. Cell Failure Mechanisms

Post-test examinations are conducted on engineering-scale cells, fabricated by industrial contractors and by ANL, to determine cell failure mechanisms, in-cell corrosion reactions, and electrode morphology. These results are evaluated, and appropriate recommendations are made for improving cell reliability and performance.

During this year, 30 multiplate cells fabricated by Eagle-Picher for the Mark IA battery program were subjected to post-test examinations. Operation was terminated because of electrical short circuits in 19 cells and declining coulombic efficiency in eight cells. Three cells had completed the scheduled testing without failure. However, a short circuit (or partial short circuit) was identified in each of the cells whose operation was terminated due to declining coulombic efficiency, and one of the cells that had reached the end of scheduled testing was also found to have developed short circuits. Therefore, 28 of the multiplate cells had developed short circuits.

The following general observations were made from the post-test examinations of the multiplate cells: the typical negative electrodes expanded in thickness by 20-25%, the separators and negative electrodes were deficient in electrolyte, and varying degrees of Li-Al agglomeration occurred in the negative electrodes. The failure mechanisms of the multiplate cells are summarized in Table 6. The major cause of short circuits was the extrusion of active material from the positive electrode through a rupture in the particle-retainer assembly at the electrode edges, and subsequent contact with the cell can or the negative electrode. This rupture was apparently caused by the pressure exerted by the expansion of the negative electrodes and the absence of adequate restraint on the edges of the electrodes. Another common failure mechanism was the development of short circuits in the electrical feedthroughs. In five feedthroughs, bridges formed across the top of the upper insulator due to the presence of electrolyte in this area, thereby resulting in a short circuit. Methods of avoiding these failure problems are under investigation.

During FY 1979, 30 engineering bicells, fabricated by both ANL and industrial contractors, were subjected to post-test examinations. Operation of these cells was terminated principally because of electric short circuits, although, in a few cases, loss of capacity, broken conductors, or declining coulombic efficiency were the causes. A summary of the cell failure mechanisms is presented in Table 7; this table also includes the engineering

Table 6. Failure Mechanisms for Multiplate Cells

Causes	No. of Cases
Extrusion of active material from positive electrode	10
Short circuit in electrical feedthrough	6
Metallic deposits in separator	4
Equipment malfunction	4
Difficulty in cell assembly	2
Rupture in separator	2
End of test[a]	3

[a] One of these cells was found to have a short circuit caused by a metallic deposit in the separator.

cells examined in FY 1978. As can be deduced from this table, the two major causes of short circuits in 1978--cutting of separators by the current collectors and problems with cell assembly--were not a difficulty during 1979. Corrective actions to prevent extrusion of active material and short circuiting in the feedthrough are under investigation.

VI. MATERIALS AND COMPONENTS DEVELOPMENT

Efforts in this part of the program are directed toward investigating the cell chemistry, developing various cell components (electrode separators, current collectors, and other cell hardware), and testing potential cell materials. The results from these studies form the basis for recommending materials, components, and cell design.

A. Cell Chemistry

The cell-chemistry studies are directed toward solving the chemical and electrochemical problems that arise in the cell and battery development work, and toward acquiring an understanding of the processes that occur in the cells.

Table 7. Failure Mechanisms of Bicells

Mechanism	Number of Cases FY 79	Number of Cases FY 78
Extrusion of active materials (inadequate confinement)	7	5
Metallic copper deposits in separator[a]	1	3
Metallic[b] and/or sulfide deposits across separator	2	4
Separator cut by honeycomb current collector	2	11
Ruptured separator (BN felt) & nonuniform expansion of electrodes	2	0
Equipment malfunction[c]	0	2
Short circuit in feedthrough	2	4
Cell assembly difficulties	0	10
Unidentified		
Declining coulombic efficiency	3	1
Short circuits	0	3
Loss of capacity/poor utilization	2	3
End of test	9	6
TOTAL	30	52

[a] FeS cells with Cu_2S additive; one cell used a copper current collector.

[b] Other than copper.

[c] Overcharge, temperature excursion, or accidental polarity reversal.

The discharge of FeS electrodes in an electrolyte of LiCl-KCl eutectic leads to the formation of Li_2S and iron at full discharge, but intermediate compounds of $LiK_6Fe_{24}S_{26}Cl$ (J phase) and Li_2FeS_2 (X phase) have been found to form in electrodes that are only partially discharged. The J phase is formed through a reaction with the KCl in the electrolyte and adversely affects electrode kinetics. Basic science studies by Saboungi et al.[4] showed that the formation of the J phase in the FeS electrode is strongly dependent on temperature and the composition of the electrolyte. Therefore, cyclic voltammetry studies were conducted to investigate the charge and discharge reactions of the FeS electrode vs. Li-Al in LiCl-KCl electrolyte of three compositions--58.2 (eutectic), 63.8, and 66.7 mol % LiCl--and at temperatures of 389 to 495°C. The cyclic voltammograms indicated that (1) the kinetics of the electrode reactions in eutectic electrolyte are improved as the temperature is increased from 389 to 495°C, and (2) the kinetics of the electrode reactions at 451°C are markedly improved as the LiCl content of the electrolyte is increased from 58.2 to 66.7 mol % LiCl. These findings have been further substantiated in small-scale cell tests.

In another study of the FeS electrode, (8 A-h) Li-Al/(1 A-h) FeS cells (eutectic LiCl-KCl electrolyte) were used to measure the transition potentials at various temperatures of the following phase transitions: J to X phase, J to Li_2S, and X to Li_2S. The following equations were then derived by a least-squares fit of the data:

$$E_{J\rightarrow X} = 1149.9 + 0.2289T \text{ (above 748 K)}$$

$$E_{J\rightarrow Li_2S} = 1359.9 - 0.0519T \text{ (below 748 K)}$$

$$E_{X\rightarrow Li_2S} = 1454 - 0.1776T$$

where E is in millivolts and T is in degrees kelvin. Equations for the transition potentials of the transitions of FeS to J phase, FeS to X phase, and FeS to Li_2S and Fe will be derived in the future.

During operation of an Li-Al/FeS_2 cell, the composition of the FeS_2 electrode traverses the Li_2S-FeS-FeS_2 triangle in the Li-Fe-S phase diagram (shown in ANL-79-64, p. 29). To further study this triangle, powders of Li_2S, Li_2FeS_2, FeS, and FeS_2 were equilibrated with LiCl-KCl salt at 450°C in graphite crucibles. The salt, which was present in an amount approximately equal in weight to the powders, served as an inert vehicle to facilitate equilibration. Corrections were made to overall powder compositions for minor weight losses, which were assumed to be due to sulfur. The products were examined metallographically and by X-ray diffraction to identify the phases present. The findings of these studies have been incorporated into the phase diagram shown in Fig. 8. The points C, D, E and F correspond to $Li_7Fe_2S_6$, $Li_{12}Fe_4S_{11}$, Li_2FeS_2, and $Li_3Fe_2S_4$, respectively. The line CDE appears to correspond to a solid solution: no abrupt change in metallographic appearance occurs in this region. X-ray diffraction analysis of samples at room

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[4] M. L. Saboungi, J. J. Marr, M. Blander, J. Electrochem. Soc. 125, 1567 (1978).

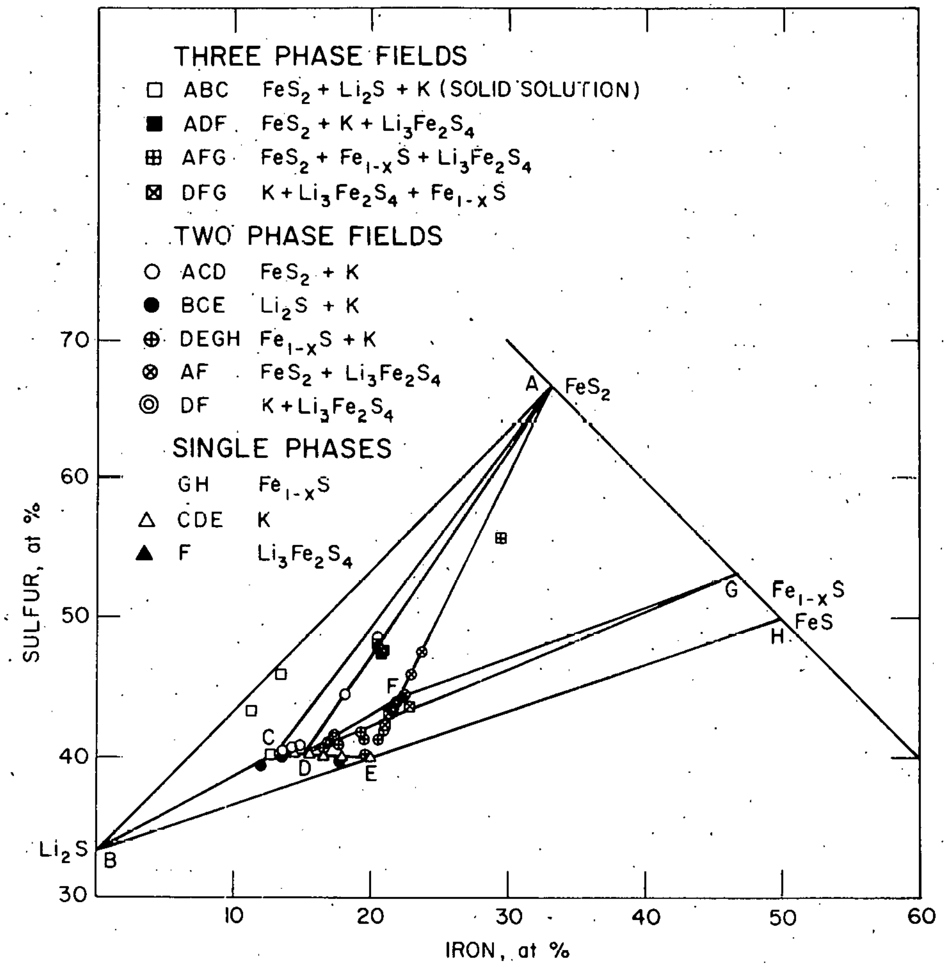

Fig. 8. The Li_2S-FeS-FeS_2 Triangle in the Li-Fe-S Phase Diagram

temperature were not useful in confirming the existence of this solid solution; future X-ray diffraction data obtained with special equipment might resolve this question.

As mentioned previously, post-test examinations of Li-Al/FeS multiplate cells have shown that Li-Al agglomerations form in the center of the negative electrode; this agglomeration is not normally observed in the negative electrode of cycled bicells. It is thought that the Li-Al agglomeration might be, in part, responsible for the high rate of capacity decline observed in the Mark IA cells. In the next year, the nature and degree of agglomeration in the Li-Al electrode will be investigated by a new technique, iodine vapor etching, in which the depth of penetration of lithium into the aluminum of a negative electrode can be detected. In other studies, metallographic and chemical analyses, as well as ion microprobe analysis, indicated a significant lithium concentration gradient in both bicells and multiplate cells, with the gradient being steeper in the multiplate cells. Iodine vapor etching will also be used to futher investigate the lithium gradient.

B. Separator Development

The separator is a key component of the cell, and it must meet several requirements, including compatibility with the electrode materials and electrolyte, good wettability by the electrolyte, adequate mechanical strength, acceptable cost, suitable porosity and thickness, and lack of electronic conductivity. In the past, BN fabric has been used successfully in engineering cells; however, the projected cost in mass production precludes its use in commercial cells. Consequently, two types of potentially low-cost separators are being studied--felt and sintered ceramic.

Bonded BN felts are being fabricated by the Kennecott Copper Corporation. At the present time, this felt is made by hand using a 30.5-cm (12 in.) square-sheet mold. These felts can be produced in any thickness and typically are 92 to 94% porous. Stress-strain measurements were made on this BN felt to estimate its ability to withstand stresses during cell operation. The felts were reduced to half thickness at compressive stresses of about 150 kPa, underwent plastic deformation at stresses above 175 kPa, and were reduced to a powder at compressive stresses of 690 to 1035 kPa. As previously reported, these felts have been successfully tested in engineering-scale cells and will be used in the cells for the first phase of the Mark II program. The Kennecott Copper Corporation is presently developing a new process that will produce continuous lengths of BN felt at a projected cost of about $10/m^2 in quantities greater than 10^6 m^2/yr.

Procedures have been developed for the fabrication of porous, sintered ceramics of Y_2O_3 and MgO for separator applications. Such plates were prepared with porosities up to about 60% and good mechanical properties; higher porosities resulted in weak and nonuniform structures that were not suitable for separator applications. Separators of MgO and Y_2O_3 have been tested in 50-A-h cells, which have shown acceptable performance. At present, however, no further efforts are planned on the development and testing of this type of separator.

C. Current Collector Development

Low-carbon steel has been found to be a satisfactory current collector in Li-Al electrodes, but can be used only for a limited period in FeS electrodes. At present, iron-base alloys developed at ANL and nickel are under investigation for longer-term use as the FeS current collectors. The three iron-based alloys are Fe-4.5 wt % Mo, Fe-10 wt % Mo-20 wt % Ni, and Fe-15 wt % Mo-30 wt % Ni (designated ANL-5-0, ANL-10-20, and ANL-15-30, respectively). All three alloys have shown very low corrosion rates in static corrosion tests (i.e., immersion of the alloy in a bath of FeS and molten electrolyte for a preselected period of time) and small-scale cell (50 A-h) tests. However, of the three alloys, ANL-5-0 has the most attractive combination of properties with regard to corrosion rate, resistivity, and potential for low cost; therefore, it is being tested in engineering-scale cells (see Section IV.A).

Although nickel has shown low corrosion rates in static corrosion tests, corrosion tests of this material in small-scale cells (50 A-h) has produced conflicting results. In cells assembled in the semi-charged or uncharged state, post-test examinations of the nickel current collector showed severe localized intergranular attack; but no evidence of this type of attack was observed in cells that were assembled fully charged. In fact, this charge condition generally results in the deposition of a thin layer of iron on the nickel surface. Studies are continuing in an effort to determine the mechanism for this unusual behavior.

The only current collector material that has been used successfully in FeS_2 electrodes is molybdenum, which is expensive and difficult to fabricate. Therefore, major efforts are being directed toward the development of conductive ceramics for use as a coating material on inexpensive metallic current collectors in FeS_2 electrodes. During the past year, static corrosion tests were conducted to determine the compatibility of the following materials with the FeS_2 electrode: TiN, TiC, and TiB_2 formed by hot pressing; TiN (with a thin underlayer of TiC), TiC, TiCN, and TiB_2 applied by chemical vapor deposition to substrates (low-carbon steel); MoS_2 and $MoSi_2$ applied by RF sputtering to substrates; and duplexes of TiC plus TiN applied by chemical vapor deposition to substrates. The only materials found to be completely compatible with the FeS_2 electrode environment were hot-pressed samples of TiN and TiC. Of the coated samples tested, the TiN with a thin layer of TiC showed the most promise. The common mode of failure for the coated samples was cracking and spalling at the sample edges followed by rapid corrosion of the substrate by the sulfide. At this time, it appears that the presence of chloride from the electrolyte and residual stresses between the coating and substrate at the edges and corners initiate coating failure, which eventually leads to corrosion of the substrate by the sulfide. Studies are continuing to identify techniques to prevent spalling and cracking of the coatings.

VII. SYSTEMS DESIGN AND ANALYSIS

The approaches taken in the design of battery systems and components differ significantly for the electric-vehicle and stationary energy-storage applications. The work in progress for each application is discussed below.

A. Electric-Vehicle Propulsion

The Li/FeS batteries under development for electric-vehicle propulsion will be tested in the laboratory under a variety of modes, including computer-simulated road conditions, prior to in-vehicle tests. Preliminary in-vehicle testing at ANL using a van as a test-bed will be followed by extensive in-vehicle testing by outside contractors and vehicle manufacturers. In order to evaluate battery performance under road-load conditions, an instrumentation package has been developed by ANL that is compact and can be installed in a van or automobile. A general block diagram of the instrumentation package is given in Fig. 9. The on-board package includes a microprocessor-controlled data acquisition and recording system, a signal integrator/display unit, a signal level monitor/alarm unit, and an operator visual/audible driving schedule meter. This equipment logs measurements of battery and vehicle performance on magnetic tape, while displays furnish an immediate visual indication of battery charge and energy transfer, as well as vehicle speed and range. The off-board support system provides a graphical display of recorded road-test data as a function of battery operating time on a cathode ray tube terminal.

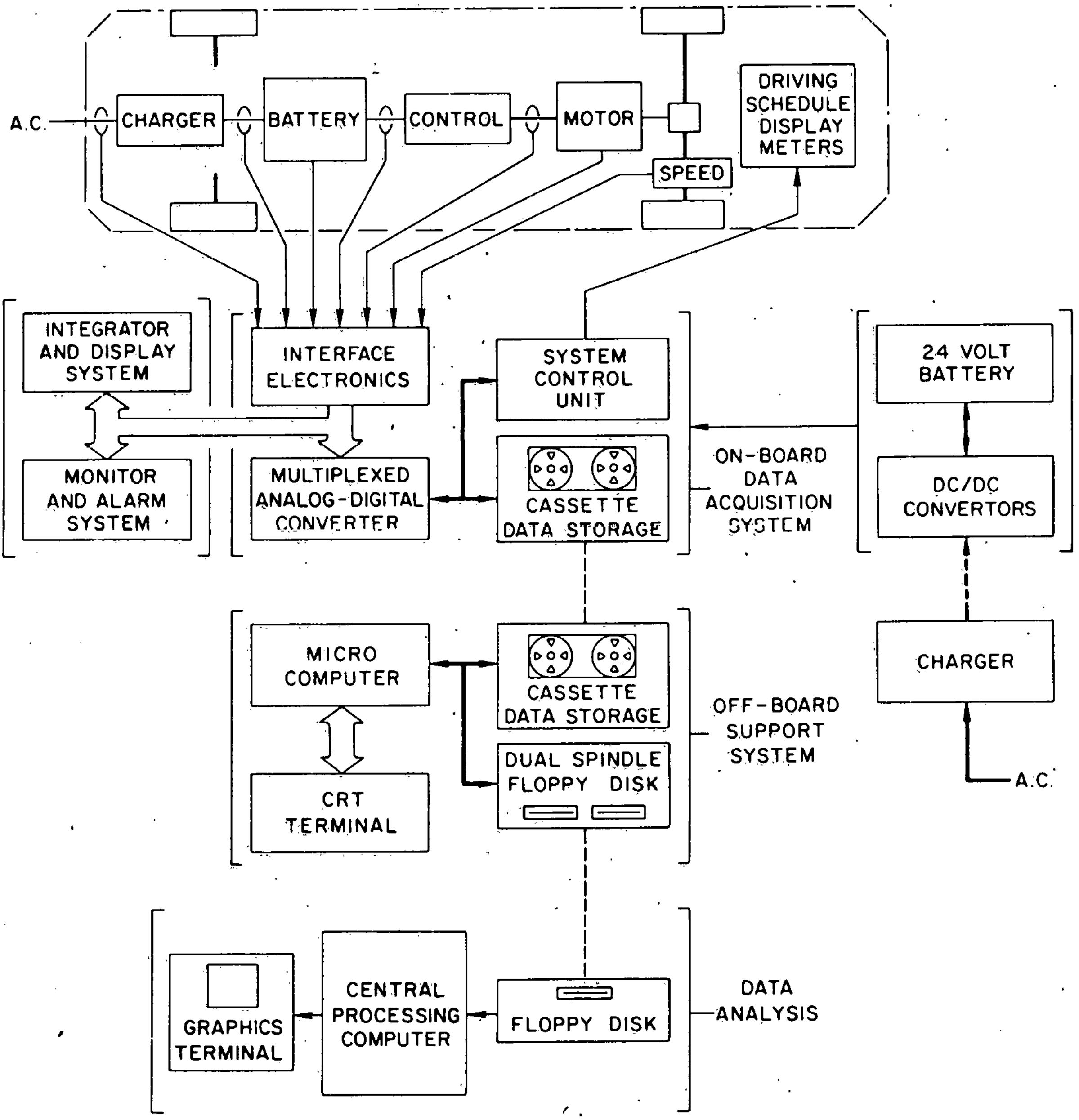

Fig. 9. Block Diagram of Data-Acquisition and Processing System for In-Vehicle Battery Tests

B. Stationary Energy Storage (SES)

In 1978, a conceptual design of a 100-MW-h SES battery having Li-Al/FeS or Li-Si/FeS cells was developed as a result of a joint effort between ANL and Rockwell International. In this design, the submodule, which was the basic replaceable unit for the battery, consisted of ninety-six 2.5-kW-h cells. However, a study by Rockwell indicated that the cost for the battery hardware, $60-88/kW-h (cell and converter costs not included), was too high.

In the above design, a significant portion of the cost (about 25%) was contributed by the electronic charge-equalization scheme, which was the same as that developed for electric-vehicle batteries. In 1979, an alternative method of equalization, in which fixed resistance shunts are used on each cell, was developed. This equalization scheme adds little equipment cost to the system and only sacrifices about 4% of the coulombic and energy efficiencies. With this scheme, equalization can be completed on the weekends with the battery in a discharged state. Along with this new equalization scheme, three different sizes for the submodules were investigated: a 120-kW-h submodule consisting of 100 cells, a 1,020-kW-h submodule consisting of 408 cells,* and a 30-kW-h submodule consisting of one cell. The cost of battery hardware for these three new designs was estimated to be $20 to 40/kW-h, which is much lower than that for the original design. Some questions remain on the assumed capabilities of the cells and the feasibility of the battery hardware for these designs.

At present, there are no data on the cell failure rate required for a low-maintenance battery. An estimate indicated that, for a battery lifetime of 10 years, not more than about 5% of the total cells should have failed. This may be difficult to achieve, although the cell reliability that will probably be required for the electric-vehicle batteries is of the same order. This long time to failure favors smaller cells than might otherwise be optimum for this application.

VIII. CALCIUM/METAL SULFIDE BATTERY

The objective of this program is to develop high-performance cells that use inexpensive, abundant materials while maintaining the performance levels required for electric vehicles or load leveling. These cells are expected to follow the lithium/iron sulfide cells into commercial production. The goals for next year are to achieve a specific energy above 100 W-h/kg at the 5-h rate and a capacity decline rate of less than 10% in 100 cycles (or 1200 h). The ultimate goals for the calcium cell are a specific energy of 160 W-h/kg, a peak specific power of 200 W/kg, a lifetime of 1000 cycles, and a materials cost (in 1979 dollars) of $15/kW-h.

During the past year, effort has been concentrated on the development of Ca_2Si and $CaSi/FeS_2$ cells. The overall reaction for the Ca_2Si/FeS_2 cell is $Ca_2Si + FeS_2 \rightarrow 2CaS + Si + Fe$, the theoretical specific energy for this reaction being 790 W-h/kg. For the $CaSi/FeS_2$ cell, the overall cell reaction is $2CaSi + FeS_2 \rightarrow 2CaS + 2Si + Fe$ and the theoretical specific energy is

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*Design developed by Rockwell International.

630 W-h/kg. In both cases, the electrolyte is molten 33 mol % LiCl-12 mol % NaCl-37 mol % $CaCl_2$-18 mol % $BaCl_2$ (mp, 383°C), and the separator is BN fabric or felt.

During this year, the conductivity of the LiCl-NaCl-$CaCl_2$-$BaCl_2$ electrolyte was measured to be 1 Ω^{-1}-cm^{-1}, which is about two thirds of the conductivity of LiCl-KCl at 450°C. Therefore, for equivalent power capabilities, it will be necessary to use somewhat thinner electrodes or separators in calcium cells to compensate for the slightly higher salt resistance.

Small-scale (about 4-A-h) cells were tested to determine the active material utilization of Ca-Si and FeS_2 electrodes. The utilization of the FeS_2 electrode was found to be fairly high, 64% at a discharge current density of 60 mA/cm^2, and was increased to 72% by the addition of a small amount (7 mol %) of CoS_2. However, these tests also indicated that the utilization of the Ca-Si electrode is low, 50% at a discharge current density of 60 mA/cm^2. It was concluded that this negative electrode for the Ca/MS cell will require further improvement if the program goals are to be met.

Cyclic voltammatry studies indicated that the resistance of the FeS_2 electrode could be lowered by the addition of E-coke flour, a high-surface-area carbon; this additive will be tested in large-scale cells.

During 1979, three engineering-scale Ca-Si/FeS_2 bicells were fabricated and tested at 450 to 500°C. The highest specific energy achieved by these cells was 67 W-h/kg at the 5-h rate, but a doubling of the resistance (8 mΩ to 16 mΩ) during the early cycles of these cells and a fading capacity limited the lifetime to about 2000 h. The specific energy of the cells declined by about 25% per 1000 h of operation.

Post-test examinations identified two lifetime-limiting mechanisms for these cells: reaction and compaction of the separator near the negative electrode to form a dense layer, and formation of a nonadherent reaction layer, probably an iron silicide, on the negative current collectors (mild steel). The cause of the reaction in the separator was the high calcium activity compound, Ca_2Si. In a cell now in operation, the charging of the negative electrode has been limited to CaSi instead of Ca_2Si, and no resistance increase has occurred. Preliminary tests have indicated that alternative negative electrodes such as $CaAl_2$ or $CaMg_2Si$ might solve both of the above problems. These alternatives will be tested in large cells in future experiments. The post-test examinations also revealed that no CaS had escaped from the positive electrode and deposited in the separator; in Li-Al/FeS cells, large amounts of Li_2S have been found in the separator. This good active-material retention was expected from previous tests in which the solubility of CaS in the LiCl-NaCl-$CaCl_2$-$BaCl_2$ electrolyte was found to be about one tenth of the solubility of Li_2S in LiCl-KCl electrolyte. Furthermore, sulfur vaporization losses from FeS_2-Li_2S mixtures in LiCl-KCl were about a factor of ten greater than from FeS_2-CaS mixtures in the quaternary electrolyte.

In summary, significant progress has been made in developing high-performance Ca-Si/FeS_2 cells, and major problems to be solved have been identified. Continued research on calcium cells is expected to lead to a system that can meet the long-term program goals. The major areas of future work will be the development of improved negative electrodes, current collectors, and separator materials.

ADDENDUM: PUBLICATIONS--1979

A. Open-Literature Publications

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A Charging System for the LiAl/FeS Electric Vehicle Battery
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High-Performance Batteries for Electric-Vehicle Propulsion and Stationary Energy Storage

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D. Papers Presented at Scientific Meetings

D. L. Barney

Advances in Lithium/Metal Sulfide Batteries

Presented at Gordon Research Conf. on Electrochemistry, Santa Barbara, CA, January 7-12, 1979

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Lithium/Metal Sulfide Batteries

Presented at ACS/CSJ Pacific Chem. Congress, Honolulu, HI, April 1-6, 1979

J. E. Battles

Technology of Materials for Advanced Li-Al/Iron Sulfide Secondary Batteries

Presented at Am. Soc. for Metals Materials and Processing Cong., Chicago, IL, November 13-15, 1979

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Technology of Materials for Advanced Li-Al/Iron Sulfide Secondary Batteries

Presented at Seminar--Illinois Institute of Technology, Chicago, IL, November 29, 1979

A. A. Chilenskas

Lithium/Metal Sulfide Load-Leveling Battery Plant Design

Presented at DOE Battery and Electrochemical Contractors' Conf., Arlington, VA, December 10-12, 1979

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Battery Development for Electric Vehicles
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Presented at Third Electric and Hybrid Vehicle Program Contractors' Meeting, Arlington, VA, June 25-27, 1979

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