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LITHIUM/IRON SULFIDE BATTERIES FOR
ELECTRIC-VEHICLE PROPULSION AND
OTHER APPLICATIONS

Progress Report for
October 1979—March 1980

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LITHIUM/IRON SULFIDE BATTERIES FOR ELECTRIC-VEHICLE PROPULSION AND OTHER APPLICATIONS

Progress Report for
October 1979-March 1980

ABSTRACT

This report covers the research and development activities of the program at Argonne National Laboratory (ANL) on lithium/iron sulfide batteries during the period October 1979-March 1980. Although the major emphasis is currently on batteries for electric-vehicle propulsion, stationary energy-storage applications are also under investigation. The individual battery cells, which operate at 400-500°C, are of a vertically oriented, prismatic design with two or more positive electrodes of FeS or FeS₂, facing negative electrodes of lithium-aluminum or lithium-silicon alloy, and molten LiCl-KCl electrolyte. The ANL program consists of cell chemistry studies, materials engineering, and component and auxiliary systems development. Important elements of this program are studies of the effects of design modifications on cell performance and post-test examinations of cells.

During the reporting period, cell and battery development work has been aimed primarily at the first phase of the Mark II electric-vehicle battery program, which consists of an effort to develop high-reliability cells having boron nitride felt separators. Later in the Mark II program, the cells will be tested in 10-cell modules. Work on stationary energy-storage batteries during this period has consisted mainly of conceptual design studies.

SUMMARY

Cell Modeling

In cell modeling studies, empirically based equations were used to relate physical and chemical characteristics of lithium/iron sulfide cells and the mode of cell operation with the specific energy as a function of cycle life. The performance of 84 Li-Al/FeS multiplate cell designs was projected from these equations. In other efforts, a computer program, which mathematically models the competing effects of electrochemical and electronic voltage losses within an electrochemical cell, is being used to predict the optimum current collector weight for a Li-Al/FeS cell.

Capacity Loss Studies

The objective of this work is to provide design recommendations to reduce the rate of capacity loss in Li-Al/FeS cells during cycling. An engineering-scale Li-Al/FeS bicell, EPRE-1, was assembled with electrodes similar to

those of the Mark IA multiplate cell (reported previously)--a 97 A-h positive electrode and a 108 A-h negative electrode. Another cell, EPRE-2, was assembled with an identical positive electrode to that of EPRE-1 but with a 208 A-h negative electrode. Both cells had reference electrodes implanted in them to study electrode polarization. Cell EPRE-1 showed the typically high capacity-loss rate that had been observed for the Mark IA cell, whereas Cell EPRE-2 showed no measurable capacity decline through 50 cycles and over 95% utilization of the positive electrode. The reference-electrode data show less polarization of the negative electrode in the second cell.

A strong correlation between the initial negative-electrode utilization and the rate of capacity decline has been established for the Mark IA-type cell design. At negative-electrode utilizations up to 60%, the rate of capacity decline is low, but, as higher utilizations are demanded by the cell design, the capacity-decline rate becomes progressively higher.

Cell Swelling Studies

Studies are under way to provide recommendations that would minimize the extent of cell and electrode swelling. As part of these studies, tests have been initiated to investigate the particle rearrangement and densification behavior of negative electrode compositions in the presence of molten electrolyte and an external load. The results from these tests should be useful in analyzing electrode swelling problems and related phenomena such as the formation of skeletal structure and agglomeration that have been observed in negative electrodes.

An elastic stress and displacement analysis was conducted on a typical cell container to determine the deformation. In a low-carbon steel can, with dimensions of 18.7 x 18.7 x 3.7 cm and a wall thickness of 0.0625 cm, an internal pressure of 175-350 kPa (25-50 psi) produced stresses and displacements that were unacceptably high. The stresses and deformations can be prevented by clamping the square faces so that they are prevented from bending.

Electrode swelling under different cell operating modes is being determined with an apparatus that measures the linear expansion of electrodes in small-scale cells. Under a constant constraining pressure of 140 kPa (20 psi), a positive electrode showed no expansion at a current density of 50 mA/cm². When the current density was lowered to 15 mA/cm², no deformation was observed during discharge under a constraining force of 70 kPa (10 psi). Therefore, the linear deformation of the positive electrode appears to be related to the discharge current density. An instrument has been recently developed to measure the force at zero deflection of the cell-container walls while an engineering-scale cell (e.g., 17.8 x 17.8 cm) is cycling.

Failure Analysis

These experiments are based largely on results of the Mark IA failure analysis, and are concerned mainly with potential short-circuiting mechanisms and their effects, electrolyte leakage problems, properties of high-temperature insulation, arcing under various conditions and feedthrough failure.

The degree of gas leakage through the seal of the electrical feedthrough in a cell of a battery at operating temperature has been in question. Therefore, vertical loads of up to 19 kg were applied to a horizontal stainless-steel rod attached to the positive terminal of a Mark IA cell at operating temperature; this torque caused no significant change in the leak rate of the feedthrough (9×10^{-6} cm³/sec). In a subsequent experiment, a horizontal force was applied to the tip of the positive terminal on this cell at 25°C such that the rod was bent about 1.5 mm off normal; again, the leak rate through the feedthrough did not change. This experiment will be repeated with the cell at 450°C.

One possible cause of failure noted in the Mark IA failure analysis was arcing. Breakdown voltages across a 0.75-mm gap were measured in pure argon and in argon contaminated with battery and cell material vapors at temperatures up to 465°C and pressures up to 175 kPa (10 psig). General trends noted included (1) an increase in breakdown voltage with pressure, (2) a lower breakdown voltage at 465°C than at 25°C, and (3) little effect of vapors from LiCl-KCl electrolyte or braze alloy on the breakdown voltage. The results indicate little likelihood of arcing across a 0.75-mm gap in a battery at 465°C in argon at potentials less than 275 V.

Post-Test Examinations

In this period, 22 multiplate cells and 26 bicells were subjected to post-test examinations; these cells were fabricated and tested either by ANL, Eagle-Picher Industries, Inc., or Gould Inc.

For the multiplate cells, the major cause of short circuits (9 cells) was the extrusion of active material at the edges of one electrode and subsequent contact with the opposite electrode; measures are being directed toward correcting this design deficiency. In two multiplate cells, the use of excessive LiAlCl₄ wetting agent in the separator resulted in metallic aluminum deposits bridging the separators. The major cause of failure for the bicells was also extrusion of active material at the edges (7 cases); localized protrusions in the negative electrode which ruptured the separator caused short circuits in five cells.

Microscopic examinations of small laboratory cells have indicated that FeS₂ does not nucleate on or within Z-phase (Li₃Fe₂S₄) particles during charge as would be expected, since Z phase formation is the first step in the discharge of FeS₂. The FeS₂ nucleation occurred only on the surface of Fe_{1-x}S particles. This behavior may be a major factor in the irreversibility observed in FeS₂ cells.

Reexamination of multiplate cells from the Mark IA and Mark II programs revealed an average expansion of 22% for the positive electrodes, 18% for the inner negative electrodes, and 29% for the outer negative electrodes. This result agrees with metallographic observations that less agglomeration occurs in the outer negative electrodes than that in the inner ones.

Electrode Development

Post-test examinations of multiplate cells revealed that Li-Al agglomerations form in the negative electrode. As a result, small, deep-bed Li-Al electrodes have been prepared for laboratory tests to investigate, in a controlled manner, the variables that affect agglomeration. In this report period, baseline conditions for agglomeration in small, deep-bed Li-Al electrodes were established. In other negative-electrode tests, the effects of two additives, Mg and Cd, to an aluminum electrode (later charged with lithium) were evaluated. The Mg additive (0.66 at. %) led to more severe capacity decline and more complex morphology than were observed in the pure Al electrode. An Al electrode saturated with Cd (0.002 at. %) showed essentially the same performance as the pure Al electrode.

In FeS electrode studies, the transition potentials of FeS to Li_2FeS_2 (X phase), X phase to Li_2S and Fe, and FeS to Li_2S and Fe were measured as a function of temperature. For these measurements, a LiAl/FeS experimental cell with LiF-LiCl-LiBr eutectic electrolyte was used. The first two transition potentials were determined to be

$$E_{\text{FeS} \rightarrow \text{X}} = 1331.6 + 0.03T$$

$$E_{\text{X} \rightarrow \text{Li}_2\text{S} + \text{Fe}} = 1417.8 - 0.127T$$

where E is in millivolts and T is in degrees Kelvin. These two transition potentials can be combined to yield the third transition potential,

$$E_{\text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe}} = 1374.7 - 0.0485T$$

This transition potential, together with well-known thermodynamic values from the literature, have allowed the most precise determination of the Gibbs free energy of formation for Li_2S to date: -102.6 kcal/mol at 700 K and -100.1 kcal/mol at 800 K.

Cyclic voltammetry results have shown that the electrochemical formation of FeS_2 from Z phase ($\text{Li}_3\text{Fe}_2\text{S}_4$) is kinetically hindered. Further voltammetry tests indicate that the overpotential associated with the formation of FeS_2 can be reduced from 120 to 70 mV by changing the electrolyte composition from the LiCl-KCl eutectic to the LiCl-KCl-LiF system. This reduction of the overpotential may improve the cycle life of the Li-Al/ FeS_2 cell couple.

Separator Property Studies

A recent batch of BN felt (presently used as the separator material in Li-Al/FeS cells) supplied by Kennecott Copper Co. was characterized for thickness, compressibility, and flexibility. The measurements showed considerable

nonuniformity in the thickness, compressibility, and flexibility. Thickness values ranged from 1.88 to 2.39 mm. The data indicated a correlation between thickness, porosity, and flexibility--the thinner felts being less porous and flexible. This problem was discussed with Kennecott, and the most recent shipment showed an improvement in felt uniformity.

Gould Inc. delivered ten identical engineering-scale FeS bicells (Q series) with BN felt separators to ANL for cycle-life testing. The honeycomb metal structure, previously used by ANL inside electrodes to provide additional support to the fine-mesh screen on the electrode faces, was eliminated from the cells. Of these ten cells, the longest operating cell was cycled for 550 cycles (3150 h), with only an 8% decline in capacity, before exhibiting low coulombic efficiency; the remaining cells were cycled for 44 to 265 cycles (200 to 1950 h) with little decline in capacity. Post-test examinations revealed a wavy electrode/separator interface. A number of structures were suggested to Gould that would have the compressive strength required to prevent collapse of the electrode.

Six engineering-scale FeS bicells were fabricated and cycle-life tested at ANL. All of these cells had carbon-bonded positive electrodes (10 vol % carbon), BN felt separators, and honeycomb structures in the electrodes for internal support. To date, these cells have exhibited good acceptance of the BN felt separator.

Efforts are in progress to develop, evaluate, and optimize ceramic powder (MgO) separators for application in Li-Al/FeS cells. In this period, an experimental apparatus was used to measure the conductivity of MgO powder samples with porosities of 34 to 94%. In addition, a new MgO powder with a high surface area (70 m²/g) was used to obtain a separator layer with a porosity of 70% in engineering-scale cells (typical porosity of MgO powder in past cells was 45%). Testing of these cells is in progress.

Current Collector Development

Static corrosion tests were completed on fifteen candidate materials for current collectors in the FeS electrode. The tests consisted of immersing these materials in an equal volume mixture of FeS and electrolyte at 400 to 500°C for up to 1000 h. Through these tests, six steel alloys and nickel-plated steel were identified as having potential for long-term use in FeS electrodes.

Two of the iron alloys--Fe-4.5 wt % Mo (ANL-5-0) and Fe-10 wt % Mo-20 wt % Ni (ANL-10-20)--and nickel were tested as current collectors and frames for the FeS electrode of 50 A-h cells assembled in the charged, uncharged, and semicharged states. The ANL-5-0 alloy components showed a significantly higher corrosion rate in cells assembled uncharged than that in cells assembled either charged or semicharged; this high corrosion rate indicated that the ANL-5-0 alloy components in cells assembled uncharged would be unacceptable. The ANL-10-20 alloy components for cells assembled in all three states of charge showed acceptable corrosion rates. The corrosion rates for the nickel

components were significantly lower in cells assembled charged than in those assembled semicharged. However, it was discovered that the high corrosion rate in the nickel components of the semicharged cell could be prevented by the addition of an excess of fine (75-100 μm dia) iron powder to the positive electrode.

Efforts are being directed toward the development of conductive ceramics for use as a coating material on inexpensive current-collector substrates for FeS_2 electrodes. Examinations of TiN- and TiC-coated steel (AISI 1008), after static corrosion testing had been completed, have indicated that coating failures are initiated at the corners and the edges of the specimens. Other studies have indicated that high-compressive residual stresses between the substrate and coating are a mechanism for coating failure. The resultant stress and the corrosion media result in stress corrosion and spallation of the coatings. Static corrosion tests have also shown that coating stability is independent of whether the substrate is low-carbon steel (AISI 1008) or the ANL-5-0 alloy, but does depend on the coating thickness. Current collectors of TiN-coated low carbon steel were tested in the FeS electrode of 50 A-h cells. Post-test examinations of these cells after 15 to 30 days of cycling showed no evidence of corrosion.

Three engineering-scale (about 145 A-h) Li-Al/FeS bicells were fabricated in the uncharged state with BN felt separators and current collectors of nickel (Cell R-47), low-carbon steel (Cell R-48), and ANL-5-0 alloy (Cell R-53) in the positive electrode. After 200 to 750 cycles, all three cells have shown similar performance, indicating little effect of the different current-collector materials. Further tests of these materials in engineering-scale cells are under way.

A new approach to electrode current collection and confinement of active material is being investigated. In this approach, a mechanically perforated metal sheet is formed into two rectangular cups so they can telescope together to form a box around the electrode plaque. Two Li-Al/FeS multiplate cells with this perforated-sheet assembly and BN felt separators have been assembled and tested. The tests to date indicate excellent promise for this newly developed component.

Cell and Battery Testing

At least six state-of-the-art cells of identical ANL design are being tested to obtain limited statistical data on their performance and lifetime. In this report period, twelve Li-Al/FeS bicells of identical design were operated between cutoff voltages of 0.90 V on discharge and 1.61 V on charge. As of this time, the operation of nine cells has been terminated; the other three are still in operation. In sum, the twelve cells have been operated for an average of 256 cycles and shown an average capacity loss of 8.3%. The three cells still in operation have achieved 328, 376, and 228 cycles at an average capacity-loss rate of 0.02% per cycle.

Tests are continuing at ANL on the multiplate cells fabricated by Eagle-Picher for the Mark IA program. During the Mark IA program, the cells were deep cycled to obtain performance and capacity-loss data under stringent conditions. Fourteen Mark IA cells were tested under less severe conditions (70-A constant current discharge for 4 h) to determine the effect on performance. This testing mode resulted in a specific energy of 85-90 W-h/kg; cell operation was terminated after an average of 88 cycles due to low coulombic efficiency. It was concluded that this shallower mode of cycling did not result in any significant improvement in performance or lifetime. Qualification testing of the Mark IA cells was conducted at 25, 75, and 150 cycles. This testing indicated that the sharp decline in specific energy with cycling previously observed in the Mark IA cells was related to capacity loss, particularly at low discharge rates.

The major emphasis of the two Mark II contractors--Eagle-Picher Industries, Inc. and Gould Inc.--has been on building reliable cells. The target is for the contractors to produce groups of 12 identical status cells which will be tested to measure whether they meet certain performance and cycle-life requirements.

Eagle-Picher has been searching for a method to prevent extrusion of active material, a common mode of failure in the Mark IA cells. To prevent this problem, Eagle-Picher incorporated a square bar around the perimeter of the electrode plaque and then welded photoetched metal screens, which covered the faces of the plaques, to the square bar. Testing of multiplate cells with this design (BN felt separators) indicated that additional edge support was needed; therefore, 16 Li-Al/FeS multiplate cells were built with a channel overlapping the bar and photoetched sheet at the electrode edges. At present, ten of these 16 cells are being tested at ANL. However, this cell design is not satisfactory because the electrode hardware is too heavy. Future cells built by Eagle-Picher will have lighter weight components.

For the Mark II program, Gould initially built eleven cells having two positive plates and BN felt separators. The lifetimes of these cells were very short; post-test examinations showed a failure of the wire screen used to wrap the electrodes. To prevent this failure mode, modifications have been made to the electrode frames to provide better edge support. A group of eight such cells has recently been placed on operation at ANL.

Argonne is preparing facilities capable of independently testing two 10-cell modules for the Mark II program.

Cost Studies

Work is continuing on the identification of potential markets for lithium/iron sulfide batteries as a function of cost and timing. In a previous study (1977), the sizes of the near-term markets for this battery were projected for transit buses, postal and delivery vans, mining vehicles, and submersibles. This study is being updated and expanded to include school buses and forklift trucks.

Auxiliary Systems Development

A charger/equalizer for batteries of up to 16 cells has been designed. After a prototype charger/equalizer has been successfully tested, six additional units will be fabricated and tested.

In thermal management studies, detailed open-circuit thermal mapping of the Mark IA cell as a function of depth of discharge and charge has been completed. These data were then used to calculate the average heat generation rate of the cell during cycling. For the specific cycling conditions chosen, the average heat generation was found to be 15 W during discharge and zero during charge (i.e., irreversible heating is cancelled by entropic heating). The procedure for calculating heat generation in a cell was then used to estimate the heat generation during discharge of a five-cell module. These calculated data were then compared with the measured temperature data obtained from the 50th discharge cycle of the five-cell module fabricated by Eagle-Picher for the Mark IA program; good agreement was obtained between the estimated and measured values.

In another thermal management effort, Union Carbide Corp. is developing a load-bearing insulation for high-temperature batteries.

I. INTRODUCTION

Lithium/iron sulfide batteries are being developed by Argonne National Laboratory (ANL) and its contractors for electric-vehicle propulsion and stationary energy-storage applications such as load leveling on electric utility systems or storage of electrical energy produced by solar, wind, or other sources. The widespread use of electric vehicles would conserve petroleum fuels, and a side-benefit would be realized in decreased air pollution in densely populated areas. The use of batteries for load leveling could save petroleum by reducing the need for gas turbines to meet peak power demands.

The battery cells that are currently under development consist of Li-Al or Li-Si negative electrodes, FeS or FeS₂ positive electrodes, and molten LiCl-KCl electrolyte. The melting point of the electrolyte at the eutectic composition (58.2 mol % LiCl) is 352°C, and the cells are operated at 400-500°C.

The major requirements for an electric-vehicle battery are high specific energy (W-h/kg), high volumetric energy density (W-h/L), high specific power (W/kg), and high volumetric power density (W/L). Economic considerations call for a minimum battery lifetime of about three years (about 1000 deep discharge cycles or equivalent) and maximum cost of about \$50-60/kW-h.* Stationary energy-storage batteries have less severe specific-energy and specific-power requirements, but this application demands a longer lifetime (about 10 years and 3000 cycles) and a cost goal of \$45-55 kW-h. At present, the major emphasis is on the development of the electric-vehicle battery; subsequent development of the stationary energy-storage battery is expected to benefit from the technology introduced by the electric-vehicle battery program.

The program on the electric-vehicle battery involves the development, design, fabrication, and testing of a series of full-scale lithium/iron sulfide batteries, designated Mark IA, II, and III.

The main objective of the Mark IA battery, which was fabricated by Eagle-Picher Industries, Inc. and delivered for testing in May 1979, was to evaluate the technical feasibility of the lithium/iron sulfide system for the electric-vehicle application and to identify potential problem areas. During startup heating prior to testing, the Mark IA battery, which consisted of two 20 kW-hr modules containing 60 cells each, developed a short circuit in one of the modules, and this resulted in a progressive failure of all of the cells.

After a detailed analysis of the Mark IA failure was performed, a decision was made to proceed with the Mark II program. A major factor in this decision was the availability of boron nitride felt, which has much greater potential as a low-cost electrode separator material than the boron nitride fabric that was used in the Mark IA cells. The Mark II program has been planned as a two-phase effort. The first phase is aimed at the development of high-reliability

*Costs given in 1980 dollars.

cells and 10-cell modules. Although cell performance and lifetime are expected to approach the Mark II goals, no specific-energy or specific-power requirements have been placed on the modules. The second phase of the Mark II program will be concerned with the development of interconnected modules and full-scale electric-vehicle batteries.

The program is currently in the first phase of the Mark II battery development. Two industrial firms, Gould Inc. and Eagle-Picher Industries, Inc., have been awarded contracts to implement this phase of the program. Both contractors are developing multiplate cells having boron nitride felt separators and conducting preliminary studies on the development of modules. The performance goals for the Mark II battery are listed in Table 1. The Mark II battery has somewhat higher performance goals than the Mark IA, but the major objective is to develop designs and materials that have the potential for low cost in mass production. On the basis of recent cell test results, consideration is being given to raising the peak power goals for the Mark II, which would make the battery suitable for use in passenger cars as well as vans and buses.

Table 1. Performance and Lifetime Goals for the Mark II Battery

	Goal
Specific Energy, ^a W-h/kg	
Cell	125
Battery	100
Energy Density, W-h/L	
Cell	400
Battery	200
Peak Power, ^b W/kg	
Cell	125
Battery	100
Battery Heat Loss, W	150
Lifetime	
Deep Discharges	500
Equivalent kilometers	95,000
Equivalent miles	60,000

^aCalculated at the 4-h discharge rate.

^bPeak power sustainable for 15 s at 0 to 15% state of discharge; at 80% discharge, the peak power is 70% of the values shown.

The Mark III battery is expected to demonstrate even higher performance and longer lifetime than those of the Mark II and will be suitable for evaluation and demonstration in a passenger automobile.

The internal program at ANL, which is covered by this report, consists of cell chemistry studies, materials engineering, and component and auxiliary systems development. Important elements of this program are studies of the effects of design modifications on cell performance and post-test examinations of the cells. Appendix A presents a summary of the performance and lifetime for the ANL cells tested in this period, and Appendices B and C present a performance summary for the contractor-fabricated cells tested at ANL.

II. CELL DEVELOPMENT

Developmental efforts are in progress to improve the performance and lifetime of the Li-Al/FeS_x cell for electric-vehicle applications. Means of improving this cell are sought through cell modeling studies, studies of previously discovered problems (e.g., significant capacity decline during cycling and cell swelling), and studies of the failure mechanisms of previously operated cells.

A. Cell Modeling Studies (E. C. Gay, D. R. Vissers)

This effort includes statistical analyses of cell performance and lifetime test results, mathematical correlations of cell performance and lifetime with cell design parameters, and modeling of the electrochemical processes occurring within the cells and electrodes.

1. Engineering-Scale Cell Model (Macro) (W. E. Miller, F. J. Martino)

As was reported in ANL-79-94, p. 98, the Mark IA cells achieved relatively high specific energy within the initial 20 cycles (typically about 100 W-h/kg at 4-h rate); however, they also exhibited a significant decline in specific energy during extended cycling (0.25% per cycle over an average of 110 cycles). Therefore, the cell model described in ANL-79-94, pp. 107-109 was used to determine the optimal multiplate cell design with respect to specific energy. For this model, empirically based equations were used to relate physical and chemical characteristics of the cell and the mode of cell operation to the specific energy as a function of cycle life. The coefficients in this equation were derived by multiple regression analysis of performance and lifetime data obtained from a number of previously operated cells having a wide variety of designs and operating modes. The design variables included volume fraction of salt in the electrodes, negative-to-positive capacity ratio, electrode thickness, electrolyte composition, active material composition, number of electrode plates, separator thickness, and cell resistance; operating mode variables included number of deep discharge cycles, discharge rate, discharge current density, cut-off voltage, coulombic efficiency, and operating temperature.

These empirical equations were subsequently used to predict the specific energy for up to 800 cycles of eighty-four Li-Al/FeS multiplate cell designs. The following design variables were investigated: positive-electrode thickness (0.28 to 0.52 cm), volume fraction of salt in the positive electrode (0.38 to 0.67), positive-electrode loading density (0.7 to 1.6 A-h/cm³), negative-electrode thickness (0.28 to 1.14 cm), and negative-to-positive capacity ratio (1.0 to 1.3); all other design variables were held constant. The preliminary results indicated that the optimal specific energy will be achieved by a cell with thin electrodes, a negative-to-positive capacity ratio of greater than one, and an initial capacity loading density of 1.4 to 1.6 A-h/cm³ for the positive electrode.

2. Electrochemical Model (Micro)

(J. Newman, R. Pollard)*

A computer program has been developed by Globe-Union Inc.¹ 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 of the positive current collector (low-carbon steel) in a Li-Al/FeS cell (Mark II type) on the specific energy and power. At present, ANL is measuring the electrochemical voltage losses in small-scale (20 A-h) Li-Al/FeS cells with very low electronic resistance; these new estimates of the electrochemical voltage losses will be used in the mathematical model to optimize the current collector design.

B. Capacity Loss Studies

(L. Redey,[†] S. Higuchi,[‡] T. D. Kaun, F. J. Martino, W. Moore,**
A. Claveria, P. Eshman, H. Shimotake, W. E. Miller)

The objective of this work is to provide design recommendations to reduce the rate of capacity loss in Li-Al/FeS cells during cycling. The first step in this investigation has been to develop a satisfactory reference electrode, which would permit a determination of which electrode is primarily responsible for the capacity loss. This reference electrode was described in ANL-79-94, pp. 121-124. In this report period, work was continued on improving the instrumentation needed for recording the relaxation potential of working electrodes with the reference electrode. The entire reference electrode system, when completed, will feature the following: (1) simultaneous data recording on eight channels, (2) 50- μ s to 1000-s sample intervals, with 270 x 500 sample values recorded on magnetic disc, (3) signal resolution of better than 1 mV at all speeds and electrode combinations, and (4) data reproducibility for the entire measuring circuit of better than 1 mV for cell testing periods of 6 to 8 months. The system is being developed to evaluate cells of up to 300 A-h.

In general, the Mark IA cells showed significant capacity decline during cycling (typically 20% within 200 cycles). In an earlier study (ANL-79-94, p. 126), a reference electrode was inserted into an engineering-scale Li-Al/FeS bicell with Matrix-D-type^{††} Mark IA electrodes. The theoretical capacities for the positive and negative electrodes of this cell (designated EPRE-1) were 97 and 108 A-h, respectively. The measurements made with the reference electrode indicated that the capacity of the cell was limited by the positive electrode during charge and the negative electrode during discharge; furthermore, the power of the cell was found to be limited by the positive electrode. Both Cell EPRE-1 and the Matrix-D-type Mark IA cell exhibited similar rates of

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^{††}See ANL-79-94, p. 21 for further description of this type of cell.

capacity decline--0.15%/cycle.* In a subsequent test, reference electrodes were implanted in a Li-Al/FeS bicell identical in design to FPRE-1 except that the theoretical capacity of the negative electrode was doubled, from 108 to 216 A-h; consequently, this recent cell (EPRE-2) has a negative-to-positive capacity ratio of 2.22. As shown in Fig. 1, this cell exhibited very little capacity decline over 55 cycles, when cell operation was terminated due to a temperature controller malfunction; in addition, the positive electrode utilization for this cell was 95%, which is the highest utilization ever obtained in a Li-Al/FeS cell. Measurements with the reference electrode indicated (1) that the negative electrode was essentially unpolarized during cycling and (2) that essentially all the polarization developed by the cell was present in the positive electrode. Therefore, the cell capacity was limited on both charge and discharge by the positive electrode. The observations made concerning this cell indicate that the capacity fading observed in Cell EPRE-1 as well as the Mark 1A cells was caused by the capacity decline of the negative electrode.

Fig. 1. Cell Capacity as Function of Cycle Life for EPRE Cells

In Cells EPRE-1 and 2, potential gradients between the top and bottom electrode edges on the order of several millivolts were observed during cycling. The magnitude of these gradients was found to change with current density and state of charge. Future studies will be initiated to investigate these gradients, which result, in part, from a nonuniform current distribution across the vertical faces of the electrodes.

*Capacity decline rates are given throughout this report, and it should be noted that these rates are not constant throughout the cell lifetime but decrease as the cycle life increases.

Analysis of performance data suggested a correlation between capacity stability and initial negative utilization. Figure 2 shows the capacity stability for a Mark IA cell (capacity ratio, 1.0), a Matrix-D Mark IA cell (capacity ratio, 1.1), and Cell EPRE-2 (capacity ratio, 2.2) as a function of initial negative electrode utilization. As shown in this figure, the capacity stability was improved as the initial negative utilization was decreased, the optimum being 60% negative utilization. In addition, lowering the discharge depth of the Matrix D cell to 280 and 235 A-h resulted in a significant decrease in the capacity-decline rate. These results are applicable only to cells fabricated with 46 at.% Li-Al alloy in the negative electrode and operated in eutectic electrolyte at 465°C. Past studies at ANL have previously indicated that a more stable capacity can be achieved in cells with LiCl-rich electrolyte at operating temperatures above 465°C.

Fig. 2. Capacity Decline in Negative Electrode as Function of Initial Negative (46 at.% Li-Al) Utilization

C. Cell Swelling Studies

(H. Shimotake, J. E. Battles, W. E. Miller)

The objective of this effort is to develop recommendations that would minimize the extent of cell and electrode swelling. An effort is being made

to determine the relative contributions of gas pressure and electrode expansion forces to swelling of the cell, and to relate the electrode swelling forces to the compositions and physical characteristics of the electrodes.

1. Mechanism of Electrode Swelling
(G. Bandyopadhyay, T. M. Galvin)*

Tests were initiated to investigate the particle rearrangement and densification behavior of negative-electrode compositions in the presence of molten electrolyte and an external load. The results from these tests should be useful in analyzing electrode swelling problems and related phenomena (such as the formation of a skeletal structure and agglomeration) that have been observed in negative electrodes of previously operated cells. As part of this effort, preliminary experiments were performed to study the volume changes in cold-compacted Li-Al (17.5 wt % Li) and aluminum containing varying amounts of salt. Weighed amounts of Li-Al or Al powder (-50 +150 size fractions) were dry mixed with suitable amounts of LiCl-KCl, and the powder was cold pressed to a constant size (21-mm diameter, 13-mm height). The samples were then fired at 450°C for 48 h in an argon-filled glove box. The porous specimen sizes were measured at room temperature after firing.

Significant volume shrinkage through particle rearrangement occurred after firing in the Li-Al compacts (containing 25 and 30 vol % porosities in the unfired samples) when a sufficient amount of salt (28 to 37 vol % solid salt in the unfired compact) was present. The presence of excessive amounts of salt (>37 vol % solid salt) led to complete particle separation in the Li-Al compacts. Previous testing (ANL-78-94, p. 157) demonstrated that Li-Al is easily wetted by molten LiCl-KCl; therefore, particle rearrangement and separation were expected. Microstructural examination of polished sections indicated that liquid LiCl-KCl wetted the Li-Al particles, and that no sintering occurred among these particles.

The aluminum compacts (30 and 35% porosity in the unfired samples) did not exhibit significant volume shrinkage during the firing process. When the solid salt content in the original compact was >35%, the specimens were deformed, but complete particle separation was not observed. The lack of particle rearrangement and separation in these compacts is probably due to incomplete wetting of aluminum particles by the LiCl-KCl eutectic. Microstructural examination of the aluminum compacts indicated significant sintering between the particles (Fig. 3). It should be noted that "agglomeration", as shown in Fig. 3a, and neck formation between particles within an open structure (sintering), as shown in Fig. 3b, did not require any external load or electrochemical process. Since sintering in these compacts did not result in any

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Fig. 3. Microstructure of Fired Alumina Compacts. (a) Compact with 66.5 vol % Al, 3.5 vol % salt, and 30 vol % Porosity; (b) Compact with 49 vol % Al, 21 vol % salt, and 30 vol % Porosity.

volume shrinkage, it was speculated that the sintering occurred primarily by a surface diffusion mechanism in which the pores do not shrink; instead their shape changes as the sintering progresses.*

In the above experiments, the specimens used were porous and no external stresses were present during the firing process. In actual electrodes, the electrolyte is expected to fill all the pores, and the electrodes may be

*Evaporation-condensation mechanism or transport through the molten phase can also lead to sintering between particles without shrinkage. However, the temperature in these experiments was too low for the evaporation-condensation mechanism to be operative, and sintering by transport through the molten salt is unlikely because of incomplete wetting of aluminum particles by the molten phase.

subjected to significant stresses due to gas expansion, electrolyte melting, and electrode swelling. Consequently, experiments are in progress to study fully dense Li-Al and Al compacts containing varying volume fractions of salt, with and without an external load.

2. Stress Analysis on Cell Can (S. Majumdar)*

An elastic stress and displacement analysis was conducted on a typical cell can to determine the deformation (if any) under any internal stresses, with and without some externally applied constraining force on the cell-can faces. The observations made as a result of this analysis are as follows:

1. In a low-carbon steel cell can, with dimensions of 18.7 x 18.7 x 3.7 cm and a wall thickness of 0.0625 cm, an internal pressure of 175-350 kPa (25-50 psi) produced stresses and displacements that were unacceptably high. The stresses and deformations can be reduced by clamping the square faces so that they are prevented from bending; however, the stresses in the rectangular side plates will still be sufficiently high to cause plastic deformation. The plastic deformation can be minimized by increasing the thickness of the side plates.

2. An internal pressure of 175-350 kPa (25-50 psi) is estimated for the present cell can design. The stresses and strains in the cell can and the clamping force depend very strongly on the magnitude of the internal pressure. It is necessary to determine experimentally the mechanisms which are responsible for generating the internal pressure. The effect of the clamping force on the mechanical integrity of the internal cell components should also be determined. A comprehensive knowledge about the mechanical behavior of the electrolyte within the cell will be necessary before the cell can, the electrolyte, and the electrodes can all be incorporated into a single mechanical model.

3. The behavior of the rectangular side plates depends, to a great extent, on the effectiveness of the clamping force in preventing the square faces from bending. Too high a clamping force might cause buckling or excessive bending of the rectangular plates due to internal pressure, particularly at elevated temperatures where creep buckling is a possibility. An optimum level of clamping force should be determined by a combined experimental and analytical approach.

4. A modified cell can design could minimize the bending stresses. For example, plastic deformation in the rectangular side plates can be reduced by replacing the side plates with curved shells so that the internal pressure loading is resisted by membrane stresses rather than by bending.

*Materials Science Division, ANL.

5. The present analysis is based on the elastic theory of bending of thin plates. Consequently, the treatment of the large stresses that are generated at the reentrant corner of the junction between two plates is beyond the scope of this analysis. These high stresses should be minimized by providing appropriate radii at the junctions. Furthermore, the present analysis does not address the problem of mechanical failure of the cell can caused by stress-corrosion cracking, creep rupture, creep buckling, corrosion fatigue, and/or ratchetting. These failure modes could be extremely important in determining the long-term life of the cell can.

3. Determination of Cell Swelling Forces

(K. E. Anderson, J. E. A. Graae,* I. Pollack,†)

Electrode swelling under different cell operating modes is being determined with an apparatus that measures the linear expansion of small-scale cells. This apparatus is schematically represented in Fig. 4. For these

Fig. 4. Device for Measuring Linear Expansion of Electrodes

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†Engineering Division, ANL.

measurements, a restraining load is applied to one of the electrodes in a small-scale cell undergoing charge-discharge cycles. The cell consists of a pair of small cylindrical electrode pellets (0.6-cm dia) divided by a separator layer. The deformation exhibited by the electrode of interest is determined with a linear voltage differential transformer (sensitivity: 58 MV = 0.001 in.); the deformation of the counter electrode is isolated from this measurement.

In this report period, the linear expansion was measured in an FeS positive electrode having an initial loading density and thickness similar to those in a typical engineering-scale cell. The results, to date, indicated that most of the electrode expansion occurs during the first discharge. Under a constant pressure of 140 kPa (20 psi), the positive electrode showed no expansion at a current density of 50 mA/cm². When the current density was lowered to 15 mA/cm², no deformation was observed during discharge under a constraining pressure of 70 kPa (10 psi). Therefore, the linear deformation of the positive electrode appears to be related to the discharge current density. It was observed that nonuniform electrode expansion may take place in engineering-scale cells at higher current densities due to nonuniform current distribution in the electrode plate. The expansion which occurred during the first discharge did not recede during subsequent charges, even though the electrode was under a constant constraining force.

The expansion forces within the cell in combination with the internal restraining forces (frames, screens, etc.) result in the production of some net force on the can wall. At this time, it is not possible to analytically predict this net force; yet this measurement is needed for both cell and battery hardware design. One approach being taken now is to take force measurements on the outside of the cell-can wall while a cell is cycling. The design of an instrument to do this job has been completed. The instrument will measure the forces necessary to hold the cell-can wall at zero deflection while a cell is cycling. The instrument is versatile in that it will accommodate cells with face sizes of 12.7 x 17.8 cm, 17.8 x 17.8 cm, 12.7 x 25.4 cm or smaller dimensions and thicknesses up to 7 cm.

4. Correlation of Electrode Expansion, Cell Design, and Operating Mode (E. C. Gay)

A multiple regression analysis is being developed to relate the relative expansion of positive and negative electrodes to cell design and operating variables. For this analysis, 29 cells were examined after post-test examination at ANL (see Section II. D). Nineteen of these cells were bicells assembled and tested at ANL and the remainder were Eagle-Picher multiplate cells. Most of these electrodes did not show uniform expansion, and attempts to estimate the electrode expansion were not successful. Future work in this area will be limited to a small electrode area, the expansion of which can be controlled more readily.

D. Failure Analysis (W. E. Miller)

These experiments are based largely on results of the Mark IA failure analysis, and are concerned mainly with potential short-circuiting mechanisms and their effects, electrolyte leakage problems, properties of high-temperature insulation, arcing under various conditions, and feedthrough failures.

1. Cell and Battery Failure Experiments (V. M. Volba, G. W. Redding, J. F. Weber, J. D. Arntzen, M. A. Slaweki)

In previous tests (ANL-79-94, pp. 95-96), two sheets of Muscovite (white) mica insulation were sandwiched between two steel plates which contained a reservoir for supplying electrolyte saturated with Li-Al to the mica sheets. The two sheets of mica were brought together at one edge to form a butt joint, just as joints were made in the Mark IA battery. These tests showed a current of approximately 5 A with only 0.1-V potential difference between the plates at 450°C. Similar tests were conducted using Phlogopite (amber) mica; with this insulation, the water of hydration is released at temperatures 300-400°F above those for Muscovite mica. The results from the recent tests were similar to those obtained with the Muscovite mica; therefore, there appears to be no benefit in using the more expensive Phlogopite mica in future batteries.

The degree of gas leakage through the seal of the electrical feedthrough in a cell at operating temperature has been in question, especially when the positive terminal rod is under a lateral load due to the pressure exerted through the intercell connector of a battery. Therefore, a horizontally oriented stainless steel rod (about 1-cm dia) was attached to the feedthrough of a Mark IA cell (Cell EPMP-7-190), and a vertically oriented push rod was attached at a point on this rod about 9 cm from the feedthrough. This cell was heated from room temperature to 445°C and loads of 7.5 to 40 lb (3.4 to 19 kg) were applied through the push rod. The initial leakage rate was about 6×10^{-4} cm³/s at 25°C. As shown in Fig. 5, the lateral loads had no appreciable effect on the gas leakage from the cell. In further tests (>340 h in Fig. 5), with the cell at room temperature, a force was exerted perpendicular to the positive terminal rod, and this caused a permanent bend in the rod of 0.15 cm. Nonetheless, an increase in the leak rate of the feedthrough was not observed. In the future, a similar test will be conducted with the cell at operating temperature.

In the above tests, the pressure in Cell EPMP-7-190 was monitored during heat up. Figure 6 shows the internal pressure of this cell as a function of temperature. As shown in this figure, the change in pressure exhibited between the melting point of the electrolyte (about 350°C) and the operating temperature (about 450°C) accounted for nearly 30% of the total change in pressure.

Tests were conducted in which short circuits were initiated in a Mark IA-type cell between the feedthrough housing (negative potential) and the positive terminal rod. These short circuits were initiated by three methods-- formation of a bridge with a metal bar, formation of a metallic bridge through electrolyte corrosion, and an externally applied electrical

Fig. 5. Cell Internal Pressure when Load Applied to Feedthrough

Fig. 6. Internal Pressure as Function of Temperature in an Eagle-Picher Mark IA Cell

short circuit. The first type of short circuit was applied to a cell at ANL, and the other two types were applied to cells at Eagle-Picher. After the short circuit, the maximum temperature on the cell was found at the feed-through: 640°C for the mechanical short, about 775°C for the electrolyte induced short, and 800°C for the externally induced short.

A series of experiments has been initiated to examine arcing. Breakdown voltages across a 0.075-cm gap between two iron rods (3-cm dia) were measured in pure argon and argon contaminated with battery and cell-material (e.g., LiCl-KCl and silver braze) vapors at temperatures up to 465°C and pressures up to 175 kPa (25 psia). The breakdown voltages were measured with a DC power supply (0 to 2000 V). To develop a data base for comparison purposes, initial breakdown voltages were measured at 25°C in a vacuum (30 in. Hg) as well as atmospheric pressure; for these conditions, data from Paschen's curves² indicated that breakdown voltage would occur at about 800 V rms (i.e., alternating current). Figure 7 shows the breakdown voltage as a function of temperature at about 112 kPa (1 psig); as shown, the voltage decreased somewhat as the temperature was increased. Figure 7 also shows the breakdown voltage as a function of pressure at 25 and 465°C. As shown in this figure, the voltage increased as the pressure was increased, and it was less at 465°C than at 25°C. There was little effect of the vapors from LiCl-KCl or braze on the breakdown voltage. These results indicate very little likelihood of arcing occurring across a 0.075-cm gap in a battery at 465°C under a positive pressure of argon at voltages less than 275 V. The maximum potential in the Mark IA module was 79 V.

Fig. 7. Breakdown Voltage as a Function of Temperature and Pressure

2. Failure Modes and Effects Analysis (V. M. Kolba)

This effort is being conducted to provide cell and battery developers with an identification of the failure modes of various parts of the system and their probability so that corrective action can be taken to maximize overall battery reliability.

During the course of the failure analysis of the Mark IA battery, it became apparent that supplemental data on potential failure mechanisms and their effects were needed. As a result, the information obtained from the failure-analysis experiments (see above) as well as the failure analysis itself (see ANL-79-94, p. 102) will be used to obtain a reliability analysis for the Mark II. For this reliability analysis, a design description will be derived for a Mark II-type Li-Al/FeS battery, and, based upon this design, a failure modes and effects analysis (FMEA) will be conducted. This FMEA will identify the basic potential sources of failure in this battery and the failure consequences, which could be hazardous or lead to poor reliability of the system. The FMEA will then be used as input for a fault-tree analysis. For the purposes of the initial FMEA, the battery system has been divided into four parts: cell, insulated container, assembled battery including hardware, and charger/equalizer. The effects on these components by outside sources (e.g., vehicle, road operation, crashes) will be neglected in this phase of the study.

E. Post-Test Examinations

The objective of this work is to obtain information on causes of cell failure, short-circuiting mechanisms, design and fabrication defects, electrode morphology, swelling phenomena, corrosion rates, and other information, using metallography, chemical analysis, electron and ion microprobe methods, etc.

1. Cell Failure Mechanisms (F. C. Mrazek, N. C. Otto, J. Fellner,* J. E. Battles)

For this period, 22 multiplate cells and 26 bicells were subjected to post-test examinations. These cells were fabricated and tested by Eagle-Picher, Gould, and ANL.

The failure mechanisms for the multiplate cells are summarized in Table 2; this table includes those cells examined in the past six months (first half of FY 1980) as well as the cells examined in FY 1979. The cells examined in this period included 8 cells fabricated by Eagle-Picher for the Mark IA program, 10 cells fabricated by Eagle-Picher for the Mark II program, 3 cells fabricated by Gould for the Mark II program, and one cell fabricated by ANL. A more detailed description of the findings from the post-test analysis is given in Appendix D.

As can be deduced from Table 2, the major cause of short circuits was the extrusion of active material from one electrode and subsequent contact

*Student from the University of Wisconsin.

Table 2. Failure Mechanisms for Multiplate Cells

Causes	Number of Cases	
	This Period	FY 1979
Extrusion of active material from positive electrode	9	10
Short circuit in electrical feedthrough	2	6
Metallic deposits in separator	2	4
Equipment malfunction	2	4
Low capacity	1	0
Difficulty in cell assembly	1	2
Rupture in separator	0	2
Unidentified short circuits	5	0
End of test	0	3 ^a
TOTAL	22	30

^aOne of these cells was found to have a short circuit which was caused by a metallic deposit in the separator.

with the opposite electrode. This failure mechanism apparently involves expansion of the negative electrode and the absence of adequate restraint on the electrode edges. Measures are being directed toward correcting this design deficiency.

In two multiplate cells, the use of excessive LiAlCl_4 wetting agent in the separator resulted in metallic aluminum deposits that bridged the separators. To further study this failure mechanism, several small pieces of BN felt were loaded with varying levels of the LiAlCl_4 wetting agent, heated for 2 min at 200°C , immersed in LiCl-KCl eutectic (450°C) containing several large pieces of Li-Al , maintained in this bath for 10 min, and finally removed and examined. Metallographic examination of specimens with the recommended quantity of LiAlCl_4 ($6\text{--}7\text{ mg/cm}^2$) showed them to contain very few, if any, metallic particles; specimens with three to ten times this amount of wetting agent had massive amounts of aluminum dispersed throughout the separator. A BN felt sample containing ten times the recommended quantity of LiAlCl_4 (about 60 mg/cm^2) was exposed to molten LiCl-KCl electrolyte which did not contain LiAl . Microscopic examination of this sample showed a complete absence of aluminum precipitates in the BN felt. From these results, it appears that the aluminum metal deposits are caused by a reaction between LiAlCl_4 and lithium from the LiAl in the LiCl-KCl electrolyte. Since the short circuits in the two cells examined were random in nature, the high concentrations of aluminum are

probably the result of localized zones of high LiAlCl_4 concentration. Therefore, methods which will produce a more uniform application of the wetting agent should correct this problem.

One of the multiplate cells fabricated by Eagle-Picher (EPMP-7-193) was held on open circuit, and the temperature was gradually increased to approximately 800°C , at which point the cell began to rapidly undergo self discharge. (The cells in the Mark IA battery were exposed to this high temperature during failure.) Post-test examination of this cell showed that the short circuit was caused by bridging of the BN separator by copper and iron, presumably introduced by electrochemical deposition. No evidence was found of penetration of the separator by molten LiAl or aluminum.

The cause of the short circuit was not identified in five multiplate cells. In two cells (D-13 and D-15), the center negative electrodes had expanded by almost 100%. The probable cause of the short circuits was either (1) the retainer screens had ruptured, thereby allowing extrusion of electrode material, or (2) the felt separator had been cut by the electrode channel frame, which was pushed into the separator by the expansion of the negative electrode.

A summary of the failure mechanisms from the post-test examinations of bicells is listed in Table 3, and the results of the post-test examinations are reported in Appendix E. The bicells include 12 cells from Gould and 14 cells from ANL. As with the multiplate cells, the major cause of cell failure in this period was extrusion of electrode material at the edges (7 cases); separator failure was the cause of short circuits in five cells. The examination of Gould bicells, which did not have honeycomb structures in the electrodes (see Section III. B.2), revealed a gross non-uniformity in the thickness of the electrodes. The extent of the non-uniformity appeared to increase with cycle life and was the cause for the ruptured separators observed in two cells. This behavior has not been observed in cells that used honeycomb current collectors in the positive and negative electrodes. Thus, it appears that the honeycomb current collectors have the added benefit of maintaining uniformity in the thickness and shape of the electrodes. For this reason, honeycomb current collectors (or similar structures) have been recommended for electrodes in all future cells.

2. Electrode Morphology Studies (N. C. Otto)

Post-test examinations of voltammetry cells and engineering cells have indicated that FeS_2 does not nucleate on or within Z-phase ($\text{Li}_3\text{Fe}_2\text{S}_4$) particles during charge; FeS_2 nucleation occurs only on the surface of Fe_{1-x}S particles. Electron microprobe examinations of cells terminated at different charge cut-off potentials showed that the composition of Fe_{1-x}S becomes increasingly sulfur-rich (Fig. 8) with increasing voltage until about 1.84 V, where the composition is approximately $\text{Fe}_{0.88}\text{S}$. This is the equilibrium composition of Fe_{1-x}S with FeS_2 at the cell operating temperature, and, at this composition, FeS_2 will nucleate on the Fe_{1-x}S .

Table 3. Failure Mechanisms of Bicells

Mechanism	Number of Cases	
	This Period	Through FY 1979 ^a
Extrusion of active materials (inadequate confinement)	7	29
Metallic copper deposits in separator ^b	0	13
Separator cut by honeycomb current collector	0	22
Equipment malfunction ^c	2	10
Short circuit in feedthrough	2	9
Cell assembly difficulties	1	12
Broken positive-electrode conductor	0	2
Declining coulombic efficiency	2	12
Unidentified short circuits	1	5
Loss of capacity & poor utilization	1	5
Metallic ^d and/or sulfide deposits across separator	3	9
End of test	2	17
Ruptured BN felt separator & nonuniform expansion of electrodes	5	2
	—	—
TOTAL	26	147

^aAll cells that have undergone post-test examinations through FY 1979.

^bFe₂S₃ cells with Cu₂S additive; one cell used a copper current.

^cOvercharge, temperature excursion, or accidental polarity reversal.

^dOther than copper.

Fig. 8. Composition of Pyrrhotite on Charging

Thus, the initial formation of FeS_2 does not involve Z phase in the reaction,

but rather involves the sulfidation of Fe_{1-x}S as follows:

Microscopic examination revealed that the sulfur can be provided for this reaction either by Z phase in contact with the Fe_{1-x}S or as a soluble sulfur species in the salt.

These observations support the hypothesis that the irreversibility seen on the upper plateau of FeS₂ cells is caused by the kinetics of FeS₂ nucleation. If the reaction were reversible, FeS₂ should begin to form at 1.786 V, the same voltage that the discharge reaction,

takes place. The upper plateau charge peak begins instead at approximately 1.84 V, where the Fe_{1-x}S is at a composition capable of nucleating FeS₂.

3. Electrode Expansion Studies (N. C. Otto, F. Mrazek and J. E. Battles)

Electrode expansion has been observed in the post-test examinations of all bicells and multiplate cells. The electrode expansion within a given cell can be divided into three classes: (1) negative electrode expansion and compression of the positive electrode, (2) positive electrode expansion and compression of the negative electrode, and (3) expansion of both electrodes. The most common form of electrode expansion is that of class 3 followed by class 1. Class 2 is a minor occurrence and appears to be associated with porous negative electrodes such as those fabricated from pressed aluminum wire and lithium foil. Obviously, the amount of electrode expansion would depend on a number of factors; however, the most important factors appear to be the as-fabricated electrode loading density (A-hr/cm³ or volume fraction of active material), percent utilization of the active material, compressibility of the separator, and rigidity of cell restraint during operation. With regard to the latter, a bicell showed significant expansion when it was operated after the cell restrainer plates were removed.

During this period, Mark IA and Mark II cells fabricated by Eagle-Picher were examined to obtain quantitative data on the expansion of the electrodes in multiplate cells. The expansion data are summarized in Table 4. The number of cycles completed and the phases present in the positive electrode at termination are given for each cell. The electrode expansion is reported as percent increase in thickness over the as-fabricated thickness. The data show that the outer negative electrodes expanded more than the inner electrodes. This behavior is consistent with the metallographic observation that the outer negative electrodes show much less LiAl agglomeration than the inner negative electrodes. This difference may be related to the fact that the outer electrodes are in contact with the cell can and, hence, have better current collectors. The positive electrodes showed about the same expansion as the inner negative electrodes. The data do not show a trend in the electrode expansion according to the state of charge; such a trend would be expected since the volume of the sulfides increases by almost a factor of two in discharging from FeS to Li₂S plus Fe. Since the negative electrodes have been shown to form a rigid skeletal structure during cycling, the geometric volume would be expected to show only minor changes as a function of the charge state. Perhaps, this condition minimizes changes in the positive electrode as a function of the charge state.

Table 4. Electrode Expansion in Multiplate Cells

Cell No.	Cycles	Charge State ^a	Electrode Expansion, %		
			Positive	Inner Neg.	Outer Neg.
EPMP-7-022	4	Li ₂ S	35	11	31
EPMP-7-035	101	Li ₂ S, J	30	20	38
EPMP-7-055	320	X, FeS, J	29	22	39
EPMP-7-068	69	FeS, X	27	21	24
EPMP-7-071	118	FeS, X	8	31	40
EPMP-7-094 ^b	74	Li ₂ S	65	-7	20
EPMP-7-129	78	X, FeS	20	10	17
EPMP-7-131	78	X, FeS	20	10	17
EPMP-7-164	5	X, FeS	20	10	17
EPMP-7-069 ^b	4	Li ₂ S	76	-17	-9
EP-MKII-015	93	FeS, J	18	26	34
EP-MKII-016 ^b	0	—	6	0	16
Average			22	18	29

^aJ phase is LiK₆Fe₂₄S₂₆Cl; X phase is Li₂FeS₂.

^bNot included in average.

III. MATERIALS AND COMPONENTS DEVELOPMENT

The objectives of this part of the program are 1) to provide solutions to chemical and electrochemical problems that arise in the development of cells and batteries, 2) to develop improved compositions for electrodes and electrolytes, 3) to acquire a basic understanding of the chemistry and electrochemistry of cells, and 4) to improve the performance of various cell components (e.g., separators, current collectors, and other cell hardware).

A. Electrode Development (D. R. Vissers)

The chemical, electrochemical, and physical properties of various electrode materials are being investigated.

1. Li-Al Electrode Studies (A. K. Fischer and W. R. Lehman*)

Previous post-test examinations of Li-Al/FeS multiplate cells have shown that Li-Al agglomerations generally form in the center of the negative electrode; 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.

An experimental technique has been developed to examine the variables affecting this agglomeration in a convenient and controlled manner. The technique consists of cycling deep-bed (about 2 cm) porous electrodes of ($\alpha + \beta$) Li-Al and aluminum alone. Electrode geometry, particle sizes, loading, cut-off voltages (0.2 V, IR-included, in both directions), and current density (51 mA/cm²) were kept constant for all experiments. During each half-cycle, the lithium content of each electrode was traced coulometrically, and the polarization of each electrode was determined with the aid of a ($\alpha + \beta$) Li-Al reference electrode. This electrochemical cycling was continued for one week, after which the electrodes were sectioned and examined microscopically. The deep-bed configuration appears to force agglomeration conditions to develop over a more well-defined zone and more quickly than is usually the case in the thinner engineering-cell Li-Al electrodes. Also, the procedure eliminates any effects that the positive electrode might have on the operating characteristics of the Li-Al electrode.

The coulometric investigations indicated that, after the break-in stage, the amount of lithium transported in each successive half-cycle steadily diminished, representing a capacity decline. The polarization curves generally indicated that, with cycling, the discharge process showed a greater increase in overpotential than the charging process. Microscopic examination

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showed that the originally pure aluminum electrode, which had become a Li-Al electrode during cycling, developed a severely agglomerated zone, which was bordered by a zone where the agglomeration was in a striated pattern. The other electrode, which originally contained 45 at. % lithium, developed only a moderate degree of striated agglomeration. This experiment provides the baseline conditions of capacity decline and degree of agglomeration against which the effects of electrode additives as well as of changes in conditions such as electrolyte composition, current density, and cycling pattern can be assessed.

The capacity decline observed in this system demonstrates that capacity decline processes reside in the Li-Al electrode. However, the results do not rule out the possibility that the iron sulfide electrode also contributes to the capacity decline in engineering cells.

Nuclear magnetic resonance studies³ have indicated that Li-Al has a high concentration of lithium vacancies (2.7%). Also, recent work⁴ has shown that the chemical diffusion coefficient of lithium in β -LiAl at the $\alpha + \beta$ phase boundary is extraordinarily large, about 10^{-4} cm²/sec. These facts make it reasonable to suggest that Li-Al electrode agglomeration may involve sintering by processes of vacancy diffusion. Since the working composition range of a Li-Al electrode is in the $\alpha + \beta$ region of the phase diagram, where at least some β -LiAl is always present, the compositional potential for sintering is also always present. This can remain true even when the electrode is discharged to a nominal overall composition in the α region, if interior strata remain in the $\alpha + \beta$ region.

The effects of two additives, magnesium and cadmium, to the pure aluminum electrode were evaluated. The magnesium additive (0.66 at. %) produced a more severe capacity decline and a more complex morphology in the electrode than was observed in the electrode formed from the pure aluminum; extensive agglomeration as well as a band that might be magnesium-rich was also observed in the sectioned electrode. Further examination of the electrode is in progress. An aluminum electrode saturated with cadmium (about 0.002 at. %) was also tested. The electrochemical performance of this electrode did not seem substantially different from that observed with the pure aluminum electrode; morphological examination of the electrode is in progress.

To better understand the parameters operative in the agglomeration process, a blank experiment was done which exactly duplicated the baseline agglomeration experiment except that no current was passed between the electrodes. The results of this study indicated that after one week there was no agglomeration in either of the sectioned electrodes.

2. FeS Electrode Studies (Z. Tomczuk)

The reaction sequence which occurs in the FeS electrode of the Li-Al/FeS cell operated in the LiCl-KCl eutectic was established earlier

(ANL-79-94, p. 146) by cell studies, post-test (metallographic) examinations of the FeS electrodes, cyclic voltammetry experiments, emf measurements, and thermodynamic calculations. Six possible electrochemical reactions were identified in this earlier work:

The emf's of the above six reactions were assigned the symbols E_1 through E_6 , respectively, and the values of E_2 , E_3 and E_6 were measured as a function of temperature in Li-Al(5 A-h)/FeS(1 A-h) cells with LiCl-KCl eutectic electrolyte. Efforts to measure E_1 were unsuccessful and E_4 and E_5 could not be measured because these transitions do not occur under equilibrium conditions in LiCl-KCl eutectic electrolyte. The emf values of E_4 and E_6 can, however, be measured in electrolyte free of potassium ion, such as LiF-LiCl-LiBr eutectic, where $\text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$ is not formed, and E_5 can then be obtained from the equation*

$$E_5 = 1/2(E_4 + E_6) \quad (7)$$

The emf's of E_4 and E_6 at temperatures of 740-800 K were measured experimentally in small-scale FeS cells with the LiF-LiCl-LiBr electrolyte. The cell was cycled until reproducible performance was obtained and then discharged or charged to a preselected value. The E_4 values were measured at the 80% state of charge, and the E_6 values at the 60% state of discharge. Two grams of Li_2S was added to the electrolyte before the E_6 values were measured to ensure that the electrolyte was saturated with Li_2S . A linear regression analysis of the data for E_4 and E_6 (in mV) resulted in the following expressions:

$$E_4 = 1331.6 + 0.03T \quad (8)$$

$$E_6 = 1417.8 - 0.127T \quad (9)$$

where T is in degrees Kelvin. Substituting these two equations into Eq. 7 yields

$$E_5 = 1374.7 - 0.0485T \quad (10)$$

*This equation was derived in ANL-79-94, p. 146.

The emf values of E_4 and E_6 are equal at 549 K; this finding indicates that Li_2FeS_2 in the electrolyte is unstable below 549 K and stable above it. The E_6 values obtained earlier in the Li-Al/FeS cell with LiCl-KCl eutectic differ only slightly (about 3 mV at 800 K) from those obtained in the present study. From available free energy data for $(\alpha + \beta)$ Li-Al⁵ and FeS⁶ and the calculated value of E_5 , the free energy of formation of Li_2S was calculated to be -102.6 kcal/mol at 700 K and -100.1 kcal/mol at 800 K.

3. Ni_3S_2 Electrode Studies

Investigations were carried out on a Li-Al/LiCl-KCl/ Ni_3S_2 small-scale cell to evaluate its cell potential as a function of temperature. This investigation was carried out because the $\text{Ni}_3\text{S}_2/\text{S}^{2-}$ half-cell couple is routinely being used as a reference electrode to monitor the electrode potentials in engineering cells (ANL-79-94, p. 122). The cell was cycled at 465°C until reproducible performance was obtained. It was then placed in the 90% state-of-charge condition, and the emf was measured as a function of temperature (643-806 K). A linear regression analysis of the data showed that the emf (in mV) for the $\text{Ni}_3\text{S}_2/\text{S}^{2-}$ half-cell couple vs. $(\alpha + \beta)$ Li-Al can be expressed by:

$$E_{\text{Ni}_3\text{S}_2/\text{S}^{2-}} = 1306.46 + 0.083T \quad (11)$$

These results are in reasonable agreement (about 2 mV) with measurements previously obtained with small reference electrodes (ANL-79-94, p. 123); furthermore, they indicate that loss of Li_2S from the reference-electrode compartment does not appear to be a serious problem.

4. FeS₂ Electrode Studies (Z. Tomczuk)

Cyclic voltammetry studies are being conducted to develop an understanding of the chemistry and electrochemistry and to improve the capacity retention capabilities of the FeS₂ cell.

Previous tests with small-scale FeS cells (ANL-79-94, p. 70) had indicated that 62.7 mol % LiCl-28.2 mol % KCl-9.1 mol % LiF might be an acceptable alternative to the LiCl-KCl electrolyte. In this period, cyclic voltammetry tests were conducted using the FeS₂ electrode and the LiCl-KCl-LiF electrolyte. The voltammetry cell was similar to that described in ANL-79-94, p. 151 except that the positive electrode contained 220 mg of FeS₂ (instead of about 90 mg) and the electrolyte was LiCl-KCl-LiF. The temperature range investigated was 412 to 441°C, and the voltage region was between 1.0 and 2.0 V vs. $(\alpha + \beta)$ Li-Al.

A representative voltammogram is shown in Fig. 9. The shape and number of anodic and cathodic waves are very similar to those obtained in the LiCl-KCl eutectic electrolyte (see ANL-78-94, p. 169). However, the waves

Fig. 9. Typical Voltammogram for FeS_2 Electrode in LiCl-KCl-LiF Electrolyte

are better resolved, and the voltage separation between the start of the major anodic wave (at about 1.82 V) and the start of the major cathodic wave (at about 1.75 V) is only 70 mV; this voltage separation is about 50 mV less than that observed earlier in the voltammetry cell with LiCl-KCl eutectic electrolyte. This small voltage difference indicates that the degree of irreversibility of the transitions between FeS_2 and $\text{Li}_3\text{Fe}_2\text{S}_4$ (Z phase) is lowered in cells with the lithium-halide rich electrolyte. This reduction of the overpotential may improve the cycle life of the Li-Al/FeS_2 couple.

The anodic wave starting at about 1.73 V, which is associated with Z phase formation, disappears if the cell is charged at a constant potential of either 1.716 or 1.698 V, but not at 1.609 V. In addition, this wave reappears on subsequent cycling. This result indicates that the potential for Z phase formation is about 1.7 V, a value which is in excellent agreement with earlier cell work (ANL-79-94, p. 150). However, the constant-potential charging did not affect the irreversibility of the transitions between FeS_2 and Z phase. Thus, the irreversibility of the $\text{Z} + \text{FeS}_2$ transition is not related to Z phase formation. The irreversibility of the transitions between FeS_2 and Z phase was also found to depend on the discharge cutoff voltage; the irreversibility ranged from a maximum of about 70 mV with the 1.05 V cutoff (Fig. 9) to a minimum of 20 mV with a 1.66 V cutoff.

Other results of this study indicated that (1) the coulombic efficiency of the cell decreased with operating time when a 2.0-V charge cutoff was used, and (2) the cell operating temperature did not affect the shape or number of waves obtained in the voltammogram.

In conclusion, this work indicates that LiCl-KCl-LiF is a possible alternative to the LiCl-KCl electrolyte for the LiAl/FeS₂ cell system. However, the capacity decline and irreversibility of the Z to FeS₂ transition were not completely eliminated with the LiCl-KCl-LiF electrolyte system. Thus, future work will be directed toward positive-electrode additives which will allow FeS₂ formation to occur at the reversible potential.

B. Separator Property Studies

(J. E. Battles, W. E. Miller, H. Shimotake)

The electrode separator must be an electronic insulator, remain non-conductive, and be compatible with the cell materials (i.e., Li-Al, electrolyte, and iron sulfides). Other requirements of the separator include adequate mechanical strength, acceptable cost, and suitable porosity and thickness. 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--BN felt and MgO powder.

1. Characterization of BN felts

(J. Fellner*)

The present BN felt separators are hand-made at the Kennecott Copper Co. using a 12-in. square Williams sheet mold. A Fourdrinier felt machine is being set up and should be in operation by the end of April. The present felts have a nominal thickness of 2 mm, a porosity of 91 to 93%, and a basic weight of about 32 mg/cm². As previously reported (ANL-79-94, p. 156), characterization of the felts indicated reasonable uniformity in the thickness, weight and porosity. However, the B felts received in recent months have shown great nonuniformity in thickness, compressibility and flexibility. For the most recent batch (160 sheets), the thicknesses of the felts ranged from 1.89 to 2.39 mm; the average thickness was 2.10 mm. These felts were reasonably uniform in weight. The data indicated a correlation between thickness, porosity and flexibility--the thinner felts being less porous and less flexible. The problem of nonuniform felts has been discussed with Kennecott, and efforts are under way to improve the uniformity.

2. In-Cell Testing of BN Felt

(T. D. Kaun, J. D. Arntzen, V. McCann,† A. Jackson‡)

Gould Inc. delivered ten identical engineering-scale FeS bicells (Q series) with BN felt separators to ANL for cycle-life testing. These cells

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had design features which Gould expects to incorporate into their Mark II cells. The BN felt (unfired) had an area of 450 cm², a thickness of 2.2 mm, and a basis weight of 60 mg/cm². These cells were assembled with half-charged active materials, positive electrode additives of carbon and molybdenum powder, and an electrolyte of 65.6 mol % LiCl-34.4 mol % KCl. The theoretical capacities were 117 A-h for the positive electrode and 154 A-h for the negative electrodes. The honeycomb metal structures, previously used inside electrodes to provide additional support to the fine-mesh screen on the electrode faces, were eliminated from these cells.

The performance and lifetime of these cells are given in Table 5. Some of them required as many as 100 cycles to attain peak capacity; therefore, the operating time is more representative of the lifetime than the number of cycles. The longest operating cell was Q-7, which cycled for 3150 h (550 cycles), with only an 8% decline in capacity, before exhibiting low coulombic efficiency. The remaining cells were operated for 200 to 1950 h (44 to 265 cycles) with little decline in capacity before failure. Post-test examinations revealed a wavy electrode/separator interface. A number of structures were suggested to Gould by ANL that would have the compressive strength required to prevent collapse of the electrode.

Another group of six identical engineering-scale FeS bicells (KK series) was fabricated and cycle-life tested at ANL. The design of these cells is similar to that of a previously tested cell, KK-15 (ANL-78-94, pp. 132-133).

Table 5. Performance and Lifetime of Gould Q-Series Cells

Cell No.	Lifetime ^a		Peak Capacity, A-h	Peak Energy, W-h
	Cycles	Time, h		
Q-1	82	700	72	85
Q-2	165	1420	74.5	89
Q-3	265	1950	70	83
Q-4	177	1600	87	105
Q-5	133	940	72	84
Q-6	175	1450	78	92.5
Q-7	550	3150	54-61	62-71
Q-8	247	1920	66	77
Q-9	235	1725	66	77
Q-10	44	200	56	66

^aThe operation of all cells has been terminated due to either declining coulombic efficiency (<95%) or a short circuit.

In brief, the FeS positive electrode was formed by the carbon-bonding technique (10 vol % carbon) and had a capacity loading of 1.4 A-h/cm³, the electrolyte was 67.4 mol % LiCl-32.6 mol % KCl, and the separator was BN felt with a thickness of about 2 mm and a porosity of 84%. Unlike the Gould electrodes, the ANL electrodes contained the usual honeycomb structure for internal support and current collection. As of this date, three of the six cells are still in operation. One of the cells has operated for 475 cycles and another cell for 600 cycles.

3. Characterization of Ceramic Powder

(H. Ohno, F. J. Martino, G. K. Ruiz,* W. E. Moore)

Efforts are in progress to develop, evaluate, and optimize ceramic powder (MgO) separators for application in Li-Al/FeS cells.

The effective conductivity of a ceramic powder separator will vary with the volume fraction electrolyte in this electrochemically inert, porous bed. The effective conductivities are related to the conductivity of the electrolyte and the porosity of the porous media by the following relationship:

$$K = K_0 \phi^n$$

where K is the effective conductivity, K_0 is the electrolyte conductivity, and ϕ is the porosity. In ANL-79-94, pp. 130-133, an experimental apparatus was described in which the conductance of a separator material wetted with LiCl-KCl at the cell operating temperature could be measured; and this device was used to measure the effective conductivity of MgO powder samples with porosities of 34 to 94%.

Figure 10 shows the experimentally determined values of K/K_0 for MgO powder and BN felt of varying porosities at 400 and 450°C; these separator materials had been wetted with either LiCl-KCl eutectic or LiCl-rich electrolyte. Also shown in this figure are the curves of K/K_0 vs. ϕ for $n = 1, 1.5$, and 2.5. In the high porosity region ($\phi > 0.7$), the experimental values of the effective conductivities decline sharply with declining porosities, closely following the $n = 2.5$ curve. However, at a porosity near to 0.65, these values follow the $n = 1$ curve. The departure of the conductivity ratio from the $n = 2.5$ curve at low porosity appears to be a unique feature of molten salt systems. The electrolyte composition, whether eutectic or LiCl-rich, did not have an appreciable effect on the effective conductivity. At a temperature of 450°C, the separator materials showed a sharper decline in K/K_0 with decreasing porosity than did materials at 400°C.

Earlier tests (ANL-78-94, pp. 134-135) had shown that the separator layer of MgO formed in engineering-scale cells had a relatively low porosity, about 45%, which resulted in high ohmic resistances. Recently, a new MgO powder with a higher surface area (70 m²/g) than that of the previously used powder became available. This powder was vibratory loaded into a 2-mm thick annulus between the electrodes of an engineering-scale (150 A-h) FeS bicell (M8IWA); this procedure resulted in a separator with a porosity of 70%. Testing

*Student from Northwestern University.

Fig. 10. Conductivity Ratio of Porous Ceramic Separators

of this cell showed that the resistance was about the same as that of similar bicells with BN felt separators. However, the coulombic efficiency of this cell declined to 85% after only 9 cycles, indicating the development of a short circuit. Post-test examinations revealed the absence of separator material at the electrode-to-separator interface. In the future, small-size cells with this separator material will be tested.

C. Current Collector Development

(J. E. Battles, H. Shimotake, W. E. Miller)

The AISI 1008 or 1010 low-carbon steels presently used in FeS electrodes do not appear to have adequate corrosion resistance to achieve the Mark II lifetime goals. For FeS₂ electrodes, the only material that can be used satisfactorily for current collectors is molybdenum, which is expensive. Therefore, efforts are in progress to identify and/or develop alloys and protective coatings for current collectors in FeS and FeS₂ cells that satisfy both technical and cost requirements.

1. Current Collector Materials for FeS Electrodes

(J. A. Smaga, Y. M. Jeanneret*)

To increase the corrosion resistance of low carbon steel and nickel in the FeS electrode, methods such as alloying additions, protective coatings, and mechanical surface treatments are under consideration.

a. Static Corrosion Tests of Candidate Materials

Static corrosion tests were completed for fifteen candidate materials. The tests consisted of immersing these materials in an equal-volume mixture of FeS and LiCl-KCl at 400 and 500°C for periods of 500 or 1000 h. The corrosion rates, which are based on gravimetric measurements, and the findings of microscopic examinations are summarized in Table 6. The results of earlier tests at 450°C are also included for comparison purposes.

Commercially pure grades of aluminum, titanium, and zirconium had very high corrosion rates ($>1000 \mu\text{m/yr}$), even at 400°C. The sulfidation attack of electrolytic tough-pitch (ETP) copper was greatly accelerated by increasing the temperature to 500°C. The ETP copper also developed internal porosity due to the reaction of Cu_2O impurities with trace amounts of hydrogen to form pockets of steam. The extremely high reaction rates for these four metals make them unsuitable candidates for alloying with iron.

The moderate corrosion rates found for the low-carbon steel (AISI 1008) are significantly lower than the previously measured rate of $620 \mu\text{m/yr}$ for 1008 steel from another source. Differences in the final fabrication steps of the two stocks of steel sheet are believed responsible for this discrepancy in corrosion rates. Mechanical treatments, such as cold rolling and shot peening, will be examined as possible ways of reducing the intergranular attack of low carbon steel. Intergranular penetration of the $65\text{-}\mu\text{m}$ layer on the chromium-plated steel samples did not result in substrate attack for the exposure times examined, but substrate attack is probable for longer test exposures. The overall test results for electroless nickel-plated steel samples were positive: the nickel layer was breached only for the $12\text{-}\mu\text{m}$ nickel-coated sample tested at 500°C. This coating failure, however, did result in intergranular attack of the steel substrate at the edges of the sample.

Of the seven alloys tested, Fe-2.25 Cr-1 Mo, a member of the Crolloy class of alloys, was the only material to show a serious corrosion problem. This alloy developed a reaction band, probably internal sulfidation, which extended as deep as $150 \mu\text{m}$ below the surface after 1000 h at 500°C. The severity of this reaction is not reflected by the low corrosion rates. The experimental alloy, ANL-5-0, showed minor surface attack at the lower temperatures, but some susceptibility to intergranular attack and embrittlement at

*Co-op student from the University of Wisconsin at Madison.

Table 6. Results of Static Corrosion Tests for FeS Collectors

Material	Corrosion Rate, ^a $\mu\text{m/yr}$			Remarks
	400°C	450°C	500°C	
Aluminum	1300	--	>6400	Severe sulfidation attack
Copper (ETP)	16	150	6100	Severe porosity and sulfidation at 500°C
Titanium	4300	--	>5500	Severe sulfidation attack
Zirconium	4700	--	16000	Severe sulfidation attack
1008 Steel	64	140	250	Intergranular attack, 30 to 70 μm deep
Cr-plated 1008	28	--	20	Localized intergranular attack of coating
Ni-plated 1008 (12 μm)	+17	--	+1.8	Substrate of 500°C sample attacked
Ni-plated 1008 (25 μm)	+27	--	+87	Iron deposition, no substrate attack
Fe-2.25Cr-1Mo	11	--	58	Probable internal sulfidation
ANL-5-0 ^b	10	12	86	Surface attack, some intergranular attack
ANL-10-20 ^c	+29	+9.1	+40	Both surface attack and iron deposition
ANL-15-30 ^d	+30	+18	+33	Iron particle deposition
52 Alloy	+24	+23	+16	Iron particle deposition
Kovar	+26	+23	+11	Iron particle deposition
MP-35N	+35	+25*	+74	5- to 10- μm Fe deposition layer

^aFor most materials the listed corrosion rate is the average for two or more tests conducted for 500 hours or more. Values preceded by a ">" indicate that complete reaction of the sample occurred in less than 500 hours. Values preceded by a "+" indicate a net weight gain due to the deposition of iron.

^bThis alloy was developed at ANL and consists of Fe-4.5 wt% Mo.

^cThis alloy was developed at ANL and consists of Fe-10 wt% Mo-20 wt% Ni.

^dThis alloy was developed at ANL and consists of Fe-15 wt% Mo-30 wt% Ni.

500°C. The deposition of iron was the major reaction noted for ANL-10-20, ANL-15-30, 52 alloy, Kovar, and MP-35N. This incremental corrosion effect occurs at comparatively low rates and is not considered detrimental to the long-term corrosion resistance of these alloys. In other work, static corrosion tests were conducted at 450°C for 500 h on nickel and low carbon steel (1008) samples in LiCl-KCl and either FeS, Li₂S, or Li₂S plus Fe. Figure 11 illustrates the different forms of reaction observed for the three test conditions. In the FeS environment, the nickel and steel underwent iron deposition and intergranular attack, respectively. In the Li₂S tests, both materials formed sulfide scales, Ni₃S₂ in the case of nickel and J phase (about K₆LiFe₂₄S₂₆Cl) for steel. For the third environment, equivalent ampere-hours of iron powder and Li₂S were mixed in the electrolyte, which approximates the positive electrode in the fully discharged condition; no reaction was observed for either nickel or low carbon steel.

b. In-Cell Testing

Two of the experimental alloys, ANL-5-0 and ANL-10-20, were tested as positive-electrode collectors and framing components in 50 A-h test cells. During this period, post-test examinations were completed for three test cells, 3C-14, -15, and -16, which had been operated for 92 to 154 days. The measured corrosion rates for the components from these cells and three previous test cells (ANL-79-94, pp. 160-161) are listed in Table 7. (For a complete performance summary of these cells see ANL-79-39, p. 86 and ANL-79-94, p. 159.)

The corrosion resistance of the ANL-5-0 components showed a strong dependence on the assembled state of charge of the cell. The corrosion rate for the collectors were 15, 43, and 210 µm/yr per side for the cells assembled in the charged, semicharged, and uncharged conditions, respectively. The frames also showed the same effect of assembled charge state on corrosion. In all instances of measurable attack, corrosion of the ANL-5-0 components was a more or less uniform reaction over the exposed surfaces. The collector from

Table 7. In-Cell Corrosion Rates for ANL-5-0 and ANL-10-20 Alloys

Cell	Charge State at Assembly	Positive Components	Days	Mean Corrosion Rate, ^a µm/yr	
				Collector	Frame
3C-10	Charged	ANL-5-0	31	15	15
3C-14	Semicharged	ANL-5-0	150	43	31
3C-16	Uncharged	ANL-5-0	92	210	65
3C-11	Charged	ANL-10-20	31	+16	+12
3C-15	Semicharged	ANL-10-20	154	+11	10
3C-13	Uncharged	ANL-10-20	90	+22	-

^aValues preceded by "+" represent the rate of formation of an adherent iron particle layer.

a

b

c

Nickel tested at 450°C in LiCl-KCl and (a) FeS, (b) Li₂S, (c) Li₂S + Fe

a

b

c

50 μm

1008 Steel tested at 450°C in LiCl-KCl and (a) FeS, (b) Li₂S, (c) Li₂S + Fe

Fig. 11. Corrosion Behavior of Nickel and Low Carbon Steel in Three Different Environments

cell 3C-16 also formed an adherent, 5- μm -thick sulfide layer. The frames from cells 3C-14 and -16 exhibited one unusual feature--the pattern of the BN fabric weave was etched into the outer surfaces of the frames. The high corrosion rates found for the components from cell 3C-16 indicate that ANL-5-0 is unsuitable for long-term use in uncharged cells unless some modification can be made in the alloy/electrode system to reduce the reaction rate.

The ANL-10-20 components from all three cells showed acceptably low rates of reaction. The predominant reaction was the formation of an iron-particle deposition layer. In cell 3C-11, the iron layer incompletely coated the component surfaces, averaging a net thickness increase of about 1.5 μm . In cell 3C-15, a fully developed 5- μm layer was formed. The outer surfaces of the frames, however, showed a mild degree of alloy dissolution, resulting in a net thickness reduction of 4 μm . The collector from cell 3C-12 had formed an iron particle layer over the central portion of the alloy substrate, but dissolution of the alloy occurred toward the edges. The rates of reaction were approximately equivalent for both reactions. Because of the additive nature of the iron deposition reaction, no impairment in the long-term corrosion resistance of ANL-10-20 is foreseen.

In previous studies (ANL-79-39, p. 86), six 50 A-h test cells, four assembled semicharged (3C-1, -2, -4, -5) and two assembled charged (3C-8 and -9), were fabricated with nickel collectors and frames. As shown in Fig. 12, the corrosion rates measured in the collectors and frames of these cells produced conflicting results. The cell assembled semicharged showed detrimental intergranular reaction, which formed severe depressions over as much as 35% of the collector surface (see Fig. 13). In contrast, the cells assembled charged did not show evidence of this type of attack, but had formed a thin layer (4 to 6 μm) of iron on the nickel surface. Microscopic examination of the positive electrode revealed that intergranular reaction had occurred in the semicharged cells because of incomplete reaction of the iron particles, which originally were 100 to 300 μm in diameter. Another 50 A-h test cell (3C-17) with nickel structural components was assembled semicharged; however, the 75- to 100- μm -dia iron particles used for the positive electrodes were much finer than those of the previous cells in order to increase the surface area of the iron particles available for reaction. Cell 3C-17 was operated for 64 days (118 cycles) at 50 mA/cm² before operation was voluntarily terminated. During operation, it maintained a coulombic efficiency greater than 99% and had an average utilization of 45%. Post-test examination of the nickel components revealed both deposition and dissolution. The collector showed an average dissolution rate of -9 $\mu\text{m}/\text{yr}$ per side and an average iron deposition rate of +22 $\mu\text{m}/\text{yr}$ per side. The frame showed an average deposition rate of +18 $\mu\text{m}/\text{yr}$ and an average dissolution rate of -14 $\mu\text{m}/\text{yr}$. These results demonstrate that nickel components can be used in FeS electrodes regardless of the state of charge at assembly.

2. Current Collector Coatings for Li-Al Electrodes (J. A. Smaga)

Conductive coatings are under consideration as a method of preventing reaction between the collector material and aluminum from the negative electrode. The coatings must be compatible with the cell environment, serve as a

Fig. 12. Mean and Maximum Thickness Changes Found for the Nickel Components Used in the FeS Electrodes of Seven Test Cells.

barrier to the diffusion of aluminum, must be easily applied to low-cost base-metal substrates, and have potential for low cost and long life. Once the preparation of necessary glove-box facilities is completed, metallic and non-metallic materials will be identified for compatibility with the LiAl electrode, and planned testing of coated substrates will begin.

3. Current Collectors for FeS₂ Cells

(G. Bandyopadhyay, T. M. Galvin, J. T. Dusek)*

Efforts are being directed toward the development of conductive ceramics for use as a coating material on inexpensive current collectors for FeS₂ electrodes. In FY 1979 (ANL-79-94, p. 162), static corrosion tests were conducted to assess several candidate coating materials. For these tests, the coatings were applied to substrates of AISI 1008, either by chemical vapor deposition or rf-sputtering, and then immersed in a bath of FeS₂ and

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Intergranular Attack of Nickel Collector from FeS Cell
Assembled Semi-charged

Iron deposition on Nickel Collector from FeS Cell
Assembled Fully Charged

Fig. 13. Photomicrographs of the Nickel Collectors from
Cells 3C-1 (upper) and 3C-9 (lower)

LiCl-KCl (equal volume) at 500°C. None of the coated samples showed completely satisfactory corrosion resistance. Nonetheless, the samples coated with TiC and TiN (with a thin layer of TiC) by chemical vapor deposition did show some promise; in addition, hot-pressed samples of monolithic TiC and TiN showed excellent corrosion resistance. 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.

In this period, further tests of TiC- and TiN- coated samples were conducted. The results of these tests are summarized below:

1. Measurement on the coated specimens by X-ray diffraction analysis indicated that high compressive stresses between the coating and substrate were present. These stresses and the corrosion media result in stress corrosion and spallation of the coatings.

2. The corrosion rate of the coating material was not strongly dependent on the type of substrates (AISI 1008 steel or ANL-5-0 alloy) that were used. Coating stability was, however, strongly influenced by the coating thickness.

3. Coated screens (60-mesh AISI 1008 steel), which might be used as particle retainers inside the cell, exhibited poor stability in static corrosion tests; this finding indicates that the geometry of the specimens plays a significant role in the coating stability.

The test conditions in cycled cells are considerably milder (*i.e.*, lower temperature and sulfur activity) than those in the static tests. Therefore, three 50 A-h test cells with positive current collectors and frames of TiN-coated, AISI 304 stainless steel and one 50 A-h cell with a monolithic TiN current-collector plate were fabricated; in addition, some of the cells had coated positive particle retainers. Operation of all four cell was terminated because of declining coulombic efficiency after 15 to 30 days of cycling (50 mA/cm²). Post-test examination of these cells revealed that the positive current collectors and frames did not undergo corrosive attack; however, the coated particle retainers had undergone severe reaction.

The above results indicate that coated positive current collectors and frames have potential application in FeS₂ cells. The long-term stability of these components can probably be improved by the following changes: design the collectors and frames without sharp corners and edges, maintain slightly iron-rich FeS₂ as the positive electrode, and optimize the quality of the coating.

Several Fe-Mo-C and Fe-Mo-B alloys (modified ANL-5-0 compositions) are being prepared for corrosion testing in the FeS and FeS₂ environments. The carbon or boron addition to the Fe-Mo alloy should lower the iron activity, thereby resulting in improved corrosion resistance. The Materials Processing and Development Group at the Materials Science Division of ANL has successfully prepared the Fe-Mo-C alloy in sheet form with about 4.5 wt % molybdenum and 0.2 wt % carbon. Additional Fe-Mo-C alloys with as much as 1 wt % carbon as well as Fe-Mo-B alloys will be prepared in the future.

4. Engineering-Cell Testing of Current Collectors
(L. G. Bartholme, T. D. Kaun, P. F. Eshman)

In previous ANL cells, low-carbon steel has been routinely used as the current collector material for the FeS electrode. The corrosion studies described above indicated that nickel and the Fe-Mo alloy (ANL-5-0) also have the potential to provide current collection for long periods. Subsequently, three engineering-scale Li-Al/FeS bicells, designated R-47, -48, and -53, were fabricated in the uncharged state with similar designs except for the current collector material--nickel for R-47, low-carbon steel for R-48, and Fe-Mo for R-53. All three cells had BN felt separators, LiCl-KCl electrolyte (LiCl rich), and theoretical capacities of 219 A-h for the negative electrode and about 145 A-h for the positive electrode. Cells R-47 and -48 were operated for 753 cycles and 525 cycles, respectively, and showed nearly identical performances. Table 8 presents the performance of these two cells at different points in their cycle history. In both cells, resistance (3.8 m Ω at full charge) did not increase appreciably during cycling. Post-test examination of the low-carbon steel collector in Cell R-48 showed a corrosion rate of only 25 μ m/yr; no measurable corrosion was observed on the nickel current collector. The third cell, R-53, was operated for 386 cycles and showed similar positive utilization (about 70% at 4-h rate) but a higher resistance (4.4 m Ω) than those of the other two cells.

Table 8. Performance Summary of Cells R-47 and R-48 during Cycling

Cell Designation	R-47	R-48
Current Collector Material	Ni	Steel
Pos. Electrode Cap., A-h	146	144
Cycle Life	753	525
Life Time, Days	464	333
Cell Resistance, Ω -cm ²		
50 cycles	1.08	1.06
200 cycles	0.89	1.03
400 cycles	0.95	0.95
600 cycles	1.08	--
Utilization, %		
50 cycles	60	56
100 cycles	57	56
200 cycles	55	57
300 cycles	60	56
400 cycles	55	57
500 cycles	56	56

As a follow-up to these tests, two more bicells were fabricated with the same design and materials as those of Cells R-47 and 48, but with a reduced positive-electrode thickness (theoretical capacity of about 65 A-h). These two cells, R-51 (nickel collector) and R-57 (steel collector), were operated for 690 and 326 cycles, respectively, and also showed nearly identical performance: positive utilization of about 70% at the 4-h rate and cell resistance of about 3.5-4.5 m Ω at full charge.

The above-mentioned five cells, particularly the ones with steel collectors, showed unexpectedly stable cell performance, with little corrosion of the collectors over an extended period of cycling. It is believed that the formation of a passive film protected the low-carbon steel collectors. For future evaluation, cells similar to R-47, -48, and -51 have been constructed and recently placed into operation. The performance of these three cells (R-61, -62, and -63) will be presented in the next report.

A new approach to electrode current collection and confinement of active material is being investigated. In this approach, a mechanically perforated metal sheet is formed into two rectangular cups so they can telescope together to form a box around the electrode plaque (see Fig. 14). This cell design eliminates the need for steel screens on the electrode faces, picture-frame assemblies around the electrode edges, and honeycomb collector structures within the electrode. Cell assembly is accomplished by inserting a separator layer between the electrodes enclosed by the perforated sheet, compressing this stack to obtain the required separator thickness, and then inserting this entire assembly into the cell container through the top (see Fig. 15). The advantages of this design concept are reduced costs for cell hardware, additional support for the fragile BN felt separator, and easier cell assembly.

Fig. 14. New Current Collector Design. (The electrode terminal is in two halves, each attached to an electrode face.)

Fig. 15. Assembled Cell with New Current Collector Design

The first engineering-scale (120 A-h) multiplate cell utilizing mechanically perforated cages, designated LC-MP-4, contained two positive-electrode plaques (12.5-cm square) of carbon-bonded (10 vol%) FeS. The perforated sheet had a thickness of 0.25 mm, a hole size of 0.76 mm, and 35.6% open area; a nickel cage was used on the positive electrode and iron on the negative electrode. The negative-electrode cage was welded shut, whereas the positive electrode cage was not. The performance of this multiplate cell was good: a specific energy of 75 W-h/kg at the 4-h rate (86% utilization) and a specific power of 110 W/kg at the 50% state of charge. Operation of this cell was terminated after only 125 cycles due to declining coulombic efficiency. Post-test examinations (see Appendix D) revealed that the electrode edges were insufficiently restrained and that some active material from the negative electrode had penetrated through the perforated sheet. In the next cell, LC-MP-5, various design modifications were incorporated to improve the perforated plate cage. These modifications included the following: the two cage halves were not welded shut for either the positive or negative electrodes (to allow some

electrode expansion) and metal-strip reinforcements were provided at the electrode edges. This cell is still being operated after 180 cycles and has shown slightly higher specific power but lower specific energy than LC-MP-4. Another cell, LC-MP-6, has been fabricated with a perforated plate cage having holes of 1.12-mm dia (open area 36%) and pressed electrode plaques (12.5 x 17.5 cm) obtained from Gould. This cell has been placed into operation, and its performance will be reported in the next period.

IV. CELL AND BATTERY TESTING

The results of testing at ANL of engineering-scale cells fabricated by ANL and its subcontractors are described below. The primary objective of these tests is to determine periodically the performance and lifetime characteristics of state-of-art cells and to monitor the progress of the Mark II subcontractors by measuring the performance and lifetime of their cells and battery modules.

A. Status Cell Program

(F. J. Martino, W. Moore, M. Fitzgibbons,*
E. C. Gay, H. Shimotake)

At least six state-of-the art cells of identical design are being tested to obtain limited statistical data on their performance and lifetime.

During the past six months, twelve Li-Al/FeS bicells (SM8F01 to SM8F12) of identical design were operated at 460°C, charge and discharge cutoff voltages of 0.90 V and 1.61 V, respectively, and charge and discharge current densities of 37 and 74 mA/cm², respectively. The design for this cell is the same as that of a previously tested ANL cell reported in ANL-79-39, p. 30 (Cell M-8). For this cell design, the positive electrode has a capacity loading of 1.4 A-h/cm³; the electrolyte is 66.7 mol % LiCl-33.3 mol % KCl; and the separator is BN felt treated with LiAlCl₄ to improve wettability. Testing of the status cells was terminated whenever one showed a loss in specific energy of >20% or a decline in coulombic efficiency to below 95%.

As of this time, the operation of nine cells has been terminated; three cells are still in operation. The twelve cells have been operated for an average of 256 cycles and shown an average capacity loss of 8.3% (0.03%/cycle). The best six cells have been operated for an average of 367 cycles and shown an average capacity decline of 2.7% (0.01%/cycle). The three cells still in operation have achieved 328, 376, and 228 cycles at an average capacity loss of 0.02%/cycle.

An interesting aspect of these cells was their ability to recover the lost capacity at lower charge current densities (<37 mA/cm²). For example, Cell SM8F10 had shown a 6% capacity loss after 300 cycles. Nearly all of this capacity loss was recovered by one charge cycle at 18 mA/cm²; continued charging at this current density over the next four cycles resulted in complete recovery of the energy loss. After resumption of normal cycling for about 24 cycles, the capacity-loss percentage had returned to the previous level of 6%. Similar results were obtained in four other cells. This finding implies that current-limited, constant-voltage charging may produce less energy decline with cycling for these cells than constant current charging.

All of these status cells underwent thermal cycles,[†] some as many as eight times. The data are being examined to determine the effects of thermal cycling

*Student from Northwestern University.

†Between normal operating temperature (450°C) and room temperature.

on performance. Most cells showed no lasting effects of thermal cycling, but a few have shown a significant decline in capacity. For example, Cell SM8F03 declined in capacity from 81 to 68 A-h after a single thermal cycle.

B. Mark IA Cell Tests

(T. D. Kaun, J. D. Arntzen, W. A. Kremsner, W. E. Miller)

Tests are continuing at ANL on the multiplate cells fabricated by Eagle-Picher for the Mark IA program. During the Mark IA program (see ANL-79-94, pp. 16-22), the cells were deep cycled (to a discharge cutoff voltage of 0.9-1.0 V) to obtain performance and capacity-loss data under stringent conditions. This mode of cycling produced a high initial capacity, 350 A-h at a 70-A constant-current discharge, but an appreciable capacity decline rate, 0.25%/cycle. In subsequent tests, 14 Mark IA cells were tested under less severe conditions (70-A constant current discharge for 4 h) to determine the effect on performance and lifetime. This testing mode resulted in a specific energy of 85-90 W-h/kg; cell operation was terminated after an average of 88 cycles due to low coulombic efficiency (<95%). Post-test examinations revealed that cell failure was brought about by rupture of the retaining screens and subsequent extrusion of active material; this was the prevailing cell-failure mechanism in earlier Mark IA cells. It was concluded that this shallower mode of cycling did not result in improvement in performance or lifetime.

In further tests, two Mark IA cells were subjected to even shallower cycling--70-A constant-current discharge for 3.5 h and constant-voltage charge. This mode of cycling resulted in a slightly improved lifetime, about 150 cycles.

The above Mark IA cells all had Cu_2S additive in the positive electrode and LiCl-KCl eutectic electrolyte. In the Mark IA program, Eagle-Picher fabricated a few cells with LiCl-KCl electrolyte having a LiCl content above that of the eutectic and no positive-electrode additives. Two such cells are being cycled with 70-A discharges in 4 h and constant-voltage charges, and these cells have attained more than 300 cycles.

Qualification testing (*i.e.*, evaluation of specific energy and specific power at different cycling rates) of the Mark IA cells was conducted at 25, 75, and 150 cycles. This testing indicated that the sharp decline in specific energy with cycling observed in the Mark IA cells was related to capacity loss, particularly at low discharge rates. At the 4-h discharge rate, specific energy declined from 95 W-h/kg at cycle 25 to 80 W-h/kg at cycle 75. Furthermore, an increase in cell internal resistance from 1.4 m Ω at cycle 25 to 1.5 m Ω at cycle 75 reduced the peak specific power from 80 to 73 W/kg at the 50% state of charge.

C. Mark II Cell Tests

(T. D. Kaun, W. A. Kremsner, J. D. Arntzen, W. E. Miller)

The major emphasis for the two Mark II contractors--Eagle-Picher and Gould--is on building reliable cells. The target is for the contractors to produce groups of 12 identical status cells which will be tested to measure their performance and cycle life. The target peak capacity will correspond to a specific energy of about 90 W-h/kg at the 4-h rate.

To meet this objective, Eagle-Picher has been searching for a method to prevent extrusion of active material, a common mode of failure in the Mark IA cells. To prevent this problem, Eagle-Picher incorporated a 3-mm square bar around the perimeter of the electrode plaque, and then photoetched metal screens, which covered the faces of the plaque, were welded to the square bar. These electrode assemblies were inserted into multiplate FeS cells with BN felt separator treated with LiAlCl_4 wetting agent. A high percentage of these cells had short circuits after the electrolyte filling operation; as a result, the cell filling techniques and equipment are being improved at Eagle-Picher. Two of these cells did operate for over 90 cycles, and post-test examination showed that a failure had occurred in the weld that attaches the photoetched screen to the square bar. In 16 subsequent cells, Eagle-Picher constructed a channel around the electrode perimeter for additional edge support. These cells were delivered to ANL to be filled with electrolyte and tested. At present, 11 of these cells are being tested. The first cell to be tested (EPMK-II-032) has accumulated 191 cycles. The peak specific energy of this cell, 75 W-h/kg at the 4-h rate, has decreased to 70.8 W-h/kg within 110 cycles, which corresponds to a decline rate of 0.05% per cycle. To date, these ten cells have an average specific energy of 70 W-h/kg at the 4-h rate. The design of these cells results in a heavy weight; the use of lighter-weight components is expected to give a specific energy of 90 W-h/kg.

For the Mark II program, Gould initially built eleven cells (D-series) having two positive plates and BN felt separator. The design for these cells was presented in ANL-79-94, p.33. The lifetimes of these cells were very short, the failure mode generally being a rapid loss of coulombic efficiency due to a short circuit. Post-test examination of four cells showed a failure of the wire screen used to wrap the negative electrodes. In subsequent Gould cells (referred to as the "12 design"), a retainer-basket assembly was adapted to enclose the electrode plaque. Four cells of this type were delivered to ANL for testing, and all but one of them failed due to the development of a short circuit early in testing. The cell still in operation (D-12) is maintaining a coulombic efficiency of >99% after 106 cycles; the peak specific energy was 80.3 W-h/kg at the 4-h rate and the present value is 78 W-h/kg.

Another group of eight cells (D-24 through D-31) with the Gould "12 design" was delivered to ANL for testing. One of the eight cells had a relatively low cold resistance and developed a short circuit in the first few cycles. Another cell has shown a low capacity thus far, but there is no evidence of a short circuit. The other six cells, during start-up cycling with 20-A discharges (9-10 h rate), duplicated the performance recorded at Gould during the five fill and formation cycles (85-90% utilization of the positive electrode). These cells are attaining an average specific energy of 87 W-h/kg at the 4-h rate.

D. Qualification Tests of Mark II Phase I Modules

(W. E. Miller, V. M. Kolba, G. L. Chapman, G. W. Redding,
J. F. Weber, J. Thomas,* D. Horast†)

Near the end of phase I of the Mark II battery program, each subcontractor will deliver 10-cell modules to ANL for qualification testing. At present, ANL

*Computer group at CEN.

†EBR-II Project, ANL.

is preparing facilities capable of independently testing two such modules. The sixty-cell equalizers from the Mark IA program have been rebuilt to handle these modules. In addition, Robicon programmable power supplies have been modified to include a status board and watchdog; the latter component is a backup control system which shuts down the battery module in case the primary control system fails. A prototype watchdog has been recently fabricated and is being checked out; three additional units will be fabricated. The Robicon power supplies, cell equalizers, and system software will be checked out using EV-106 or equivalent lead-acid batteries.

V. COST STUDIES AND AUXILIARY SYSTEMS DEVELOPMENT

Work is continuing on the identification of potential markets for lithium/iron sulfide batteries as a function of cost and timing.

The Mark IA experience has indicated a strong need for additional thermal management evaluation and design work as well as evaluation of high-temperature electrical insulation for cells, lead wires, and other battery components. Lower cost systems for battery charging and equalization are also needed. The work conducted in these areas is presented below.

A. Commercialization studies

(A. A. Chilenskys, R. B. Swaroop,* S. Nelson†)

In a previous study (ANL-78-94, pp. 17-18), the sizes of the near-term (about 1985) markets for the lithium/iron sulfide battery were projected for the following applications: transit buses, postal and delivery vans, mining vehicles, and submersibles. This study is being updated and expanded to include the applications of school buses and forklift trucks. In addition, sensitivity analyses are being performed to estimate the conditions needed (battery manufacturing cost, sales volume, price of liquid fuels) to penetrate these various market sectors. These near-term markets will be important in supporting the lithium/iron sulfide batteries produced by pilot production facilities.

Further cost projections for the lithium/iron sulfide battery will be made as the Mark II program evolves potentially low-cost materials and fabrication methods. Cost-saving alternatives will also be sought as part of the ANL in-house program.

B. Charger Development

(W. H. Deluca)

A charger/equalizer system capable of accommodating batteries of up to 16 cells has been designed. Figure 16 shows a block diagram of this system, which consists of three basic units: main charger, equalizer, and controller. The main charger is a programmable current-regulated power supply. Different power supplies may be used as needed to satisfy battery-voltage and charge-rate requirements. The equalizer contains voltage-monitoring and current-bypass circuitry to accommodate up to 16 cells; additional equalizers may be added to the system for batteries containing more than 16 cells. The controller is a microprocessor-based unit that establishes overall system operation. The controller continuously monitors cell voltage status, automatically adjusts battery charge current, and initiates current shunting. The controller will be preprogrammed to provide a full bulk, taper and equalization charge sequence as shown in Fig. 17. For laboratory operation, the controller will also be programmed to allow user communication via a printer/keyboard terminal for charge parameter modification and operational status/performance reporting.

*Division of Energy and Environment, ANL.

†Private consultant.

Fig. 16. Block Diagram of ANL Equalizer/Charger

Fig. 17. Current Waveform for Battery Charging

A fully assembled equalizer/charger chassis has been successfully operated. This unit utilizes two types of printed circuit boards (PCB) to facilitate fabrication and maintenance. One PCB contains the individual cell voltage-monitoring and current-bypass circuitry, and the second PCB is used to provide the interconnector wiring for 16 of the cell-circuit PCB's. Procurement of additional PCB's and component parts has been initiated to fabricate and assemble six 16-cell equalizer units. A microprocessor-based charge-control unit is being fabricated and preprogrammed by the Omnibyte Corporation (West Chicago, Illinois) according to ANL specifications. Delivery of this unit is expected in early April, 1980. A remotely programmable, current-regulating power supply has been purchased from Electronic Measurements, Inc. (Neptune, NJ) to be used as the system's main charger. The output capability of the main charger permits the charging of up to 12 cells at a maximum rate of 120 A. A Texas Instruments printer/keyboard terminal has been procured for user communication with the charge control unit.

Upon receipt of the charge-control unit, testing of the fully assembled prototype charging system will begin. System performance testing will be aided by the intrinsic preprogrammed reporting and diagnostic capabilities of the charge control unit. After the prototype charging system has been successfully tested, procurement of six additional systems will be initiated. Two of these units will be furnished to the Mark II battery contractors for field testing at their facilities.

C. Thermal Management Studies

(M. Farahat, E. R. Hayes, G. W. Redding)

The objective of this task is to provide input into the design of thermal management systems for lithium/iron sulfide batteries. These studies consist of the development of a model to be used for calculating heat loss and cell temperatures within a battery, and experiments using one of the Mark IA insulated jackets to verify (or modify) calculations made for heat loss and cell temperature. In addition, efforts are under way at Union Carbide Corp. to develop a load-bearing insulation.

1. Battery Modeling

An integral part of thermal modeling for the lithium/iron sulfide battery is cell heat generation. Cell heating depends upon cell overpotential during charge and discharge, which, in turn, depends upon the current. To date, there is no reliable analytical model to predict cell polarization resistance; hence, an empirical approach has been taken in the present modeling effort.

Detailed open-circuit mapping was conducted on a Mark IA cell being discharged at a current of 70 A and charged at 40 A. Figures 18 and 19 show

Fig. 18. Open-Circuit Mapping during 70-A Discharge

Fig. 19. Open-Circuit Mapping during 40-A Charge

this open-circuit mapping as a function of discharge and charge, respectively. In these figures, the area between the cell voltage and open circuit potential represents the irreversible heat generation during that cycle. The reversible heat generation rate can be expressed as $\pm KI$, where I is the current in amperes and K is a constant previously determined (experimentally and theoretically) to be about 0.11 V. The positive sign is for discharge and the negative sign for charge.

These data were then used to calculate the heat generation rates during discharge and charge, which are plotted in Fig. 20. The average heat generation rate was about 15 W during discharge and zero during charge (*i.e.*, irreversible heating is cancelled by entropic heating). From this figure, it was concluded that (1) the heat generation rate is higher during discharge than that during charge, and (2) the heat generation rate increases substantially near the end of discharge and the beginning of charge due to an increase in polarization resistance.

The procedure for calculating heat generation in a cell was then used to estimate the heat generation during a 70-A discharge of a five-cell battery module. Based upon the calculated heat generation as well as component-weight and specific-heat data, it was possible to estimate the average temperatures in the five-cell module during this discharge. These estimated average temperatures were then compared with three temperature measurements made inside the Mark IA five-cell module (ANL-79-94, p. 26) during its 50th discharge (auxiliary heaters off). As shown in Fig. 21, good agreement exists between the calculated and measured temperatures of this module during discharge.

Fig. 20. Heat Generation during Charge and Discharge

Fig. 21. Estimated and Calculated Temperatures within Five-Cell Module

2. Heat-Loss Measurements

Heat-loss measurements will be conducted on the undamaged vacuum-foil insulated case (without cells) from the Mark IA battery. As shown in Fig. 22, this case has been equipped with a Min K plug and several thermocouples, attached both inside and outside the insulated case, to monitor temperature; an ion pump (25 L/s) is used on each end of the case to ensure a consistent vacuum level. For the heat-loss measurements from this case, the internal temperature will be varied between 400 and 500°C; in addition, the effect on the temperature of various sizes and types of penetrations through the plug will be tested.

Fig. 22. Setup for Heat-Loss Measurements in Mark IA Module

3. Development of Thermal Insulation

Union Carbide Corp. (Linde Division) is developing a load-bearing insulation for high-temperature batteries. The requirements of such an insulation are that it be capable of withstanding pressures of 95 kPa (15 psi) and temperatures of 450°C, be lightweight (about 290 kg/m³), and have a thermal conductivity of 2.38×10^{-3} W/m-K (140 Btu/h-ft-°F) or lower. Three candidate insulation systems that have been tested appear promising: (1) an insulation board composed of fiber-glass sheets compressed together, with no radiation

foils; (2) Linde's Super Insulation (fiber glass and aluminum foil) with load-supporting Fiberglass* paper sheets (8% of total area) and 40 radiation foils; and (3) Linde's Super Insulation with Min-K† 2000 peg supports and 120 radiation foils. The latter two insulations are illustrated in Fig. 23. Table 9 shows the results of the insulation tests for the three developmental insulations along with commercially available insulations.

THICK-THIN AND PEG-SUPPORTED INSULATION SYSTEMS

NOTE: THICK-THIN SPACER IS PRODUCED IN A CONTINUOUS PAPER MAKING PROCESS.

Fig. 23. Load-Bearing Thermal Insulation

*A product of Owens-Corning Co.

†A product of Johns Manville Co.

Table 9. Pressure-Supporting Vacuum Thermal Insulation

Description	Thermal Conductivity, ^a W/m-K	Density, kg/L	Percent Compression at 95 kPa Load
Glass Mat (no foils)	3.88×10^{-3}	0.35	7
Paper Spacer (40 foils)	1.64×10^{-3}	0.24	21
Min-K Pegs (120 foils)	1.75×10^{-3}	0.18	6
Min-K 2000 ^b	18.16×10^{-3}	0.32	7
Microtherm 20 CR ^c	14.19×10^{-3}	0.32	2

^aMeasured at $T_H = 840^\circ\text{F}$ and $T_C = 75^\circ\text{F}$.

^bA product of Johns-Manville.

^cA product of Micropore International.

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APPENDIX A.

PERFORMANCE SUMMARY FOR ANL-FABRICATED CELLS

Appendix A. Performance Summary for ANL-Fabricated Cells

Cell Number ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline In						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.	
SM8F01 LiAl/FeS 174/120 A-h 1.39 kg	82	95	4	8	99	82	101	129	11	8	20	21	Status cell with BN felt separator, LiCl-rich electrolyte, and positive capacity density of 1.40 A-h/cm ³ .
SM8F02 LiAl/FeS 174/120 A-h 1.40 kg	83	97	4	8	98	84	119	241	2	2	9	11	Same as SM8F01.
SM8F03 LiAl/FeS 174/120 A-h 1.38 kg	83	100	4	8	98	84	205	433	4	5	10	4	Same as SM8F01.
SM8F04 LiAl/FeS 174/120 A-h 1.39 kg	82	95	4	8	99	83	68	120	18	16	4	5	Same as SM8F01.
SM8F05 LiAl/FeS 174/120 A-h 1.39 kg	81	97	4	8	99	84	40	82	20	23	0	4	Same as SM8F01.
SM8F06 LiAl/FeS 174/120 A-h 1.40 kg	81	95	4	8	99	83	>176	>328	1	1	0	0	Same as SM8F01.
SM8F07 LiAl/FeS 174/120 A-h 1.39 kg	78	93	4	8	99	83	197	409	2	2	7	6	Same as SM8F01.
SM8F08 LiAl/FeS 174/120 A-h 1.39 kg	82	96	4	8	99	81	179	365	3	2	7	3	Same as SM8F01.

(contd)

Appendix A. (contd)

Cell Number ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline In						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.	
SM8F09 LiAl/FeS 173/119 A-h 1.39 kg	82	98	4	8	99	80	147	290	5	7	8	4	Same as SM8F01.
SM8F10 LiAl/FeS 173/210 A-h 1.40 kg	82	96	4	8	99	81	>198	>376	2	3	0	0	Same as SM8F01.
SM8F11 LiAl/FeS 174/120 A-h 1.39 kg	81	96	4	8	99	83	>118	>228	19	18	0	0	Same as SM8F01.
SM8F12 LiAl/FeS 174/120 A-h 1.39 kg	84	99	4	8	99	84	42	75	8	8	10	10	Same as SM8F01.
M-15 LiAl/FeS 174/88 A-h 1.38 kg	69 60	81 68	4	8	99	83	31	57	4	4	1	1	Status type cell with 1.0 A-h/cm ³ positive theor. cap. density, BN felt separator, and LiCl-rich electrolyte.
M81WA LiAl/FeS 174/120 A-h	70	85	8	8	76	83	9	9	0	0	34	50	Status type cell testing MgO powder in place of BN felt separator. Quick separator wetting with 3.5 mΩ at 50% charge.
M8NoH LiAl/FeS 174/120 A-h 1.32 kg	98 90 82	120 108 93	8 4 2	8 8 8		98 83		88 147	2	2	10	7	Status type cell with all honey-comb structures removed. 82 W-h/kg at c/4 rate; 84 W/kg at 50% charge.

(contd)

Appendix A. (contd)

Cell Number ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline In						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.	
M8NoHP LiAl/FeS 174/120 A-h 1.36 kg	89	110	8	8									Status type cell with no honeycomb structure in positive electrode. 71 W-h/kg at c/4 rate; 85 W/kg at 50% charge.
	82	98	4	8	93	77	>68	>131	0	1	0	2	
	70	79	2	8									
MMP-4 LiAl/FeS 480/344 A-h 4.15 kg	270	331	8	8									Multiplate cell with no honeycomb structures, photochemically etched sheet on all electrode faces, BN felt separator, and two 5" x 7" positive electrodes. 75 W-h/kg at c/4 rate.
	264	312	4	8	98	82	>44	>60	1	1	2	1	
	242	277	2	8									
MNP1 LiAl/FeS 120/120 A-h 1.32 kg	90	108	8	8									Bicell with electrodes of equal theoretical capacity, BN felt separator, LiCl-rich electrolyte, and no honeycomb in negative electrode.
	72	84	4	8	99	83	>5	>7	0	0	0	0	
R-47 LiAl/FeS 210/144 A-h 1.78 kg	90	108	4.5	14.5	100	85	>464	>753	21	22	20	17	Bicell with BN felt separator, LiCl-rich electrolyte and nickel current collector.
R-48 LiAl/FeS 210/144 A-h 1.78 kg	82	100	4.0	10.8	100	88	333	525	3	5.5	2	7	Similar to R-47 but iron collector.
k-51 LiAl/FeS 86/62 A-h 0.95 kg	48	52	4.0	6	99	90	274	690	17	16	5	6	Similar to R-48 but 30% thinner positive electrode.
R-53 LiAl/FeS 143/143 A-h 1.6 kg	74	88	4.0	9.4	99	85	173	386	0	0	2	1	Similar to R-48 but with ANL alloy for collector.
R-54 LiAl/FeS 208/145 A-h 1.68 kg	80	98	4.0	10	99	80	95	124	20	19	20	21	Similar to R-48 but with LiF-LiCl-KCl electrolyte.

(contd)

Appendix A. (contd)

Cell Number ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline In						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.	
R-55 LiAl/FeS-TiS ₂ 210/141 A-h 1.6 kg	80	90	4.0	10	98	84	54	97	22	20	20	19	Similar to R-48 but with TiS ₂ additive in pos.
R-56 LiAl/FeS-TiS ₂ 207/146 A-h 1.75 kg	77	89	4.4	10	97	81	29	25	18	18	31	30	Similar to R-55 but with LiF-LiCl-KCl electrolyte.
R-57 LiAl/FeS 85/66 A-h 1.16 kg	41	50	3.7	5.4	99	84	145	326	0	0	0	0	Similar to R-48 but with 35% thinner pos.
R-58 LiAl/FeS-N 172/122.9 A-h 1.42 kg	65	74	3.3	6.9	96	60	>101	>292	20	22	20	12	Nickel powder additive in pos.
R-59 LiAl/FeS ₂ 167/121 A-h 1.67 kg	103	140	5.2	11	97	74	43	65	13	12	20	20	Positive electrode assembled with Li ₂ FeS ₂ and salt; molybdenum collector.
R-60 LiAl/FeS 145/95.9 A-h 1.41 kg	57	74	3.8	8.1	99	85	112	245	9.5	8.5	19	16	Similar to R-50 but with photo-etched sheet on pos.
R-61 LiAl/FeS 221/140 A-h 1.78 kg	97	115	4.1	9.7	99.5	83	>86	>130	0	0	0	0	Similar to R-48.
R-62 LiAl/FeS 221/140 A-h 1.78 kg	95	113	4.0	10.0	99	84	>72	>110	21	20	25	20	Similar to R-47.

(contd)

Appendix A. (contd)

Cell Number ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	% Decline In		
											A-h Eff.	W-h Eff.	
R-63 LiAl/FeS 97/65.3 A-h 1.19 kg	45	55	4.5	6.0	99	84	>37	>65	0	0	1	0	Similar to R-57.
KK-17 LiAl/FeS 175/115 A-h 1.35 kg	101 81	123 96	10 4	10 8	99	84	>280	>600	16	16	2	2	BN-felt separator test cell with carbon-bonded FeS electrode. Capacity loss due to thermal cycles. Design patterned after Cell KK-15.
KK-18 LiAl/FeS 175/115 A-h 1.35 kg	81	96	4	8	99	84	>63	>120	1	1	0	0	BN-felt separator test cell with carbon-bonded FeS electrode.
SKKF19 LiAl/FeS 175/116 A-h 1.34 kg	100 82	122 97	10 4	10 8	99	84	80	159	-	-	-	-	BN-felt separator test cell operated at Varta in W. Germany. Underwent 12 thermal cycles.
SKKF20 LiAl/FeS 175/115 A-h 1.35 kg	82	97	4	8	99	84	>225	>475	11	11	5	5	BN-felt separator test cell with carbon-bonded FeS electrode.
SKKF21 LiAl/FeS 175/115 A-h 1.35 kg	72	85	4	8	96	80	52	95	0	0	9	9	BN-felt separator test cell with carbon-bonded FeS electrode.
SKKF23 LiAl/FeS 175/117 A-h 1.35 kg	82	96	4	8	99	84	150	283	3	3	10	10	BN-felt separator cell test with carbon-bonded FeS electrode.

(contd)

Appendix A. (contd)

Cell Number ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline In						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.	
EPRE-1 LiAl/FeS 108/97 A-h 1.3 kg	90	108	5	10	>99	86	157	322	24.8	24.1	20	30	Reference electrode bicell. Built with hardware similar to Eagle-Picher multiplate cell with fading capacity on cycling. Furnace malfunction 650°C.
EPRE-2 LiAl/FeS 268/97 A-h 1.3 kg	93	111	5	10	99	85	30	51	0	0	-	-	Similar to EPRE-1 but with twice the capacity in neg.
LC-MP-4 LiAl/FeS 175/116 A-h 1.65 kg	102	129	5	5	99	87	47	124	20	24	34	30	Low-cost cell design for BN felt separator. Two positive carbon-bonded FeS, three LiAl electrodes, and perforated sheet current collectors (30 mil dia, holes at faces). Peak power was 110 W/kg at 50% state of charge and resistance 2.2 Ω.
	100	123	4	5	99	86							
	95	113	2.3	5	99	84							
LC-MP-5 LiAl/FeS 175/116 A-h 1.65 kg	96	119	4	5	99	87	>70	>180	0	0	1	1	Same design as LC-MP-4. Resistance was 1.85 mΩ at 50% S.O.C. for 135 W/kg.
LC-MP-6 LiAl/FeS 275/210 A-h 2.75 kg	162	189	4	8	99	83	>68	>131	2	2	3	3	Similar design to LC-MP-4 but with 5" x 7" electrode plaque obtained from Gould in half-charged state. Feedthrough problems required three thermal cycles. Resistance is 1.55 mΩ at 50% charge.

^aCell description includes cell number, active materials, theoretical capacities of negative and positive electrodes, and cell weight.

^bThe "greater than" symbol indicates continued cell operation.

APPENDIX B.

PERFORMANCE SUMMARY OF EAGLE-PICHER FABRICATED CELLS TESTED AT ANL

Appendix B. Performance Summary of Eagle-Picher Fabricated Cells Tested at ANL

Cell Description ^a	Maximum Performance @ Indicated Rate		Life Characteristics										Remarks
			% Decline In										
	Rates, h		Initial Eff., %		Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.			
	Disch.	Charge	A-h	W-h									
EMP-7-098 LiAl/FeS 430/425 A-h 3.85 kg	206	40	4	8	97	65	13	22	-	-	-	-	NKIA baseline design except LiCl rich electrolyte (no Cu ₂ S). Erratic cell voltage output.
EMP-7-099 LiAl/FeS 430/425 A-h 3.85 kg	348	404	4	8	98	80	92	150	13	13	7	6	NKIA baseline design except LiCl rich electrolyte (no Cu ₂ S). Qualification tested.
EMP-7-100 LiAl/FeS 430/425 A-h 3.85 kg	277	324	4	8	97	79	154	340	6	7	5	5	NKIA baseline design except LiCl rich electrolyte (no Cu ₂ S). Life tested with constant voltage charge.
EMP-7-101 LiAl/FeS 430/425 A-h 3.85 kg	278	330	4	8	98	80	139	301	12	13	8	7	NKIA baseline design except LiCl rich electrolyte (no Cu ₂ S). Life test with constant voltage charge.
EMP-7-180 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	277	327	4	8	100	83	115	285	25	26	7	6	NKIA baseline design.
EMP-7-181 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	274	321	4	8	99	83	85	200	11	11	9	10	Same as above.
EMP-7-182 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	324	381	4	8	98	82	61	115	17	17	5	6	Same as above. Qualification tested.
EMP-7-190 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	283	345	8	8	99	82	41	89	0	0	16	12	NKIA baseline design. Qualification tested.

(contd)

Appendix B. (contd)

Cell Description ^a	Maximum Performance @ Indicated Rate		Life Characteristics											Remarks
			% Decline in											
	A-h	W-h	Rates, h		Initial Eff., %		Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.		
Disch.	Charge	A-h	W-h											
EMP-7-251 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	235	286	3.4	7	99	85	80	189	0	3	6	7	MKIA baseline design.	
EMP-7-253 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	278	339	4	8	98	84	38	80	8	11	7	6	Same as above.	
EMP-7-347 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	279	334	4	8	98	83	27	55	4.6	6.5	6	7	Same as above.	
EMP-7-351 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	279	332	4	8	99	83	43	90	15	15	6	6	Same as above.	
EMP-7-352 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	278	328	4	8	98	82	26	53	10	10	6	4	Same as above.	
EMP-7-355 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	278	340	4	8	98	84	34	71	0	3	10	9	Same as above.	
EMP-7-364 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	277	340	4	8	99	85	32	68	0	4	9	11	Same as above.	
EMP-7-379 LiAl/FeS-Cu ₂ S 430/425 A-h 3.85 kg	278	331	4	8	99	84	27	59	8	10	6	6	Same as above.	

(contd)

Appendix B. (contd)

Cell Description ^a	Maximum Performance @ Indicated Rate		Life Characteristics										Remarks	
	A-h	W-h	Rates, h		Initial Eff., %		% Decline In							
			Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.		
EMP-7-389 LiAl/FeS 430/425 A-h 3.8 kg	278	338	4	7	99	85	35	80	15	18	10	10	NKIA baseline design.	
EMP-7-395 LiAl/FeS 430/425 A-h 3.8 kg	278	339	4	7	100	86	30	65	5	5	10	10	Same as above.	
EMP-7-417 LiAl/FeS 430/425 A-h 3.8 kg	278	335	4	7	99	84	41	95	18	20	8	9	Same as above.	
EMP-7-418 LiAl/FeS 430/425 A-h 3.8 kg	278	338	4	7	99	85	34	80	8	11	6	6	Same as above.	
EMP-7-423 LiAl/FeS 430/425 A-h 3.8 kg	235	290	3.5	6	99	85	51	124	0	2	6	6	Same as above.	
EMP-7-425 LiAl/FeS 430/425 A-h 3.8 kg	284	344	4	7	99	85	38	54	10	14	5	7	Same as above.	
EPMKII-009 LiAl/FeS 406/405 A-h 4.7 kg	307	362	4	6	99	84	15	35	76	32	5	4	Similar to NKIA design but with BN felt separator (instead of BN fabric).	
EPMKII-021 LiAl/FeS 406/405 A-h 5.0 kg	321	376	4.5	8	99	82	>81	>137	6	6	5	4	Initial Eagle-Picher MKII cell design using 1-2mm layer of BN felt separator.	

(contd)

Appendix B. (contd)

Cell Description ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline in						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.	
EPMK11-032 LiAl/FeS 480/360 A-h 4.8 kg	310	370	4	7	100	84	>92	>191	7.7	7.8	2.0	2.4	Eagle-Picher MK11 multiplate cell design for BN felt separator (2 mm layers), LiAl and FeS cold-pressed electrodes, LiCl-rich electrolyte, photo-etched screens on electrode faces.
EPMK11-033 LiAl/FeS 480/360 A-h 4.8 kg	295	348	4	7	100	84	>89	>194	10.9	10.1	0	1.2	Same as above.
EPMK11-036 LiAl/FeS 480/360 A-h 4.8 kg	243	293	3.5	7	100	85	>64	>160	0	0	0	0	Same as above.
EPMK11-037 LiAl/FeS 480/360 A-h 4.8 kg	288	342	4	7	99	82	>65	>145	3.1	3.2	0	0	Same as above.
EPMK11-038 LiAl/FeS 480/360 A-h 4.8 kg	243	293	3.5	7	100	84	>64	>140	0	1.0	1.0	0	Same as above.
EPMK11-039 LiAl/FeS 480/360 A-h 4.8 kg	266	316	4	7	100	83	>65	>176	0.8	1.3	0	0	Same as above.

(contd)

Appendix B. (contd)

Cell Description ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline In						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^b	Cycles ^b	Capacity	Energy	A-h Eff.	W-h Eff.	
EPMKII-040 LiAl/FeS 480/360 A-h 4.8 kg	270	318	4	7	100	83	>64	>117	2.2	3.2	1.0	0	Eagle-Picher MKII multiplate cell design for BN felt separator, (two 2mm layers) LiAl and FeS cold-pressed electrodes, LiCl-rich electrolyte, photo-etched electrode faces.
EPMKII-041 LiAl/FeS 480/360 A-h 4.8 kg	281	345	4	7	100	84	>59	>128	1.1	3.8	0	0	Same as above.
EPMKII-042 LiAl/FeS 480/360 A-h 4.8 kg	268	317	4	7	100	84	>53	>80	17.9	19.2	0	2.4	Same as above.
EPMKII-043 LiAl/FeS 480/360 A-h 4.8 kg	303	365	4	7	100	86	>43	>96	16.8	18.4	0	2.3	Same as above.
EPMKII-049 LiAl/FeS 480/360 A-h 4.8 kg	306	368	4	7	100	85	>26	>49	2.0	3.3	1.0	3.4	Same as above.

^aCell description includes cell number, active materials in electrodes, theoretical capacity, and cell weight.

^bThe "greater than" symbol denotes continued operation.

APPENDIX C.

PERFORMANCE SUMMARY OF GOULD-FABRICATED CELLS TESTED AT ANL

Appendix C. Performance Summary of Li-Al/FeS Gould Cells Tested at ANL

Cell Number ^a	Maximum Performance @ Indicated Rate		Rates, h		Initial Eff., %		Life Characteristics						Remarks
							% Decline In						
	A-h	W-h	Disch.	Charge	A-h	W-h	Days ^a	Cycles ^a	Capacity	Energy	A-h Eff.	W-h Eff.	
C-2	74	87	4	4	99	76	350	1170	45	45	7	4	Gould baseline bicell with BN cloth separator and Ni current collector. Poor capacity.
C-3	110	130	7.4	7.4	99	—	317	1140	80	80	0	0	Same basic design as C-2. Terminated for corrosion evaluation.
C-7	103	125	6.9	6.9	>99	>83	400	800	50	50	—	—	Gould baseline bicell design. Hastalloy B collector with positive additives of Fe, Co, C.
D-8	143	173	6	7	99	84.5	17	24	—	—	50	50	Multiplate cell with BN felt separator. Initial attempt at new design. Cold-pressed FeS and LiAl electrodes assembled in semi-charged state.
D-9	169	205	7	8.5	99	85	15	21	0	0	—	—	Multiplate cell with BN felt separator. Cold-pressed FeS and LiAl electrodes in 1/2 charged state.
D-12	167	202	3.6	6.8	100	86	52	106	3	3	0	0	Gould MKII (BN felt separator) design. Dry-room fabricated in half-charge state.
D-24	170	208	4.3	8.7	99	87	>40	>75	5	5	0	0	Gould MKII design with two positive plates.
D-25	162	197	3.6	7.4	99	86	>38	>66	3	3	0	0	Gould MKII design. Capacity increased when temp. raised to 485°C. 100 W/kg at 50% charge.
D-26	178	216	4.5	9.0	98	86	>46	>81	6	6	0	0	Gould MKII design.
D-27	172	210	4.3	8.6	100	88	>42	>80	6	6	0	0	Gould MKII design.
D-28	127	151	3.2	6.4	100	85	5	7	—	—	—	—	Gould MKII design.

(contd)

Appendix C. (contd)

Cell Number ^a	Maximum Performance @ Indicated Rate		Life Characteristics										Remarks
			% Decline In										
	Rates, h		Initial Eff., %		Days ^a	Cycles ^a	Capacity	Energy	A-h Eff.	W-h Eff.			
											Disch.	Charge	
D-29	127	151	3.2	6.4	100	85	>47	>123	10	9	0	0	Gould MKII design. Terminated due to low capacity.
D-30	172	210	4.3	8.7	100	88	>42	>79	12	12	0	0	Gould MKII design.
D-31	165	201	4.2	8.3	100	88	>42	>81	5	5	1	0	Gould MKII design.
D-36	-	-	-	-	-	-	3	3	-	-	-	-	Gould MKII design.
D-42	177	218	4.4	8.7	99	87	>20	>33	3	3	0	0	Gould MKII design.

^aThe greater than symbol (">") denotes continued cell operation.

APPENDIX D.

SUMMARY OF POST-TEST EXAMINATIONS OF MULTIPLATE CELLS

Appendix D. Summary of Post-Test Examinations of Multiplate Cells

Cell Description ^a	Lifetime		Reasons Terminated	Comments
	Cycles	Days		
EPMP-7-028 LiAl/FeS-Cu ₂ S, E, C	78	47	Short circuit	Short circuit was caused by extrusion of positive electrode at the edges.
EPMP-7-106 LiAl/FeS-Cu ₂ S, E, C	245	116	Short circuit	Short circuit was caused by extrusion of positive electrode at edges. The electrodes were uniform in thickness except at the edges.
EPMP-7-190 LiAl/FeS-Cu ₂ S, E, C	89	41	Short circuit	No short located. Cell as-received had a cold resistance >2000 ohms. The electrodes were uniform in thickness.
EPMP-7-253 LiAl/FeS, C	80	38	Short circuit	All failure was due to a short circuit in the feedthrough. The electrodes were uniform in thickness.
EPMP-7-364 LiAl/FeS-Cu ₂ S, C	68	32	Short circuit	Short circuit was caused by extrusion of positive electrodes at edges. The electrodes were uniform in thickness except at the edges.
EPMP-7-388 LiAl/FeS-Cu ₂ S, C	96	71	Short circuit	Short circuit was caused by extrusion of positive electrodes at edges. The electrodes were uniform in thickness.
GLER D-13 LiAl/FeS, LR, SC	7	3	Low cold resistance	This cell was operated for the seven break-in cycles only. The short was located in the bottom corner of the cell; exact cause of short circuit was not identified. Thickness of the electrodes was very uniform. The negative electrode (center) showed 80% expansion in thickness. LiAlO ₂ observed on the face of each negative electrode.
GLER D-15 LiAl/FeS, LR, SC	13	7	Declining A-h	The short circuit was located at the edge about 2 in. below the top of the electrodes; the exact cause of the short circuit was not identified. The negative electrode showed about 100% expansion in thickness. Large quantities of LiAlO ₂ were present on the face of each negative electrode.
EMP-DC-5 LiAl/FeS-Cu ₂ S, C	59	31	Short circuit	Short circuit was caused by a furnace-controller malfunction which allowed cell to overheat.
EPMP-7-193 LiAl/FeS-Cu ₂ S, E	b	b	Short circuit	This cell was purposely heated to failure (850°C). Iron dendrites were in positive electrode and in separator. Current collectors were completely corroded. No Al detected in positive electrode. No Li ₂ S or Al ₂ S ₃ detected in negative electrode.

(contd)

Appendix D. (contd)

Cell Description ^a	Lifetime		Reasons Terminated	Comments
	Cycles	Days		
EPM-001FBX LiAl/FeS-Cu ₂ S, E	77	b	Short circuit	Short circuit was caused by extrusion of positive active material through screen rupture. Electrode expansion was about 20% in the negative and about 50% in the positive.
EPMK-002 LiAl/FeS, LR	18	b	Short circuit	Cause for short circuit was not identified. Cell was overheated during the electrolyte filling operation.
EPMK-003 LiAl/FeS, LR			Short circuit	Short circuit was caused by the honeycomb current collectors cutting the separator at the cell top where the electrodes were misaligned and distorted.
EPMK-005 LiAl/FeS, LR	52	b	Declining A-h efficiency	Many locations throughout the separator were deficient in electrolyte. The edges of the negative electrodes (to a depth of over 0.25 in.) were made up of a very fine nonmetallic material. These areas were dull gray in appearance in contrast to the bright metallic color normally seen in the LiAl electrode. Other negative electrodes which were prepared and stored in an inadequately pure atmosphere have shown a similar appearance.
EPMK-007 LiAl/FeS, LR	53	b	Short circuit	Short circuit was caused by extrusion of active material through ruptured screens at the edges of the electrodes.
EPMK-008 LiAl/FeS, LR	4	b	Short circuit	Short circuit was caused by extrusion of active material through a ruptured screen.
EPMK-010 LiAl/FeS, LR	2	b	Low capacity	The low capacity problem of this cell appears to have been due a severe deficiency of electrolyte in the separator. A solid electrolyte plug was observed in the electrolyte fill tube even through the top area of the cell was void of electrolyte.
EPMK-015 LiAl/FeS, LR	93	b	Short circuit	This cell contained two short circuits; 1) feedthrough, 2) extrusion of active material from negative electrode through rupture at defective weld in photo-etched screen to electrode outer frame. Center negative electrode expansion was about 35%.
EPMK-016 LiAl/FeS, LR	0	0	Short circuit	Short circuit was caused by metallic Al deposits across separators which had been treated with LiAlCl ₄ wetting agent. Condition indicated excessive LiAlCl ₄ was used.

(contd)

Appendix D. (contd)

Cell Description ^a	Lifetime		Reasons Terminated	Comments
	Cycles	Days		
EPMK-022 LiAl/FeS, LR	0	0	Short circuit	Same as EPMK-016.
GLER D-8 LiAl/FeS, LR, SC	23	16	Declining A-h efficiency	Short circuits were caused by extrusion of unrestrained negative electrodes and a crimp in positive electrode screen that cut separator. Negative electrode expansion was 73 to 93%. The positive electrodes showed a 9% expansion to 19% compression.
LC-MP-4 LiAl/FeS-C, LR	125	50	Declining A-h efficiency	Short circuit was caused by extrusion of positive electrodes at edges. The negative electrodes exhibited gross expansion, whereas the positive electrodes were compressed. The electrodes were non-uniform in thickness (wavy).

^aCell description includes cell number, active materials for negative and positive electrodes, type of electrolyte (E = LiCl-KCl eutectic; LR = LiCl-rich LiCl-KCl), and state of charge at cell assembly (C = charged; U = uncharged; SC = semicharged).

^bData not available at present.

APPENDIX E.

SUMMARY OF POST-TEST EXAMINATIONS OF BICELLS

Appendix E. Summary of Post-Test Examinations of Bicells

Cell Description ^a	Lifetime		Reasons Terminated	Comments
	Cycles	Days		
R-43 LiAl/FeS, U, LR	240	128	End of Test	Feedthrough was isolated on 5th cycle because of short circuit. Cell was then operated to end of scheduled test. Separator was two layers of BN treated with LiAlCl ₄ wetting agent. Separator was clean except for normal Fe deposits near positive electrode.
R-36 LiAl/NiS ₂ +Co ₂ S ₃ , U, E	1318	506	End of Test	A short circuit was identified at cell bottom where the current collector of the positive electrode had cut through the BN fabric separator; Li ₂ S was deposited in separator.
LC-1 LiAl/FeS+C, LR	176	99	Short circuit	Short circuit was caused by re-welding a defect in the cell can. The Li-Al in the rear position of the electrode was unreacted. Negative-electrode expansion was approximately 25%.
LC-2 LiAl/FeS+C, LR	95	55	Declining A-h efficiency	Separator was one layer of 2-mm thick BN felt. Short circuit was caused by compression of BN felt to 1/2-mm thick and the normal iron deposits near positive electrode. Negative electrode expansion was approximately 15%.
LC-3 LiAl/FeS+C, LR	150	66	Short circuit	Short circuit was caused by corrosion products that bridged the separator at the top of the cell. Electrode expansion was about 30% for the negative and about 55% for the positive electrode.
EPRE-1 LiAl/FeS+Cu ₂ S, E	322	132	Short circuit	This was a reference-electrode test cell that failed because of over-heating to about 650°C, which resulted in a short circuit.
GLER Q-3 LiAl/FeS, SC, LR	265	81	Short circuit	Short circuit was caused by expansion of negative electrode and compression of positive which caused metal strip around the positive electrode to cut the BN felt separator. The electrodes were non-uniform in thickness--10 to 60% expansion in the negative electrodes and 40% compression to 25% expansion in the positive electrodes.
GLER Q-4 LiAl/FeS, SC, LR	177	67	Short circuit	Cause of the short circuit was same as Q-3. The electrodes were non-uniform in thickness (wavy). Negative expansion was 10 to 55%. Positive electrodes varied from about 20% compression to 20% expansion.
GLER Q-6 LiAl/FeS, SC, LR	175	60	Short circuit	Short circuit was caused by extrusion of positive electrode material through ruptures in retainer screens at edges. The electrodes were non-uniform in thickness (wavy). Negative electrode expansion was 40 to 110%. Positive electrodes showed 20% expansion to 15% compression.
GLER Q-8 LiAl/FeS, SC, LR	247	80	Short circuit	Cause of short circuit same as Q-6. The electrodes exhibited moderate non-uniformity in thickness (wavy). Negative electrode expansion was 30 to 85%. Positive electrode showed 10% compression to 45% expansion.

(contd)

Appendix E. (contd)

Cell Description ^a	Lifetime		Reasons Terminated	Comments
	Cycles	Days		
GLER Q-9 LiAl/FeS, SC, LR	235	72	Short circuit	Cause of short circuit same as Q-6. The electrodes exhibited minor non-uniformity in thickness. Negative electrode expansion was 10 to 50%. Positive electrode showed 15 to 40% expansion.
GLER C-1 LiAl/FeS, U, LR	242	153	Short circuit	Short circuit was caused by extrusion of positive electrode material through ruptured screen at edge. Electrode thickness was non-uniform (wavy). Negative electrode expansion was 50 to 100%. Positive electrode was compressed by 10 to 35%.
GLER C-4 LiAl/FeS, U, LR	10	4	Short circuit	Cell failure was caused by short circuit in feedthrough.
GLER C-4A LiAl/FeS, U, LR	367	62	Declining A-h efficiency	Cause of short circuit was not identified. Cold resistance was 400 Ω as received for post-test examination. Cell showed poor A-h efficiency.
GLER C-8 LiAl/FeS, U, LR	45	23	Declining A-h efficiency	Same as cell C-4A.
GLER C-10A LiAl/FeS, U, LR	303	201	Short circuit	Short circuit was caused by gross irregular expansion and distortion of electrodes, which caused the retainer screens and BN fabric to rupture. This permitted extrusion of active material.
R-48 LiAl/FeS+C+Ni, U, LR	525	333	Short circuit	Short circuit was not identified. However, it was borated in the top 2 cm of this cell within 2 cm of the conductor rod. Low carbon steel positive electrode current collector showed a corrosion rate of 23 $\mu\text{m}/\text{yr}$. Lower-than-normal corrosion rate may have been influenced by the nickel powder addition which increased the metal-to-sulfur ratio within the electrode. Positive electrode showed both severe expansion and compression. One area of the negative electrode showed about 100% expansion.
M-8IWA LiAl/FeS, C, LR	9	8	Short circuit	Cell was operated to evaluate the use of a new form of MgO powder separator. Examination showed that most of the fine MgO powder had migrated out of the separator zone. This permitted direct contact of the electrodes and multiple short circuits.
R-50 LiAl/FeS+Ni+C U, LR	326	174	Short circuit	Short circuit was caused by extrusion of positive electrode material at the top of the cell. The addition of nickel powder may have contributed to the lower-than-normal corrosion rate of the nickel positive-electrode current collector. Electrode thickness was uniform; expansion was moderate (<25%).

(contd)

Appendix E. (contd)

Cell Description ^a	Lifetime		Reasons Terminated	Comments
	Cycles	Days		
R-52 LiAl/FeS+Ni+C, U, LR	57	26	Short circuit	The short circuit was caused by a defect or rupture in the BN felt separator. This cell used a 2-mm thick single layer for the separator. In the area of the short circuit, the felt was <0.1 mm thick; elsewhere, the separator was 1 mm thick.
R-56 LiAl/FeS+TiS ₂ +C, U, LR	20	30	Short circuit	Multiple short circuits were present throughout this cell and metallographic examination showed them to be due to the presence of a very large amount of Ti-S crystals throughout the entire separator thickness.
GLER Q-7 LiAl/FeS, SC, LR	552	132	Declining Coulombic Efficiency	The short circuit was caused by extrusion of positive electrode material through ruptured screen at edge. The negative electrode showed about 100% expansion. Positive electrode showed no expansion. The electrodes showed some waviness.
GLER X-54 LiAl/FeS, SC, LR	11	8	Short circuit	Cell failure was caused by a short circuit in the feedthrough. LiAlO ₂ was observed on the front face of negative electrodes. Expansion of negative electrodes was 50-65%. Positive electrode showed 14% expansion.
KK-16 Li-Al-Fe/FeS, C	b	b	Short circuit	Short circuit caused by overheating due to furnace failure.
R-59 LiAl/FeS ₂ , U, E	65	43	Declining A-h Efficiency	Short circuit was caused by multiple penetrations of positive material through the separator. This occurred because the stainless steel retainer screen was totally corroded and thus did not contain the positive electrode material. Li ₂ S(Fe) deposits were observed in the separator. This is typical of FeS ₂ cells.
R-53-2 LiAl/FeS, U, LR	386	172	Low capacity	Although the separator was severely compressed (0.6 mm thick) and was penetrated by positive electrode material, no evidence of a short circuit was found in this cell. The low capacity was apparently caused by an electrolyte deficiency in the positive electrode.

^aCell description includes cell number, active materials for negative and positive electrodes, state of charge at cell assembly (C = charged; U = uncharged; and SC = semicharged), and type of electrolyte (E = eutectic LiCl-KCl; LR = LiCl-rich LiCl-KCl).

^bData not available at present.