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**HIGH-PERFORMANCE BATTERIES FOR
OFF-PEAK ENERGY STORAGE AND
ELECTRIC-VEHICLE PROPULSION**

**Progress Report for the Period
January—June 1975**

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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HIGH-PERFORMANCE BATTERIES FOR OFF-PEAK ENERGY STORAGE AND ELECTRIC-VEHICLE PROPULSION

January-June 1975

ABSTRACT

This report describes the research and management efforts, for the period January-June 1975, of Argonne National Laboratory's program on high-performance lithium/metal sulfide batteries. The batteries are being developed for two applications: off-peak energy storage in electric utility networks and electric-vehicle propulsion. The battery design for the two applications differ, particularly in cell configuration and electrode design, because of the differing performance requirements. The present cells are vertically oriented, prismatic cells with two negative electrodes of a solid lithium-aluminum alloy, a central positive electrode of iron sulfide (FeS_2 or FeS), and an electrolyte of LiCl-KCl eutectic (mp, 352°C). The operating temperature of the cells is about $400\text{--}450^\circ\text{C}$.

Recent effort in the development of engineering-scale cells has been focused on designing and fabricating vertically oriented, prismatic cells and on improving the lifetime capabilities of cells. Work on electrode development has been directed toward the evaluation of the factors that influence the performance of the negative electrode and the development of new designs of vertical, prismatic iron sulfide electrodes. Materials studies have included work on improving feedthroughs and separators, corrosion tests of candidate materials of construction, and postoperative examinations of cells. Cell chemistry studies have included continuing investigations of cell reactions and the identification of advanced cell systems. Battery development work has included the design of a battery for an electric automobile and the development of battery components. The transfer of Li-Al/FeS_x battery technology to industry is being implemented through contracts with industrial firms for the manufacture of components, electrodes, and cells.

SUMMARY

Cell Development

Engineering-Scale Cells. The effort in this part of the program is directed primarily toward the development of engineering-scale, sealed Li-Al/ iron sulfide cells capable of meeting the requirements for off-peak energy storage and electric automobile propulsion. In previous work, compact, lightweight cells (150 A-hr capacity) with impressive specific energies (up to 150 W-hr/kg) were developed. Recent work has been concentrated on improving the life of these cells and on the design, construction, and testing of more advanced cells.

The first generation of engineering-scale cells (represented by the W-series cells) are cylindrical, with top and bottom negative electrodes of Li-Al alloy and a central iron sulfide (FeS_2 or FeS) electrode; they are operated in a horizontal position. The second generation cells are vertically oriented, prismatic cells (13 by 13 cm, 2 to 4 cm thick) and, like the earlier cells, have a central iron sulfide electrode and two outer Li-Al electrodes.

Cell R-1 ($\text{Li-Al/FeS}_2\text{-CoS}_2$), the first engineering-scale, sealed prismatic cell was operated for more than 47 cycles and 900 hr. The cell achieved a fairly high specific energy and featured a hot-pressed positive electrode. Of the cylindrical, horizontal cells, Cell W-8 ($\text{Li-Al/FeS-Cu}_2\text{S}$) proved to be the most durable and maintained a high degree of stability for more than 3700 hr and 121 cycles. Cell W-9 (Li-Al/FeS_2) was designed to sustain high power discharges on the upper voltage plateau ($\text{FeS}_2 \rightarrow \text{FeS}$), and thus had electrodes of unmatched capacity (sulfur capacity, 204 A-hr; lithium capacity, 112 A-hr). Cell W-9 performed well on a metropolitan driving profile in a comparative test with a lead-acid battery.

Cell W-10 was constructed to test the use of an FeS_2 electrode with a cobalt sulfide additive. Cell W-11 was also built to test the cobalt sulfide additive, as well as a new cell fabrication technique, in which multiple folds of BN and ZrO_2 fabrics were eliminated through the use of a design employing concentric hoops. Cells W-12 and W-14 were designed as thin-electrode, high-specific-power cells and were tested under driving profile loads as part of the Department of Transportation program; both cells were designed for operation on the upper voltage plateau ($\text{FeS}_2 \rightarrow \text{FeS}$). Cell W-13 was a test of a hot-pressed FeS electrode and pyrometallurgically prepared Li-Al electrode in a compact cell; the electrodes had matched capacities of 100 A-hr.

Supporting Studies. The FeS electrode offers several advantages over the FeS_2 electrode but also has certain performance limitations. It is believed that the performance of the FeS electrode can be improved, and several methods of accomplishing this are being tested. The addition of other metal sulfides is being evaluated, and copper sulfide has produced improved sulfur utilizations, in a similar manner to the addition of cobalt sulfide to FeS_2 . Another method being tested to improve the performance of the FeS electrode is the use of molten-salt electrolytes containing only lithium ions, instead of the LiCl-KCl eutectic. The elimination of potassium prevents the formation of a K-Li-Fe-S compound, which contributes significantly to excessive swelling of FeS electrodes.

Other supporting cell development work is concerned with the continuing measurements of volumetric changes in particle bed electrodes during the first electrochemical discharge. The data derived from these experiments will be useful in (1) determining the active material loading for optimum electrical performance, (2) evaluating new electrochemical additives and electrolytes, and (3) delineating the chemical phase changes, which are manifested as abrupt volumetric changes during discharge.

Electrode Development

Development of Negative Electrodes. Investigations are presently being conducted to identify the parameters that limit the performance of solid Li-Al electrodes. Studies are being conducted in Li/LiCl-KCl/Li-Al cells to determine the effect on electrode performance of volume fraction of electrolyte in the electrode, electrode thickness, and fabrication technique. The results obtained to date on electrochemically prepared Li-Al electrodes indicate that 1) the optimum volume fraction of electrolyte at full charge is near 0.2, 2) the optimum thickness of the electrode is a function of the charge and discharge rates but will probably be about 0.3 to 0.7 cm, and 3) the incorporation of a porous iron current collector into thicker electrodes (~ 0.8 cm) should improve the performance of a Li-Al/LiCl-KCl/FeS₂ cell, except at high charge rates.

Studies are also under way to identify the factors that limit the cycle life of the present Li-Al electrodes (the goal is about 1,000 cycles). The effect of electrolyte purity on cycle life is being examined first. Cell LT-1 (Li-Al/Al) utilizes the high-purity, polarographic-grade LiCl-KCl electrolyte from Anderson Physics Laboratory, which is being used in most of the cell studies at ANL. The data from Cell LT-1 will be used as a baseline to evaluate other, less expensive sources of LiCl-KCl electrolyte. Cell LT-1 has been operated for 60 cycles and 1278 hr at a current density of 0.078 A/cm². The lithium utilization is 82% and appears to be gradually improving.

Solid lithium alloys other than lithium-aluminum are being evaluated as possible alternative materials for the negative electrodes of lithium/metal sulfide cells. Investigations of a lithium-boron alloy were described previously. In a continuation of these studies, silicon, AlB₂, SiB₄ and Al-50 wt % Si were evaluated as base materials from which suitable solid-lithium alloys could be electrochemically formed. The results of these investigations indicate that all these materials except SiB₄ can be electrochemically converted to a lithium-metal alloy. However, only the lithium-silicon system seems to be worthy of further study. This system has a theoretical capacity density that is much greater than that of the Li-Al system; the achievable capacity density is also higher at low current densities (0.032 A/cm²), but a rapid decrease occurs as the current density is increased. Further work is needed to improve the lithium-loading properties of the Li-Si system during electrode charging and to characterize the reactions that occur in this system during cell operation.

Particulate Loading of Porous Current Collector Structures. Some of the present electrode designs for vertical, prismatic cells include porous current collector structures vibratorily loaded with electrochemically active materials. The preparation of such electrodes will require suitable loading techniques to insure uniformity of the electrodes not only during fabrication but also during subsequent transport of cells and batteries.

The loading requirements in terms of volume fraction of active material in the porous matrix vary considerably: from 0.60 to 0.80 for Li-Al, from 0.31 to 0.41 for discharged Li-Al (*i.e.*, Al metal); from 0.25 to 0.35 for FeS, and from 0.25 to 0.30 for FeS₂. Results of preliminary studies have indicated that the loading requirements for Li-Al and Al in iron Retimet can be achieved,

but that the physical properties of the FeS and FeS₂ powders are not suitable for obtaining the desired loading. Tests are now under way to examine the loading properties of FeS or FeS₂ blended with powdered LiCl-KCl eutectic.

Development of Positive Electrodes. In this part of the program, recent efforts have emphasized the development of vertical, prismatic electrodes that are suitable for manufacture. Current collector materials and fabrication techniques are being evaluated as part of this effort. Iron sheet/screen structures as well as porous iron have been used as current collectors in FeS electrodes, whereas vitreous carbon foam and composite structures of vitreous carbon foam and molybdenum sheet have been used as current collectors in FeS₂ electrodes. Fabrication techniques have included hot-pressing of FeS and electrolyte for the FeS electrodes, and vibratory compaction of FeS₂ powders for the FeS₂ electrodes.

Initial scale-up efforts have been quite successful for electrodes in which the active materials are vibratorily compacted in porous current collector structures. Two vertical, rectangular cells (S-80 and S-81) have been operated. Each cell has one positive electrode and two outer negative electrodes, and electrode areas of about 200 cm². A major change in cell design is the use of two separate compartments in the positive electrode. The objective of this design change is to prevent electrode mismatch, which might occur if the cell resistance between one negative electrode and the positive electrode is slightly less than that between the other negative and positive electrode. These two cells (S-80 and S-81) are presently operating satisfactorily, and measurements of their performance characteristics at various charge and discharge rates are continuing.

Cell S-77, a Li-Al/FeS₂ cell of 46.5 cm² electrode area, has a vitreous carbon foam current collector in the positive electrode and a porous iron current collector in the negative electrode. This cell has been operated for over 3546 hr and 156 cycles at the 11 hr rate (0.075 A/cm²). The cell has not shown a decrease in performance nor a decline in ampere-hour efficiency over this long operating period. The maximum lithium utilization is 80.5%. This performance is sufficient to meet the goals for the off-peak energy storage battery.

Cell PR-1, the first prismatic Li-Al/FeS cell, was tested for 1400 hr and 88 cycles. This cell had a vertical hot-pressed FeS electrode (0.6 cm thick, 58 A-hr capacity) centered between two Li-Al electrodes. The overall performance of the cell was excellent. There was no apparent settling or slumping of the positive electrode material, which is of principal concern in the design of the vertical electrodes. However, as previously observed in horizontal, cylindrical cells, swelling of the electrodes (particularly the positive electrode) occurred. Methods of minimizing electrode swelling continue to be sought.

A study was conducted to evaluate potential coating material for metal current collectors in FeS₂ electrodes. Of the coating materials investigated, TiN, TiC, Nb₂C, TaC, and FeB are particularly promising. Evaluation of these coating materials is being conducted in Li-Al/FeS₂ cells under normal discharge-charge cycling tests. Preliminary results indicated that the TiN coating on an iron substrate is stable, but a denser coating is needed. A

good quality FeB coating was obtained on a Type 304 stainless steel substrate by electrolytic deposition of boron in a molten salt bath of BaCl_2 - NaCl - $\text{Na}_2\text{B}_4\text{O}_7$ - B_4C at 900°C . An FeB-coated current collector is presently being tested in a Li-Al/ FeS_2 cell.

A study is also under way to evaluate metal sulfides as possible additives for improving the performance of FeS_2 electrodes. FeS_2 electrodes containing 15 at. % Ce_2S_3 , MnS , NiS , CoS_2 , Cr_2S_3 , V_2S_3 , ZnS , CdS , TiS_2 , and CaS , were evaluated in Li-Al/ FeS_2 cells at various current densities and temperatures. Of the additives studied, Ce_2S_3 , MnS , NiS , and CoS_2 were particularly beneficial in improving sulfur utilization.

Materials Testing and Fabrication

The effort in the materials program is directed toward the development of fabrication methods for cell components, corrosion testing of candidate materials for these components, and postoperative examination of cells to evaluate the behavior of the various construction materials as well as the lithium-aluminum and metal sulfide electrodes.

Electrical Feedthrough Development. Two types of electrical feedthroughs are currently under development: a mechanical compression type and a brazed or bonded type. A compression feedthrough, which is very similar to the Conax feedthrough used successfully in engineering-scale cells, has been designed. The new design is expected to effect cost and weight reductions and to simplify the assembly procedure; the performance is expected to be about the same as that of the Conax feedthrough. Insulators of Y_2O_3 , BeO , AlN , $\text{SiC}\cdot\text{AlN}$, and $\text{SiC}\cdot 2\text{AlN}$ are being developed as replacements for the intrinsically weak lower BN insulator presently used.

Brazed-type feedthroughs are being fabricated to our specifications by ILC Technology for testing and evaluation. The insulators are Al_2O_3 and BeO and the brazes are niobium-base alloys. Also, a ram- or crunch-type feedthrough is being fabricated to our specifications by Ceramaseal, Inc. for testing and evaluation. In this design, a metal sleeve is forced over a ceramic insulator. The advantages are simplicity, compactness, absence of a braze, and the use of a stable low-cost ceramic that is not easily brazed (e.g., AlN).

Ceramic Insulator Development. A slip-casting process for fabricating upper insulators of Al_2O_3 for the compression feedthroughs has been developed and insulators are being routinely fabricated. However, attempts to prepare lower insulators of Y_2O_3 by this process have been unsuccessful, presumably because the powder tends to hydrate. Isostatic pressing techniques have been used successfully to fabricate these insulators. Efforts are being continued to refine the fabrication process and to optimize the mechanical properties of the insulators.

Electrode Separators. Porous ceramic papers of boron nitride fibers are being developed by the Carborundum Co. (under contract with ANL) to replace the costly, woven BN fabric separators. Samples of BN paper separators have been received. These materials are presently being evaluated in in-cell tests to determine compatibility and electrical performance. The initial results have been encouraging.

Lithium-Aluminum Phase Diagram Studies. The phase relationships of the lithium-aluminum alloy system are being investigated to aid in optimizing the cell performance. Differential thermal analysis, as well as metallographic, X-ray, and chemical techniques are being employed to develop a revised phase diagram; a tentative version is included in this report. An important feature is the determination of a peritectic reaction isotherm at 330°C that limits the lithium concentration at which the alloy remains solid, at cell operating temperatures, to less than 60 at.%. Work is continuing to elucidate the aluminum-rich portion of the diagram.

Corrosion Studies. Corrosion tests of the planned-interval type were conducted on molybdenum-bearing alloys to determine their resistance to attack in a mixture of FeS_2 and electrolyte. The alloys tested were: 1) Hastelloy B (Ni-28 Mo-1 Cr-5 Fe), 2) Hastelloy C (Ni-17 Mo-16 Cr-5 Fe), 3) Fe-2.6 Mo, 4) Fe-5.8 Mo, and 5) Fe-30.1 Mo. The respective corrosion rates, measured for 750 hr of exposure at 400°C, were 76, 142, 1160, 602 and 1100 $\mu\text{m}/\text{yr}$. Previous results obtained for molybdenum and iron were <10 and 3700 $\mu\text{m}/\text{yr}$, respectively. Any of the alloys tested, even the low-cost Fe-5.8 Mo, would have a corrosion resistance superior to that of iron in FeS electrodes; iron current collectors have been used successfully in FeS type cells for more than 5 months.

Corrosion tests of candidate materials for cell housings *e.g.*, iron, nickel, AISI-1008, and Types 304 and 316 stainless steel have shown negligible attack when exposed to a 50 vol % mixture of Li-Al alloy and LiCl-KCl eutectic at 400 and 500°C. However, extensive reaction is observed when a galvanic couple is established between aluminum (discharged negative electrode) and iron in the LiCl-KCl eutectic at 500°C. The reaction rate is much lower at 400°C. Metallographic examination has shown that the morphology of the reaction product formed on the iron sample is identical to that observed in postoperative examinations of cells.

Postoperative Examinations of Cells. A large number of test cells operated to evaluate a variety of parameters have been sectioned and examined. The results of the postoperative examination are presented. In addition to the test cells, postoperative examinations were conducted on engineering-scale Cells W-8, W-9, W-12, and PR-1.

The postoperative examinations of Cells W-8 and PR-1 showed extensive reaction of the low carbon steel (AISI-1008) housing. Electron microprobe analysis identified the reaction product as an iron-aluminum intermetallic compound (probably FeAl_3 or FeAl_2). Both cells were operated at or above 500°C for some period of time during their lifetimes; reaction with the cell housing has not been observed in cells operated below 450°C.

The first evidence of a reaction with the molybdenum current collector was found in the examination of Cell W-9. X-ray diffraction analysis indicated the reaction product to be MoS_2 . The electrical feedthrough was examined and found to be in good condition. Volume-fraction analysis (using metallographic techniques) of the negative electrodes yielded values ranging from 81 to 26 vol % Li-Al alloy. These results illustrate the nonuniformity that can occur in the distribution of active material within the electrode.

Cell W-12 was physically constrained to prevent electrode swelling. The electrical short which developed after 10 cycles and 194 hr operation has been attributed to the increased conductivity of the ZrO_2 retainer cloth, caused by reaction with lithium. The volume fraction of sulfide material in the positive electrode was about 75%, which is greater than normally observed. The volume fraction of Li-Al alloy ranged from 29 to 52% in the upper electrode and 20 to 40% in the lower electrode.

The distribution of metallic lithium within the negative electrode of operated cells is an important cell parameter. For this reason, an analytical procedure has been developed for determining the metallic lithium concentration in an electrode (Li-Al alloy plus LiCl-KCl electrolyte). Details of the procedure are presented, along with results from the initial application, namely, the analysis of the negative electrodes of Cell W-9.

Cell Chemistry

Investigations of Iron Sulfide Electrodes. Laboratory investigations were continued on the formation of J phase (approximately $\text{Li}_{0.4}\text{K}_{2.8}\text{Fe}_{12}\text{S}_{13}$) in FeS electrodes, the use of copper mattes (FeS- Cu_2S mixtures) as positive electrode materials, and the use of cobalt sulfides as additives to FeS and FeS_2 electrodes. In the case of FeS electrodes, two voltage plateaus were observed as cells were charged at $\sim 430^\circ\text{C}$; these plateaus appear to correspond to the formation of J phase and its subsequent conversion to FeS. At a higher temperature of 491°C , only one voltage plateau was observed, which appeared to involve consecutive reactions to form J phase and Li_2FeS_2 , followed by the formation of FeS. Commercially available copper mattes performed very well as the active material in the positive electrodes of lithium/metal sulfide cells; the presence of Cu_2S appears to preclude the formation of J phase because of the greater stability of ternary Cu-Fe-S phases. Copper matte electrodes of this type are considered sufficiently promising to merit evaluation in engineering-scale cells. The use of CoS as an additive resulted in a significant improvement in the performance of FeS_2 electrodes but had little, if any, effect on FeS electrodes.

Five tests in which Li/ FeS_2 cells were subjected to successively higher cutoff voltages and cyclic voltammetry experiments were used to characterize the overcharge reaction of FeS_2 electrodes. The reaction was identified as the oxidation of FeS_2 to form free sulfur and FeCl_2 (complexed as KFeCl_3 or K_2FeCl_4). The porosity of the FeS_2 electrode increased and the current efficiency decreased with increasing charge cutoff voltage. The cyclic voltammetry studies indicated three anodic (oxidation) peaks and four cathodic (reduction) peaks in the potential range from 1.7 to 2.7 V vs. LiAl.

Electrochemical Characteristics of Lithium-Aluminum Electrodes. Current-interruption measurements on Li/Li-Al and Li-Al/iron sulfide cells were made to investigate the effect of diffusional overpotentials on the percent utilization of Li-Al and iron sulfide electrodes. A mathematical model representing the solid-state diffusional overpotential that arises during the discharge of Li-Al electrodes was developed. Good agreement was obtained between calculated results from the model and experimental data from the Li/Li-Al cell. Modeling studies also indicated an optimum Li-Al electrode thickness and volume percentage of electrolyte that are consistent with experimental data.

Investigations of Other Cell Systems. A 1.4-V $\text{CaAl}_4/\text{NaCl-CaCl}_2/\text{FeS}$ cell having a 3-A-hr capacity (limited by the negative electrode) was operated successfully through 14 charge-discharge cycles at 550-560°C with nearly 10% coulombic efficiency and negative electrode utilization. Lower-melting-point electrolytes and negative electrodes richer in calcium are currently being sought for this type of cell. The principal objective of this study is to develop a cell that uses low-cost, abundant materials.

Wetting and Creeping Characteristics of LiCl-KCl Electrolyte. Further studies were conducted on the wetting and creeping characteristics of LiCl-KCl electrolyte. The addition of Li_2O to the electrolyte resulted in a slight increase in its tendency to wet a porous boron nitride surface. The addition of Li_2O to the molten LiCl-KCl had little, if any, effect initially on its wetting of a polished iron surface, but after a period of about 20 min the contact angle decreased markedly from 96 to 17°. The effect of LiF addition to LiCl-KCl had no significant effect on its wetting of boron nitride and caused only a slight increase in the tendency to wet a polished iron surface. A low-temperature plasma treatment of boron nitride in NH_3 or a nitrogen-hydrogen mixture was at least as effective as high-temperature nitrogen-firing in improving the wettability of BN by molten LiCl-KCl. In the creeping tests, the LiCl-KCl showed no tendency to creep up the walls of stainless steel, nickel, borosilicate glass, alumina, or molybdenum containers. When the salt was saturated with Li_2O , however, it gradually crept up and over the walls of a molybdenum crucible.

Electrochemical Studies of Impurities in LiCl-KCl Electrolyte. Cyclic voltammetry has been developed as a suitable method for determining O^{2-} , OH^- and H_2O as impurities in LiCl-KCl electrolyte with detection sensitivities of about 10 ppm. The kinetics of O^{2-} discharge reactions at platinum, gold, and glassy carbon electrodes were examined to investigate the possible use of electrolysis as an electrolyte purification procedure. The oxidation of O^{2-} appears to occur reversibly in LiCl-KCl on platinum and gold, but irreversibly on the glassy carbon. Investigations have also been initiated on the effect of electrolyte impurities on cell performance and lifetime.

Related Physical Research Studies. Basic research studies have continued on the phases that occur in metal sulfide systems. In the Li-Fe-S system, a new phase, designated "Y", has been discovered. The Y phase appears to have a composition near that of the Z phase (approximately $\text{Li}_4\text{Fe}_2\text{S}_5$), but it is somewhat richer in sulfur. The Y phase has not yet been observed in iron sulfide electrodes. Studies of the Li-Co-Fe-S system have indicated no interactions between Li_2S and cobalt sulfides. A procedure has been developed for out-of-cell synthesis of J phase by the reaction of an $\text{Li}_2\text{FeS}_2\text{-Li}_2\text{S}$ mixture with LiCl-KCl eutectic and iron at 400°C.

Further emf studies of Li-Al alloys have shown that the emf relative to lithium decreases from 296 mV to 24 mV at 427°C (700 K) across the composition range of the β -phase (48-56 at. % Li). The increase in lithium activity is accompanied by a reversal of the temperature coefficient of the emf in going from the ($\alpha + \beta$) two-phase region to the (Li_3Al_2 -liquid) two-phase region of the lithium-aluminum phase diagram.

Potentials that were measured at a graphite electrode in molten LiCl-KCl eutectic saturated with Li_2C_2 did not agree with literature values for the

free energy of formation of Li_2C_2 , which, themselves, are in conflict. A ΔG_f° value of about -26 kcal/mol at 700 K was obtained from emf data. Cyclic voltammetry studies of molten-salt electrolytes containing additions of Li_2C_2 indicate that C_2^{2-} ions are discharged at an unexpectedly high value of 2.8 V relative to lithium.

Design, Testing, and Commercial Development of Batteries

Design of a 42 kW-hr Battery for an Electric Automobile. A design study has been conducted in cooperation with Linear-Alpha, Inc. to determine the design requirements and estimate the performance of an American-made automobile converted to electric propulsion using a Li-Al/iron sulfide battery. The car selected for this study was a 1975 Ford Mustang II that had a loaded car weight (including two passengers) of 1568 kg and was powered with either a 383 kg Li-Al/FeS battery or a 292 kg Li-Al/FeS₂ battery. The calculated performance for this car gave it an acceleration of 0 to 50 mph in 15 sec and a driving range of greater than 100 miles.

Development of Battery Components. Three methods are under consideration for the equalization of the charge of a series-connected string of unequally charged cells. These are (1) a charge current bypass method, (2) a separate cell voltage sensing method and (3) a constant voltage method. Preliminary testing of a constant voltage charging circuit was completed. The need for a computer circuit analysis program was identified and such a program, SPICE, was obtained.

Testing was continued on iron or steel elements clad with aluminum or copper, to be used as a current carrying component in the cells. Based upon results to date, the bond resistance of iron-aluminum increases at 400-450°C to values higher than those desired, whereas the resistance of the iron-copper bond is stable at these temperatures and is acceptably low.

A mobile gas chromatographic unit for the measurement of water vapor in helium glove-box atmospheres was developed and is undergoing testing. The approximate limits of accuracy for the instrument are as follows: 1-10 ppm, 100-50%; 10-25 ppm, 50-10%; and 25-100 ppm, 10-5%. The instrument is being used to monitor helium glove-box atmospheres and to calibrate existing water vapor instrumentation in the battery program.

Materials and Manufacturing Costs. An estimate of the cost of commercially manufactured cells for load-leveling in utility networks has been completed. Materials and manufacturing costs were estimated for a prismatic cell having 30-cm-square electrodes and delivering 0.92 kW-hr. Process flow-sheets as well as plant and equipment layouts were developed, and equipment sizes and man power levels were determined as a basis for estimating manufacturing costs. A factory selling price of \$27/kW-hr was estimated for a battery submodule based on a plant capable of producing 5000 0.92-kW-hr cells per day.

Commercial Development. To achieve rapid commercial availability of Li-Al/metal sulfide batteries, a transfer of technology between ANL and industrial firms is being implemented at an early stage of battery development. The transfer is being accomplished in two ways: by the temporary assignment of industrial participants from battery manufacturers to the battery program.

at ANL and by contractual arrangements with industrial firms having capabilities for the development and fabrication of separators, electrical feedthroughs, electrodes, and cells.

The development of a low-cost electrode separator of good performance is essential to the commercial success of the Li-Al/metal sulfide cells. The woven fabrics of BN fiber presently used as separators are too bulky and too costly. Three potentially low-cost methods are under consideration for fabrication of improved separators. Contracts have been let to develop fabrication methods for producing papers, mats, and composite-type separators using BN, LiAlO_2 and Y_2O_3 fibers.

The effort to develop economical electrical feedthroughs has also been expanded by contractual efforts. Three major types of feedthroughs are being investigated. These are the mechanical, brazed, and compression feedthroughs (the latter are similar to those presently in use). The ceramic materials being evaluated for the insulator bodies are Al_2O_3 , BeO and Y_2O_3 . Both conventional and niobium-based brazes are being evaluated in these efforts.

Development contracts have also been made with industrial firms to fabricate test electrodes and cells. Two such contracts have been implemented with Gould Inc. and Eagle-Picher Industries, Inc.; an additional contract is expected to be made early in FY 1976 with Catalyst Research Corp. These contracts provide for development of several different methods of fabricating electrodes e.g., powder loading (by Gould) and cold pressing (by Eagle-Picher), both in dry-box atmospheres, and fabrication and assembly in "super" dry-room atmospheres by Catalyst Research.

A study has been completed on the design and cost of a Battery Energy Storage Test (BEST) Facility. This study was a cooperative effort between ERDA and the Electric Power Research Institute. The BEST Facility will provide a site for testing advanced battery systems and power conditioning equipment for energy storage on a utility network. The recommended facility is a 160- by 180-ft building with three battery rooms, a control room, an inverter area, a shop area, data analysis rooms, and offices. Each battery room is of adequate size (60 x 80 ft each) to accommodate an advanced battery system (~1 MW, 10 MW-hr). The estimated cost of the facility is 6.4 million dollars.

I. INTRODUCTION

Lithium/metal sulfide batteries are being developed at Argonne National Laboratory, in a program for the U. S. Energy Research and Development Administration (ERDA) for use as (1) energy storage devices for load-leveling on electric utilities and (2) power sources for electric automobiles. Batteries that are currently available are too expensive for the first application and do not have sufficient energy storage and power per unit weight for the second application. The installation of batteries on electric utility networks would permit the utilities to store energy generated at night by coal-burning or nuclear baseload plants and discharge the battery to the network during the day when demand is highest. This would reduce the need for gas- or oil-burning turbine generators. Electric automobile batteries could be recharged at night using electricity produced from coal, nuclear energy, or other energy sources. The successful development of batteries for either application would reduce our dependence on foreign sources of oil.

Development efforts on the energy storage battery are broad in scope and include cell chemistry studies, materials studies, electrode development, cell development, battery development, and systems studies. The development of the car battery consists of systems design studies and a limited amount of work on cell and battery development. The program for the car battery has been supplemented by a design and cell-evaluation study for the Department of Transportation (DOT). In the DOT program, which was completed in June 1975, high performance cells developed in the ERDA program were evaluated by a computer-controlled unit that subjects the cells to power cycles of the type expected under actual driving conditions.

The performance goals that we have set for off-peak energy storage and electric automobile batteries, shown in Table I-1, have not changed in the past six months.

Table I-1. Performance Goals for Lithium/Metal Sulfide Batteries

Battery Goals	Electric Vehicle Propulsion	Off-Peak Energy Storage
Power		
Peak	60 kW ^a	40 MW
Normal	21 kW	10 MW
Voltage, V	140	1000
Specific Energy, W-hr/kg	120-160	120-150
Energy Output	42 kW-hr	100 MW-hr
Discharge Time, hr	2	10
Charge Time, hr	5	5-7
Watt-Hour Efficiency, %	70	80
Cycle Life	1000 ^b	1500 ^b
Cost of Capacity, \$/kW/hr	20-30 ^b	15-20 ^b
Heat Loss Through Insulation	150 W	100 kW

^aBased upon power required to accelerate a 1570-kg car 0-60 mph in 23 sec.

^bTentative; to be specified by systems and cost studies.

Specific energy (W-hr/kg) and specific power (W/kg) are the more important considerations for the electric automobile battery. The specific-energy goal for the off-peak energy application is not a direct requirement, but results from consideration of the goal for cost of capacity and an estimate of the projected cost per unit weight that can be expected for these batteries.

The cells presently being developed have negative electrodes of solid lithium-aluminum alloys, positive electrodes of iron sulfide (FeS or FeS_2), and a molten electrolyte of LiCl-KCl eutectic (mp, 352°C), which fills the pores in the electrode and the separator. The use of this salt requires operation of the cell at about 400 to 450°C . Boron nitride fabric has been a satisfactory electrode-separator material, and has permitted the development of compact cells in which the separator is compressed between the electrodes.

Recent experimental work on cells and electrodes has been focused on the development of prismatic, vertically oriented cells. This design is more amenable to assembly into a compact battery than the cylindrical, horizontally oriented design of previous cells. Increased emphasis is also being placed on battery design, development of battery components, and systems and cost analyses.

To increase the effort on the transfer of technology to industry, contracts are being made with industrial firms to develop fabrication procedures and to produce electrodes and cells for testing at ANL. During this period, contracts with Gould Inc. and Eagle-Picher Industries, Inc. became effective and negotiations are continuing on a contract with Catalyst Research Corp. Contracts have also been made with several industrial firms to develop improved electrode separators and electrical feedthroughs. Early involvement of industry in this manner is considered very important in terms of assuring that industrial capability for the production of lithium/metal sulfide cells is available when battery fabrication is needed.

II. CELL DEVELOPMENT

The effort in this part of the program is directed primarily toward the development of engineering-scale sealed cells capable of meeting the requirements for batteries for off-peak energy storage and electric automobile propulsion. In previous work (described in Ref. 1 and in the preceding semi-annuals, ANL-8109 and ANL-75-1) compact, lightweight cells were developed and impressive specific energies (up to 150 W-hr/kg) were achieved. This first generation of engineering-scale cells employed a cylindrical design (13-cm dia, 3 to 5 cm high, 100-150 A-hr capacity) with top and bottom Li-Al electrodes and a central FeS_x electrode. These cells, which were operated in the horizontal position at temperatures ranging from about 400-500°C, achieved excellent watt-hour and ampere-hour efficiencies and yielded stable, high performance for periods exceeding 1000 hr and 50 cycles. Recent work has been concentrated on development of a second-generation cell, which is prismatic (13 by 13 cm, 2 to 4 cm thick, 100 to 150 A-hr capacity) and designed for vertical operation. In addition, continuing efforts have been directed toward increasing the specific power and lifetime capability of the cells and developing improved assembly and startup procedures.

The effort to increase electrical performance and reliability while reducing the cost and complexity of the cells has included supporting research activities; these have been devoted to studying problems encountered in the engineering cells and to testing possible improvements in components or procedures. Cell dilatometry experiments have been conducted to study the swelling and expansion forces that occur in electrodes and cells and to identify methods of minimizing these forces. Experiments have also been conducted to identify the factors that influence lifetime, to determine the effects of metal sulfide additives to the positive electrodes, to study alternative outgassing and startup techniques, and to study candidate current collector materials. Some of the Li-Al/ FeS_2 cells were also subjected to driving profile tests using computer-controlled automatic cycling equipment (the latter tests were conducted as part of a program sponsored by the Department of Transportation).

A. Development and Testing of Engineering-Scale Cells

The first generation of engineering-scale cells, represented by the W-series cells, are cylindrical, with top and bottom negative electrodes, a central iron sulfide electrode, and an electrolyte of LiCl-KCl eutectic. A schematic drawing of this type of cell, which is operated in a horizontal position, is shown in Fig. II-1. The negative electrodes consist of porous beds of solid Li-Al alloy particles (generally, ~50 at. % Li), contained in fine-mesh stainless steel screen. The pores in the structure are filled with electrolyte. The positive electrode is a porous bed of iron sulfide (either FeS or FeS_2). A current collector structure is contained within the porous bed, and the pores are filled with electrolyte. The positive electrode particles are retained with a finely woven ZrO_2 fabric, and the positive and negative electrodes are electrically insulated from each other with BN fabric separators. The positive electrode lead passes through the cell housing; insulation from the housing is provided by a compression-type feedthrough having BN and Al_2O_3 components. The cells are 13 cm dia and 3 to 5 cm high, and generally have weighed between 0.9 and 1.7 kg.

Fig. II-1. General Design of W-Series Cells

The second generation of engineering cells are vertically oriented, prismatic cells and development work on these cells in the early stages. These cells are rectangular (13 by 13 cm, 2 to 4 cm thick) and, like the earlier cells, have a central positive electrode and two outer negative electrodes; the positive electrode feedthrough is located at the top of the cell. The major advantage of the prismatic cells is that they can be directly connected in compact battery arrays, without requiring the development of a special compact feedthrough.

Seven W-series cells and one vertical prismatic cell (R-1) have been operated in this reporting period. Table II-1 summarizes the cell tests during the past six months, including the types of cells, their physical characteristics, and their specific-energy performance. The performance of each cell is described in more detail below.

1. Long-Lifetime Cell, W-8

(C. C. McPheeters, J. D. Arntzen, H. Shimotake, L. G. Bartholme)

Cell W-8, as reported previously (ANL-75-1, p. 22), was operated to determine the effect of the Cu_2S addition on the performance of an engineering-scale cell (Li-Al/FeS + 16 mol % Cu_2S). The cell had 150 A-hr of total sulfur capacity (including the Cu_2S capacity) and 150 A-hr of lithium capacity. The positive electrode was non-compact (~ 1.5 -cm thickness compared to the usual ~ 1.0 -cm thickness) because of the necessity of providing additional space for FeS expansion.

Cell W-8 had a lifetime of 3700 hr and 121 cycles, with only a $\sim 20\%$ decline in performance observed during that period. The maximum specific energy achieved with Cell W-8 was 82 W-hr/kg during Cycle 87; the specific energy was ~ 60 W-hr/kg.

Table II-1. Physical Characteristics and Performance of Engineering Cells

	Cell Designation							
	W-8	W-9	W-10	W-11	W-12	W-13	W-14	R-1
Cell Weight, kg	1.49	1.54	1.40	1.37	0.98	1.27	0.92	0.98
Lifetime, ^a hr	3700	1511	2688	1128	150	168	>1100	>900
No. of Cycles ^a	121	76	113	43	20	9	>98	>47
Specific Energy, W-hr/kg								
Maximum	82	98	128	122	50	59	85	105
Normal	60	84	114	105	35	45	81	95
Positive Electrode								
Active Material	FeS-Cu ₂ S ^b	FeS ₂	FeS ₂ -Co ₂ S ₃ ^c	FeS ₂ -Co ₂ S ₃ ^c	FeS ₂ -Co ₂ S ₃ ^c	FeS-Cu ₂ S ^b	FeS ₂ -CoS ₂ ^c	FeS ₂ -CoS ₂ ^c
Theor. Capacity, A-hr	150	204	165	165	132	100	118	100
Current Collector	Fe Mesh	Mo Mesh	Mo Mesh	Mo Mesh	Mo Mesh	Fe Sheet	Mo Mesh	Mo Mesh
Negative Electrodes								
Active Material	Li-Al	Li-Al	Li-Al	Li-Al	Li-Al	Li-Al	Li-Al	Li-Al
Li-to-Al Atom Ratio	0.92	0.92	0.92	0.92	1.09	1.09	1.09	0.92
Preparation Method	Pyromet.	Electrochem.	Electrochem.	Electrochem.	Pyromet.	Pyromet.	Pyromet.	Electrochem.
Theor. Capacity, A-hr	150	112	150	150	68	100	60	100
Current Collector	None	SS Wire	SS Wire	Fe Screen	None	Retimet ^d	Retimet ^d	Fe Mesh
Cell Operating Temp., °C	425-500	450	450	450	450	500	450	450

^a Cells R-1 and W-14 are still in operation.^b 16 mol % Cu₂S.^c 10 wt % Co_xS_y.^d A porous metal (~5% solids) produced by Dunlop, Ltd., England.

Although no major improvement in electrical performance resulted from the Cu_2S addition, Cell W-8 was the most durable of any engineering cell yet tested at ANL, and maintained a high degree of stability over the 3700 hr of operation. The cell failed by short-circuiting during a high-temperature test (500°C instead of the normal operating temperature of 450°C). It is believed that the lifetime of Cell W-8 would have been considerably longer than 3700 hr if the cell had not been subjected to the high-temperature test.

Post-test examination included a search for the location of the short circuit using temperature-sensitive liquid-crystal paper. At room temperature, a low-power (~ 15 W) current was passed through the cell and a color change occurred in the liquid crystal paper (indicating a temperature rise) at an area between the upper two electrodes. It was concluded that a short circuit was present directly between these electrodes. Post-test examination also showed severe swelling of the positive electrode, although additional space had been provided within the electrode for the expansion of FeS . The final FeS electrode thickness was 1.5 times the initial thickness; the Li-Al electrodes were reduced in thickness (compressed) in the central area of the cell, and the Li-Al redistributed radially. It was subsequently found (see Section II.B) that the principal cause of expansion of FeS electrodes is the reaction with LiCl-KCl electrolyte to form J-phase. In future engineering cells with FeS electrodes, alternative electrolytes containing only lithium cations will be used in an attempt to achieve dimensional control.

2. Upper-Plateau Cell, W-9

(W. W. Schertz, J. W. Allen, C. C. McPheeters)

Cell W-9 was constructed with the aim of achieving sustained high power capability. Toward this end, Cell W-9 was designed to operate only on the first plateau of the FeS_2 discharge curve ($\text{FeS}_2 \rightarrow \text{FeS}$). The theoretical lithium capacity was 112 A-hr and the theoretical sulfur capacity was 204 A-hr.

The design and early performance results were presented in the preceding semiannual (ANL-75-1, p. 18). Cell W-9 performed well on the SAE-J227 metropolitan driving profile. In a comparative test with a lead-acid battery, Cell W-9 had a range of ~ 80 miles vs. ~ 20 miles under the same conditions for the lead-acid battery.

Operation of Cell W-9 was voluntarily terminated after 76 cycles and 1511 hr to allow post-test examination of a "healthy" cell. At the time of termination, Cell W-9 was gradually declining in capacity, apparently because of the same life-limiting mechanism that was encountered in many previous and subsequent engineering cells. This mechanism, which involves a gradual loss in the ability to fully charge the cell, is attributed to one of the following: (a) the lithium is seriously maldistributed or (b) part of the Li-Al electrode becomes inactive. The post-test examination of Cell W-9 was unsuccessful in identifying the cause of the life-limiting mechanism. Cell W-14, described below, was specifically dedicated to studying this life-limiting mechanism.

As seen in Table II-1, the maximum specific energy for Cell W-9 was 98 W-hr/kg and the typical value 84 W-hr/kg. It is believed that upper-plateau cells of this type will be capable of 110 to 125 W-hr/kg when fully

developed. The specific-power capability of upper-plateau FeS_2 cells is expected to be superior to that of two-plateau FeS_2 cells and FeS cells. Consequently, this type of cell is particularly attractive for the electric vehicle application.

3. Cobalt-Sulfide Additive Cells, W-10 and W-11
(C. C. McPheeters, J. D. Arntzen, W. W. Schertz, J. W. Allen)

Cell W-10 was constructed to test the use of an FeS_2 electrode with cobalt sulfide additive in an engineering cell. Previous smaller-scale experiments (ANL-75-1, p. 29) had indicated that the use of FeS_2 containing 10 wt % Co_2S_3 (nominal composition) resulted in a great improvement in capacity, power capability, and the ability to charge at higher current densities. The original intent of adding cobalt sulfide to FeS_2 had been to increase the electrical conductivity of the active material and thus reduce the amount of molybdenum current collector required. Accordingly, one of the objectives of operating Cell W-10 was to compare its current-collecting capability with that of Cell W-5, which had a similar design, including three molybdenum-mesh current collectors. The only major difference in the two cells was the cobalt sulfide addition to the positive electrode. The FeS_2 capacity was 150 A-hr, as was the lithium capacity. The negative electrodes were formed by electrochemically charging lithium into pressed aluminum wire plaques.

Cell W-10 operated for 113 cycles and 2688 hr. The electrical performance was superior to that of Cell W-5, thus demonstrating the beneficial effect of the cobalt sulfide addition. The internal resistance of Cell W-10 was lower than any previous ANL cell (5.5 milliohms), and allowed operation at higher current densities, *e.g.*, a capacity of 78 A-hr (52% utilization) was achieved at a current of 40 A (0.176 A/cm^2). During the first 1000 hr of operation, Cell W-10 could be charged effectively at 15 A (7.5-hr rate). The charging capability as well as the A-hr capacity slowly declined after 1000 hr, apparently because of the same life-limiting mechanism discussed above.

Cell W-10 demonstrated the lowest cell resistance, the highest capacity, and the highest power capability of any ANL cell tested until that time. The cobalt sulfide addition to the FeS_2 electrode in Cell W-10 resulted in a significant improvement in performance and thus it was concluded that a major reduction could be made in the amount of molybdenum current collector. Accordingly, the next cell, W-11, was operated to evaluate the performance of a $\text{FeS}_2\text{-CoS}_x$ cell with greatly reduced current collection (one molybdenum mesh current collector instead of three).

Cell W-11 ($\text{Li-Al/LiCl-KCl/FeS}_2\text{-CoS}_x$) had two principal objectives: (1) to test the performance of a cell having a $\text{FeS}_2\text{-CoS}_x$ electrode with a single molybdenum mesh current collector, as discussed above, and (2) to test a new cell-fabrication technique in which multiple folds of BN and ZrO_2 fabrics were eliminated through the use of an "embroidery hoop" design (discussed further below). In other respects, Cell W-11 was identical to Cell W-10 except that the exterior flat surfaces of the cell were restrained from expanding by steel clamping plates. The Li-Al electrode was formed electrochemically and contained 150 A-hr of lithium to match the 150 A-hr of FeS_2 capacity.

Cell W-11 was operated for 43 cycles and 1128 hr; its electrical performance was very similar to that of Cell W-10. The overall cell resistance was slightly lower than that of Cell W-10 (4.8 milliohms vs. 5.5 milliohms for Cell W-10), despite the use of only one molybdenum mesh current collector. It was concluded that the cobalt sulfide addition to FeS_2 permits a major reduction in the current collector requirements in the positive electrode.

An important feature of Cell W-11 was its improved specific power. Figure II-2 shows a power ramp taken during Discharge 7 using a computer-controlled Robicon power supply system. The current-carrying capability exceeded that of the testing system. A peak power of 116 W was estimated from these data, as shown in Fig. II-2; this peak power significantly exceeds the values of 55 and 80 W obtained in similar tests with Cells W-9 and W-10, respectively. The specific power corresponding to 116 W is 85 W/kg. The achievement of much higher specific power is expected to result from the development of more compact cells with thinner electrodes.

The design of Cell W-11 represented a major advance in the ease of fabrication of the positive electrode and also in the quality of the electrode. In previous cells, the sealing of the retainer and separator fabrics to obtain particle retention and electrical isolation of the positive electrode was achieved by tedious and inefficient folding of fabric and sewing operations. In Cell W-11 this was achieved by simply pressing the fabric between two thin hoops of slightly different diameters. Figure II-3 is a photograph of the positive electrode assembly for Cell W-11. The advantages of this electrode fabrication technique are (a) greater ease of fabrication, (b) smaller amounts of boron nitride, and (c) elimination of multiple folds of the BN and ZrO_2 fabrics which previously detracted from the electrochemical uniformity of the cell. This "embroidery hoop" technique and other separator clamping methods are being developed for the square prismatic cells.

Fig. II-2. Peak-Power Performance of Cell W-11

Fig. II-3. Positive Electrode Assembly for Cell W-11

4. Thin-Electrode Cell, W-12
(W. W. Schertz, J. W. Allen)

Cell W-12 (Li-Al/FeS₂) was a thin-electrode, high-specific-power cell that was scheduled for testing on driving profiles as part of the DOT program. Like Cell W-9, this cell was designed to operate only on the upper plateau (FeS₂ → FeS) of the FeS₂ discharge curve so that sustained power capability would be available throughout the discharge. The positive electrode contained FeS₂-10 wt % Co₂S₃, with a single molybdenum mesh current collector at the center. The negative electrodes were prepared by loading Li-Al powder into a Retimet structure. The theoretical sulfur capacity was 132 A-hr and the total lithium capacity was 68 A-hr.

Cell W-12 had a brief lifetime of only 150 hr and 20 cycles owing to the development of a serious short circuit. Post-test examination indicated that the ZrO₂ paper between the two exterior hoops of the positive electrode had become conductive, and this probably caused the short circuit. A minor design modification will eliminate this problem in future cells.

Cell W-12 achieved the highest specific power, nearly 100 W/kg, of any ANL cell. However, much higher specific power should be possible when cell resistances are reduced and engineering improvements are made. The resistance of Cell W-12 was >6 milliohms, whereas a resistance of 3-4 milliohms had been expected for this thin-electrode compact cell. The higher resistance apparently resulted from an extended evacuation of the cell at 300°C, which had been conducted prior to introduction of the electrolyte. This procedure, which was intended to reduce to amount of gases evolved, apparently resulted in a thin layer of sulfides or oxides of molybdenum on the current collector and thereby increased the contact resistance.

Alternative gas-removal methods and improved vacuum equipment will be employed in future cells.

5. Hot-Pressed Electrodes Cell, W-13
(C. C. McPheeters, T. O. Cooper, J. D. Arntzen)

Cell W-13 was a test of a hot-pressed FeS electrode in a compact cell with pyrometallurgically prepared Li-Al electrodes (Li-Al particles loaded into Retimet structures). The positive and negative electrodes were matched at 100 A-hr. Cell W-13 had a brief lifetime of only 9 cycles and 168 hr. From the beginning of operation, this cell had a serious short circuit, which gradually worsened with time. Despite this, Cell W-13 achieved a maximum specific energy of 59 W-hr/kg, which is fairly good for a thin-electrode FeS cell at this stage of development. The most promising feature of Cell W-13 was its resistance of 3.5 milliohms, the lowest yet achieved in an ANI cell. The cause of the short circuit has not yet been determined.

6. Cell W-14
(W. W. Schertz, J. W. Allen)

Cell W-14, a thin-electrode cylindrical cell, has completed 98 cycles and 1100 hr of testing and is still in operation at this writing. The cell is designed for operation on the upper voltage plateau ($\text{FeS}_2 \rightarrow \text{FeS}$), and has a theoretical capacity of 60 A-hr. This cell was tested on driving profiles as part of the DOT program.

The performance of Cell W-14 has been extremely stable, with specific energies of 80 to 85 W-hr/kg achieved over the first 600 hr of testing. The ampere-hour efficiency was nearly 100% for the first 300 hr of testing but has gradually declined to a value of 96%.

7. Prismatic Cell, R-1
(C. C. McPheeters, E. Carr,* J. D. Arntzen and T. O. Cooper)

Cell R-1, the first engineering-scale, sealed prismatic cell was the culmination of several months of development work. The new prismatic cell design, shown in Fig. II-4, required the development of new cell components (e.g., square electrodes, cell housings, etc.) and new assembly and startup procedures. Figure II-5 is a photograph of Cell R-1.

Cell R 1 is a fairly compact cell, weighing only 0.98 kg. The theoretical capacities of the $\text{FeS}_2\text{-CoS}_2$ electrode and the Li-Al electrodes were matched at 100 A-hr. The Li-Al electrodes (12.7 cm square, 0.4 cm thick) were formed electrochemically prior to cell assembly by the deposition of lithium into a pressed plaque of aluminum demister wire.

The positive electrode was assembled as follows. The active material ($\text{FeS}_2\text{-CoS}_2$) and an electron-beam-welded current collector were encased, by a folding technique, with ZrO_2 paper (particulate retainer) and BN fabric separators. The folded pack was then inserted into a 325-mesh stainless steel basket having a hole in one end for the positive lead. Additional BN fabric was provided for insulation at this end to prevent FeS_2 shorting to the basket assembly, which is at the negative potential during cell operation.

* Industrial Participant from Eagle Picher, Inc.

Fig. II-4. Design of Engineering-Scale, Prismatic Cell R-1

Fig. II-5. Prismatic Cell R-1
ANL Neg. No. 308-4090

Before installation in the cell case, the entire electrode assembly was electrochemically discharged in a horizontal orientation to immobilize the positive electrode material. This step was carried out in a formation fixture to insure the proper dimensional control. Upon completion of the discharge, the electrode assembly was placed in the cell case (Type 304 stainless steel), and various components were spot-welded in place; the cell was then sealed by welding, leak-checked, and put into operation in the vertical position.

Cell R-1 has operated for more than 47 cycles and 900 hr. The electrical performance results are summarized in Table II-1. The cell achieved a fairly high specific energy level for the first several hundred hours (~ 100 W-hr/kg), but the power capability was low owing to a broken molybdenum current lead. The fracture in the current lead apparently occurred during cell startup, owing to mechanical stresses that resulted from the new prismatic cell design. This problem will be avoided in future prismatic cells through a minor design modification. The maximum specific energy achieved with Cell R-1 was 105 W-hr/kg at a discharge current of 5 A (73% utilization), during Cycle No. 11; Fig. II-6 shows a curve of cell voltage *vs.* capacity for Discharge 11.

The initial results of Cell R-1 are highly encouraging considering that it represents the first in a new generation of cells. The problems encountered in Cell R-1 appear to be solvable. Assembly and startup will be greatly simplified as advances are made in the development of immobilized vertical electrodes. The specific energies (~ 90 to 105 W-hr/kg) achieved in this 2-cm-thick cell are equivalent to about 125 W-hr/kg for a thicker (~ 3 cm) cell because of the fairly large interelectrode distances associated with fabric BN separator. The specific energy loss resulting from the use of thin cells will become less as thin paper separators become available.

Fig. II-6. Cell Voltage *vs.* Capacity for Prismatic Cell R-1 (discharge 11)

B. Supporting Studies

1. FeS Electrode Studies (H. Shimotake, L. G. Bartholme)

The FeS electrode offers several advantages over the FeS₂ electrode. One advantage is the low cost, which is particularly attractive for applications such as large utility batteries. However, it is believed that the performance of the FeS electrode may have serious limitations, owing to diffusional resistance. This resistance results from the formation of J phase (a K-Li-Fe-S compound), which is a solid product of interaction between the LiCl-KCl electrolyte and the cell active materials. Accordingly, two different measures to reduce or eliminate J-phase formation were tested. The first method was to add a transition metal sulfide. The second method was to use an electrolyte containing only lithium ions instead of LiCl-KCl eutectic and thus eliminate potassium ions, which are necessary for formation of the J phase. These tests were conducted in 7.5-cm-dia cells.

FeS Electrodes with Additives. Cells having FeS₂ electrodes to which a transition metal sulfide has been added, particularly CoS₂, have shown a remarkable improvement in utilization of sulfur. It was hoped that the addition of a transition metal sulfide would produce similar improvements in cells having FeS electrodes--by preventing or reducing the formation of the undesirable solid J-phase and thereby reducing the diffusional resistance, by reducing the electrical resistance of the electrode, or by a combination of these two effects. The metal sulfides tested included Cu₂S, Co₂S₃, NiS and ZnS. The theoretical capacity of the positive electrode, including the additive, was 25 A-hr and that of the pyrometallurgically formed Li_{1.2}Al negative electrode was 40 A-hr. The cell capacity was thus limited by the sulfide electrode. To prepare the positive electrode, the FeS and the metal sulfide powder were mixed and encased in a cage structure consisting of a low-carbon steel ring and Armco iron mesh lined with zirconia cloth to prevent escape of the sulfide powder. The Li_{1.2}Al disk was placed at the bottom of the cup that served as the cell housing. The two electrodes were separated by a sheet of BN cloth to prevent electrical contact. All cells that were tested during this reporting period had this design.

The positive electrodes each contained 10 mol % of the additive metal sulfide. Of the additives tested, only Cu₂S produced a significant improvement in sulfur utilization. A utilization of 75% at a current density of 0.12 A/cm² was obtained at a temperature of 450°C, compared with a utilization of 60% or less for an equivalent cell without the Cu₂S addition. No improvement in utilization was achieved with the addition of Co₂S₃, NiS, and ZnS.

Titanium carbide (TiC) was also tested as an additive to FeS electrodes. This material, which is corrosion-resistant to the positive electrode environment and is also electronically conductive, was expected to improve the utilization. The test results, however, showed no improvement. In summary, among the additives tested, only Cu₂S produced a marked improvement in utilization of sulfur in FeS electrodes.

FeS Electrodes with Electrolyte Containing Only Lithium Ions. The second method tested to eliminate the J-phase was to use an electrolyte

containing only lithium ions, instead of the LiCl-KCl eutectic normally used. Two mixtures have been tested: LiF-LiCl-LiI (mp = 342°C) and LiF-LiCl-LiBr (mp = 430°C).

The performance of Cell DS-23, which employed the LiF-LiCl-LiI eutectic as the electrolyte, is compared in Fig. II-7 with that of Cell DS-11, which employed LiCl-KCl eutectic. Both cells contained an identical amount of FeS, had identical cell configuration, and were operated at the same temperature. The performance of the cell containing LiF-LiCl-LiI (DS-23) is clearly superior to that of Cell DS-11. At current densities of 0.08 and 0.16 A/cm², Cell DS-23 achieved 80% utilization while Cell DS-11 achieved only 40 to 60%. It should be noted that the utilization in Cell DS-23 was not significantly reduced at the higher current density, whereas that of Cell DS-11 was reduced from 60 to 40% by increasing the current density from 0.08 to 0.16 A/cm². It was also found that the cell temperature had little effect on the performance of Cell DS-23 in the range between 385 and 450°C.

Performance similar to that of Cell DS-23 was obtained with a cell containing LiF-LiCl-LiBr electrolyte. These results strongly suggest the importance of eliminating potassium ions from the electrolyte in order to achieve high utilization. To this end, efforts are now under way to find an electrolyte containing no potassium ions that has suitable properties and also is relatively inexpensive.

2. Electrode Dilatometry Studies (R. C. Elliott, T. O. Cooper)

Measurements have been continued of the volumetric changes that occur in particle bed electrodes during the first electrochemical discharge.

Fig. II-7. Effect on Cell Performance of All-Lithium-Ion Electrolyte: Li-Al/FeS Cell DS-23

The data derived from these experiments is expected to be useful in (1) determining the loading of active material that produces optimum electrical performance, (2) evaluating new electrochemical additives and electrolytes, and (3) delineating the chemical phase changes that are associated with the abrupt volumetric changes during discharge. The studies conducted to date have clarified several problems that have lead to improvements in cell design. The cause of the large volumetric change of an FeS electrode during early discharge was identified (in conjunction with studies carried out by the Materials Group). One possible method for control of rapid initial expansion of FeS was developed. And, finally, the additive Co_2S_3 , was found to significantly reduce the swelling of FeS_2 electrodes.

In order to isolate the cause of the large expansion of an FeS electrode, it was necessary to prepare a series of electrodes with progressively deeper discharges. These electrodes were then examined by photomicrography and X-ray diffraction. The cause of the expansion was the formation of J-phase, a complex compound consisting of potassium, lithium, sulfur, iron, and traces of chloride. The formation of J-phase results in particle-to-particle interaction which causes the electrode bed to jam against its constraints and eventually buckle. Particle-bed buckling causes the large volumetric changes observed.

A method for control of particle-bed buckling has been developed. Figure II-8 shows that as the particle size of FeS in Retimet (a commercially

Fig. II-8. Effect of Particle Size on First-Discharge Expansion: FeS in Retimet

available porous iron) is increased, the total expansion of the electrode decreases. However, the electrode with the lowest expansion is not the best electrode from a performance standpoint. Figure II-9 shows that when fine-particle-size FeS is incorporated into porous metal structures, better initial electrode performance is achieved. These results indicate that the best FeS electrode designs will probably be those in which the FeS is incorporated in porous metal current collectors. The use of such structures minimizes particle-bed buckling.

Fig. II-9. Capacity per Unit Volume of FeS-Iron Retimet Electrode as a Function of FeS Particle Size

Cobalt sulfide, an additive that was first incorporated into FeS₂ electrodes to improve the electrical conductivity of the particle bed, was also found to reduce the overall expansion during discharge. This result is shown in Fig. II-10, which compares the expansion of FeS₂ and FeS₂-10 wt % Co₂S₃ electrodes during initial discharge. The addition of Co₂S₃ to FeS₂ electrodes also improves both the specific energy and power capability.

Fig. II-10. Expansion of FeS_2 and $\text{FeS}_2\text{-Co}_2\text{S}_3$ Electrodes during First Discharge

REFERENCE

1. W. J. Walsh *et al.*, "Development of Prototype Lithium/Sulfur Cells for Application to Load-Leveling Devices in Utility Networks," *Proc. 9th IECEC, San Francisco, August 26-30, 1974*, pp. 911-915 (1974).

III. ELECTRODE DEVELOPMENT (E. C. Gay)

A. Scope

The objective of the investigations in this part of the program is to develop electrodes having the capacity density, power density, and cycle life commensurate with the goals for batteries to be used for off-peak energy storage and electric-vehicle propulsion. The major emphasis for development of negative electrodes continues to be on solid lithium-aluminum electrodes, with a smaller effort on other solid lithium-alloy electrodes. The positive electrodes contain FeS_2 or FeS as the active material and various metal sulfide additives. Cylindrical and rectangular electrodes are being investigated with major emphasis on development of the vertical, rectangular electrodes. The development efforts for the off-peak energy storage battery and the electric-vehicle battery are closely related and, in some cases, development work is carried out in the same series of experiments. The major difference is that the electrodes developed for the electric vehicle battery are thinner and are more suitable for operation at higher current density.

B. Development of Negative Electrodes

The development of negative electrodes has been focused primarily on two types of Li-Al electrodes formed by different techniques. The first type is formed by electrochemical deposition of lithium in a substrate of compressed aluminum fibers. Investigations of these electrodes have been conducted to determine the effects on performance of volume fraction of electrolyte, electrode thickness, and operation over a range of charge and discharge rates. The second type of electrode is formed by vibratory compaction of pyrometallurgically prepared Li-Al powder into a porous metallic structure; the structure serves as the current collector and also provides a means of distributing the Li-Al homogeneously. The latter consideration is particularly important in vertical, rectangular electrodes and this type of structure appears to be well suited to achieving the appropriate electrolyte loading and to maintaining the distribution of active material, without settling, during operation of the cell in a vertical configuration.

Studies have also been continued in vertical, prismatic cells to determine the effects on performance of electrolyte loading,* electrode thickness, cycle life and lifetime, and operation over a range of charge and discharge rates. The results are discussed in connection with studies of vibratorily loaded positive electrodes in Section D.

Investigations are also being conducted to identify and evaluate solid lithium-metal alloys, other than lithium-aluminum, that show promise of achieving higher performance than lithium-aluminum in Li/iron sulfide cells. To date, the systems that have been examined are binary alloys of lithium-boron and lithium-silicon, as well as ternary alloys of lithium with aluminum, boron, and silicon.

* The electrolyte loading, or volume fraction of electrolyte, in a Li-Al electrode is defined as the maximum loading at full charge.

1. Solid Lithium-Aluminum Alloy Electrodes in Li/Li-Al Cells
(D. R. Vissers, K. E. Anderson, W. Frost, J. Dorsey)

The work described herein is a continuation of a study to evaluate electrochemically formed Li-Al electrodes in terms of electrode thickness, electrolyte content, and type of current collector structure. Some of the results have been reported previously (ANL-75-1, p. 42).

The Li-Al electrodes are operated against a liquid lithium counter-electrode so that the cell performance is completely limited by the Li-Al electrode. The lithium electrode serves both as a working electrode and as a near-perfect reference electrode. The lithium (~ 15.5 A-hr) is contained in a Type 347 stainless steel Feltmetal support, with an electrode area of ~ 20 cm².

In recent studies, two Li-Al electrodes (DK-11A and DK-9) were electrochemically prepared from aluminum plaques, which were formed by pressing aluminum mesh to a thickness of 0.64 cm; the weight of aluminum was chosen to give electrolyte volume fractions in the charged electrodes of 0.2 or 0.4. Stainless steel wire (2 wt %) was incorporated into the aluminum mesh structures before pressing to serve as a current collector. The plaques were contained in housings of Type 304 stainless steel. (Earlier studies employed 0.32-cm-thick electrodes with electrolyte volume fractions of 0.2, 0.4 and 0.7.) A third electrode (DK-19) was prepared by loading aluminum powder into a porous iron structure (0.8 cm thick), which was expected to provide improved current collection. All of the Li-Al electrodes had an area of 15.6 cm². The experiments were conducted in open cells in a helium-atmosphere glovebox. The cells were operated at $\sim 425^\circ\text{C}$.

In general, the following cutoff potentials were used during cell cycling: 0.15 V during Li-Al electrode charge and either 0.40 or 0.7 during Li-Al electrode discharge (all cutoff potentials cited are IR-free voltages vs. lithium). These cutoff potentials studied are believed to be quite conservative. In normal operation of a Li-Al/LiCl-KCl/FeS₂ cell having electrodes of matched capacity, the potential of the Li-Al electrode during cell charging may reach 0.050 V, while during cell discharge the potential may reach 0.67 V. If a large excess of FeS₂ is used, the potential of the Li-Al electrode during cell discharge may reach as high as 0.97 V, whereas the electrode potential during cell charge will remain essentially unchanged from that of a cell with equal-capacity electrodes.

The capacity densities achieved by the Li-Al electrodes at various charge and discharge current densities were used to evaluate electrochemical performance. The operating conditions and results of the three cell tests, as well as comparisons with previous cell tests, are presented below.

Cell DK-11A. The Li-Al electrode of Cell DK-11A was electrochemically formed from a 0.64-cm-thick aluminum plaque, and the electrolyte volume fraction in the charged state was 0.4. The theoretical capacity density was 0.69 A-hr/cm² (0.83 A-hr/cm³). During the first 13 cycles, the Li-Al electrode was electrochemically charged at a current density of 0.025 A/cm² because earlier studies (ANL-75-1, p. 37) had indicated that thick (0.64 cm) electrochemically formed Li-Al electrodes undergo an induction period during which the capacity density gradually increases to a stable value. The

inductive cycling procedure was carried out with all of the thick (>0.32 cm) electrodes investigated in this study.

The capacity density of the cell was measured at charge current densities of 0.025 – 0.10 A/cm^2 and at discharge current densities of 0.05 – 0.20 A/cm^2 . The results of these measurements are presented in Fig. III-1. At a

Fig. III-1. Capacity Density of Cell DK-11A As a Function of Charge and Discharge Rates (temperature, 430°C ; discharge cutoff, 0.40 V)

discharge cutoff potential of 0.40 V, the capacity density for a given charge rate decreased rapidly as the discharge current density was increased. However, when high charge and high discharge current densities were used, the lithium utilization was better than when low charge and high discharge current densities were used. These results suggest that at high charge rates the lithium is "piling up" in the half of the electrode nearest the lithium electrode. This anomaly is not understood. When the discharge cutoff potential was increased from 0.40 to 0.70 V vs. lithium, the performance of the Li-Al electrode was improved by about 25%.

The effect of electrode thickness was evaluated by comparing the performance of Cell DK-11A with that of Cell DK-6, which had a similar Li-Al electrode except that the thickness was 0.32 cm (ANL-75-1, p. 44). This comparison indicates that at Li-Al electrode charge and discharge rates of 0.05 – 0.10 and 0.05 – 0.20 A/cm^2 , respectively, greater lithium utilization (fraction of theoretical capacity density) is obtained with the 0.32 -cm-thick electrode (63–79%) than is obtained with the 0.64 -cm-thick electrode (20–54%)

The capacity densities of the cells under these conditions are very similar. At lower charge and discharge rates, however, the capacity density of Cell DK-11A rises rapidly and exceeds that of Cell DK-6. These results indicate that the thicker Li-Al electrode is more extensively polarized, especially during discharge, as indicated by the capacity densities at cutoff potentials of 0.40 and 0.70 V, respectively.

Cell DK-9. The Li-Al electrode of Cell DK-9 was prepared from a 0.64-cm-thick aluminum plaque and had an electrolyte volume fraction of 0.2. The theoretical capacity density was 0.91 A-hr/cm^2 (1.09 A-hr/cm^3). The capacity density of the cell was measured at charge rates of 0.05 and 0.10 A/cm^2 , discharge rates of 0.05 to 0.20 A/cm^2 , and a discharge cutoff potential of 0.40 V. The results are presented in Fig. III-2. The performance of Cell DK-9, like that of Cell DK-11A, decreased rapidly as the discharge current density was increased, and better utilization of the Li-Al electrode was obtained at high charge and discharge current densities. When the discharge cutoff potential was increased from 0.40 to 0.70 V, the capacity density attained at a charge rate of 0.10 A/cm^2 and at discharge rates of 0.05 to 0.20 A/cm^2 increased by about 25%. This increase with increasing discharge cutoff potential indicates that the Li-Al electrode in this cell is seriously polarized during discharge.

Fig. III-2. Capacity Density of Cell DK-9 as a Function of Charge and Discharge Rates (temperature, 425°C ; discharge cutoff, 0.40 V)

The performance of Cell DK-9 was compared with that of Cell DK-4, which also had an electrochemically formed Li-Al electrode with an electrolyte volume fraction of 0.20, but the electrode thickness was 0.32 cm. At a charge rate of 0.10 A/cm^2 , the lithium utilization for Cell DK-4 (44-72%) was much greater than Cell DK-9 (31-42%).

DK-19. To date, most of the electrodes in this series of cell tests have been formed by the electrochemical deposition of lithium in an aluminum structure. However, studies of pyrometallurgically prepared Li-Al electrodes (ANL-75-1, p. 42) have suggested that the performance of thick electrodes (~ 0.8 cm) is improved by the use of a porous metal (Retimet) current collector. Consequently, Cell DK-19 was operated to evaluate the performance of a thick electrode electrochemically formed in a porous iron Retimet structure. The aluminum matrix for the electrode was prepared by vibrating granular aluminum metal ($-60+80$ mesh) into a two-layer structure of iron Retimet, 0.76 cm thick $\times$ 5.1 cm in diameter, which was spot welded to the stainless steel electrode housing. A zirconia cloth was used to contain the granular metal, and stainless steel mesh screens were used on the open face of the electrode to confine the electrode. The volume fraction of electrolyte of the electrode at full charge was ~ 0.48 , and the theoretical capacity density was 0.65 A-hr/cm^2 (0.68 A-hr/cm^3).

The capacity density of Cell DK-19 remained essentially unchanged when the charge current density was increased from 0.025 to 0.050 A/cm^2 (see Figs. III-3 and III-4) but it changed markedly with change in discharge cutoff

Fig. III-3. Discharge Capacity Density of Cell DK-19 with 0.40 V Discharge Cutoff Potential (temperature, 425°C)

potential. For example, at a charge current density of 0.10 A/cm^2 and discharge current density of 0.30 A/cm^2 , the capacity density decreased from 0.315 A-hr/cm^2 to essentially zero when the discharge cutoff potential was changed from 0.70 to $0.40 \text{ V vs. lithium}$. Cell DK-19 was operated at a higher discharge current density than Cells DK-11A and DK-9 because it was felt that better utilization could be achieved with the Retimet current collector. There is no reason to assume that at charge and discharge current densities

Fig. III-4. Discharge Capacity Density of Cell DK-19 with 0.70 V Discharge Cutoff Potential (temperature, 425°C)

of 0.10 and 0.30 A/cm², respectively, Cell DK-11A or Cell DK-9 would have exhibited higher capacity densities than Cell DK-19, which yielded a capacity density of essentially zero under these conditions.

At charge current densities of 0.025 and 0.050 A/cm² and a discharge cutoff potential of 0.70 V, the performance of Cell DK-19 was superior (see Fig. III-5) to that of Cell DK-11A, which had a similar volume fraction of electrolyte (~0.4) and a similar thickness (~0.64 cm). However, at a charge current density of 0.10 A/cm², the performance

Fig. III-5. Comparison Capacity Densities of Cells DK-19 and DK-11A (discharge cutoff potential, 0.70 V)

of the two cells was very similar. Also, at the lower discharge cutoff potential of 0.40 V, the performance of the two cells was very similar. Thus, the addition of Retimet to the electrode structure did not improve the performance of the thick (~ 0.8 cm) Li-Al electrode at high charge current densities (0.10 A/cm^2). However, at lower charge current densities (0.025 and 0.050 A/cm^2), where an 0.70 V cutoff was used, the performance was markedly enhanced. Consequently, if thick Li-Al electrodes are to be used successfully in Li-Al/ FeS_2 and Li-Al/ FeS cells, the cells should be designed to allow the Li-Al electrode to be polarized by 0.40 V during discharge, which is equivalent to the 0.70 V discharge cutoff potential used in the studies reported here.

The results of these and earlier characterization studies on the electrochemically prepared Li-Al electrodes indicate that (1) the optimum electrolyte volume fraction for the electrode is near 0.2, (2) the optimum thickness of the electrode will be a function of the charge and discharge rate but will probably be in the range from 0.3 to 0.7 cm , and (3) the incorporation of porous iron current collectors into relatively thick ($>0.3 \text{ cm}$) negative electrodes should improve the performance in Li-Al/ FeS_2 cells, except at high charge current densities.

2. Cycle Life Studies of Li-Al Electrodes (W. R. Frost, J. Dorsey, D. R. Vissers)

The objectives of this study are to determine the cycle life of the presently used Li-Al alloy electrodes and to identify the factors that limit cycle life. To limit the number of variables in the investigation, the tests are being conducted in Li-Al/ LiCl-KCl/Al cells. The first variable being studied is the purity of the LiCl-KCl eutectic electrolyte.

Cell LT-1. In the first cell operated in this series (LT-1), polarographic-grade LiCl-KCl eutectic (Anderson Physics Laboratory) is being used. This electrolyte is very highly purified and has been used in nearly all the engineering cells operated at ANL. Operation of Cell LT-1 is expected to provide base-line data for evaluating the effects of electrolyte purity.

The design of Cell LT-1, a 7.6 cm welded cell, is shown in Fig. III-6. The pyrometallurgically prepared Li-Al powder had a lithium content of $52.5 \text{ at. \%}$

Fig. III-6. Configuration for Cell LT-1

(26 A-hr) and was vibratorily loaded into two layers of porous iron Retimet (0.8 cm thick) to produce an electrode with an electrolyte volume fraction of 0.48. Aluminum powder was loaded into a counterelectrode structure consisting of three layers of iron Retimet (1.2 cm thick). The complete transfer of the lithium to this electrode would give an alloy of 53.9 at. % Li and an electrolyte volume fraction of 0.51. The aluminum electrode was cycled against a lithium counterelectrode in an open cell to precondition it and to determine its performance characteristics before it was placed into the welded cell assembly.

At this writing, the cell has completed 60 cycles and 1278 hr of operation at a current density of 0.078 A/cm^2 and a cutoff potential of 0.9 V. The lithium utilization is 82% and appears to be gradually improving with operating time. Cell cycling will continue at the same current density until the lithium utilization has been markedly reduced. A postoperative examination will then be conducted on the cell to determine the cause of failure.

A second cell, LT-2, now being constructed, will be identical to LT-1, except that the LiCl-KCl electrolyte from Lithcoa Corp. will be used. This electrolyte, which is used at Lithcoa in the production of lithium metal, has been purified by partial electrolysis at 450°C , and is relatively inexpensive. In future studies, known impurities will be added to LiCl-KCl electrolyte to determine their effect on the cycle life of the Li-Al electrode.

3. Development of Alternative Lithium Alloy Electrodes (D. R. Vissers, K. E. Anderson, W. R. Frost)

The objective of this investigation is to evaluate solid lithium-metal alloys other than lithium-aluminum for possible use as the active material in the negative electrode of lithium/metal sulfide cells. Candidate alloy systems are being evaluated by comparing their performance in electrochemical cells with that of lithium-aluminum. The systems that have been studied to date are binary lithium-boron and lithium-silicon alloys, and ternary alloys of lithium with silicon, boron and aluminum (studies of lithium-boron were presented in ANL-75-1, p. 47).

Lithium-Silicon. A review of the literature suggested that a lithium-silicon "alloy" might be a suitable negative electrode material. Six lithium-silicon compounds have been identified:¹⁻⁴ $\text{Li}_{22}\text{Si}_5$, Li_4Si , Li_7Si_2 , $\text{Li}_{10}\text{Si}_3$, Li_2Si , and $\text{Li}_{13}\text{Si}_7$. The theoretical capacities of these compounds (in terms of A-hr/g and A-hr/cm³) are all higher than the corresponding values for LiAl (see Table III-1). Osborg⁵ has reported that a number of "alloys" of lithium and silicon can be prepared by heating the elements at temperatures above 600°C under vacuum. These "alloys" are solid, hard, uniform masses of metallic appearance having the following compositions: Li_6Si , Li_4Si , Li_3Si , and Li_4Si_3 (the properties of these materials are given in Table III-2). However, only one of these (Li_4Si) has been identified¹⁻⁴ as an actual Li-Si compound.

Cell DK-13. Cell DK-13 was operated to test the feasibility of forming a lithium-silicon alloy electrochemically. The cell design and electrode structure were similar to those of Cell DK-19 (described above). A

Table III-1. Theoretical Capacities of Lithium-Metal Compounds

Compound	Density of Compound, g/cm ³	Theoretical Capacity		
		A-hr/g Alloy	A-hr/cm ³	A-hr/g Al or Si
LiAl	1.75	0.79	1.38	0.99
Li ₂₂ Si ₅	1.18	2.01	2.37	4.20
Li ₄ Si	1.20	1.92	2.30	3.82
Li ₇ Si	1.29	1.79	2.31	3.34
Li ₁₀ Si ₃	1.27	1.74	2.21	3.18
Li ₂ Si	1.36	1.28	1.74	1.91
Li ₁₃ Si ₇	1.53	1.20	1.85	1.78

porous iron structure (15.6-cm² area) was loaded with 3 g of silicon, and this electrode was operated at 435°C against a liquid lithium counterelectrode. On the assumption that Li₄Si was formed at the end of the charge cycle, the Li-Si electrode would have a theoretical capacity of 11.4 A-hr (0.73 A-hr/cm²).

Table III-2. Properties of Lithium-Silicon Alloys

Possible Compound	Composition, at. % Li	Density, g/cm ³	Freezing Range, °C
Li ₆ Si	85.9	1.0	500-550
Li ₄ Si	80.2	1.17	>625
Li ₃ Si	72.9	1.40	680-700
Li ₄ Si ₃	57.4	1.72	700-750

Note: The diffusion of lithium⁶ in silicon at 700 K is reported to be 2.11×10^{-8} cm² sec⁻¹, or about two orders of magnitude greater than it is in aluminum.

Initially, 7.27 A-hr of lithium was loaded into the silicon at a current density of 0.025 A/cm² to a cutoff potential of 0.07 V (IR-free). The emf curve for this cell showed three plateaus at about 0.35, 0.28 and 0.16 V vs. lithium. The cell resistance was 0.10 ohm. When the current density was increased to 0.064 A/cm², the capacity density decreased from 0.41 to 0.32 A-hr/cm².

To examine the Li/Li-Si emf curve further, the Li-Si electrode was charged at 0.050 A/cm² to a cutoff of 0.018 V. No break in the emf curve during this charge cycle could be observed that indicated a transition between

the Li-Si potential and that of liquid lithium. During the subsequent discharge, however, five plateaus were observed. The first plateau, near zero voltage, apparently resulted from the presence of lithium in the Li-Si electrode. The second plateau occurred at about 0.053 V. The remaining three were the plateaus described above. The plateaus (other than that of Li) suggest the presence of four different compounds. The total capacity discharged over the four plateaus was about 10.6 A-hr, (0.68 A-hr/cm²), suggesting that a compound near Li₁₅Si₄ is probably being formed in the electrode at the end of charge.

In an effort to identify the four compounds, the cell was cycled at a current density of ~0.016 A/cm². The Li-Si electrode discharge curve suggests that the compounds are Li₁₅Si₄, Li₃Si, Li₂Si and probably Li₃Si₂. The charge curve suggests that the compounds are Li₇Si₆, Li₇Si₄, Li₅Si₂ and Li₇Si₂. Further studies are being conducted in Cell DK-13 to identify these compounds.

Cell DK-17. The results described above suggested that (1) at charge and discharge rates of 0.064 A/cm², only about 50% of the lithium is utilized, if one assumes that Li₄Si is formed; and (2) the apparent composition of the polarized electrode material is near Li₂Si (theoretical lithium capacity, 1.91 A-hr/g Si). On the basis of Li₂Si formation, the DK-13 electrode would have had an apparent theoretical capacity of 5.72 A-hr (0.367 A-hr/cm²) at 0.064 A/cm². Consequently, in Cell DK-17, which was similar in design to Cell DK-13, the silicon loading of the Li-Si electrode was increased from 3 to 6 g, which would give a theoretical capacity of 11.44 A-hr (0.734 A-hr/cm²) on the basis that the material found in the electrode has an average lithium composition of Li₂Si.

The achievable capacity of DK-17 was somewhat better than that of DK-13 at the lower current densities. For example, at 435°C and charge and discharge current densities of 0.032 A/cm², the capacity was 8.5 A-hr (0.545 A-hr/cm²) with charge and discharge cutoff potentials of 0.05 and 0.50 V, respectively. At 0.064 A/cm², the capacity decreased to about 5-6 A-hr, or about the same as that achieved in Cell DK-13. When the temperature was increased to 500°C, the achievable capacity, at 0.064 A/cm² and cutoff potentials of 0.05 and 0.50 V, increased to 13 A-hr (0.833 A-hr/cm², which represents an increase of more than 100% over the achievable capacity at 435°C.

The capacity density of Cell DK-17 was next determined at discharge current densities of 0.13, 0.20, 0.30, and 0.40 A/cm², with a charge rate of 0.064 A/cm² and a temperature of 500°C. The charge and discharge cutoff potentials were increased to 0.15 and 0.70 V, respectively. The results are presented in Fig. III-7. At discharge current densities of 0.10 A/cm² or more, the capacity density is markedly reduced when the discharge cutoff potential is 0.40 V rather than 0.70 V; this finding indicates that the Li-Si electrode is significantly polarized on discharge.

In summary, the Li-Si electrode may have some potential for use as the negative electrode in Li/FeS_x cells. The achievable capacity density of the Li-Si system at 425°C is greater than the Li-Al system at current densities

Fig. III-7. Capacity Density of Lithium-Silicon Cell at 500°C

of 0.032 A/cm² or less, but decreases rapidly as the current density is increased. The performance is improved at 500°C. The Li-Si alloy system appears to contain four discrete compounds, which produce four emf plateaus during charge and discharge. The potentials of the four plateaus are at 0.35, 0.28, 0.16 and 0.053 V vs. Li. The Li-Si electrode tends to polarize more extensively than the Li-Al electrode, especially during charge. The internal resistance of the lithium-silicon electrode is greater than that of the lithium-aluminum electrode. If a practical Li-Si electrode is to be developed, techniques are needed for improving the lithium-loading properties during charging.

Studies are being continued on the characterization of the lithium-silicon compounds formed during cell operation and on further evaluation of the use of Li-Si alloys as negative electrodes in Li/FeS_x cells.

Lithium-Aluminum-Boron. The cell design used in this study was similar to that used in Cells DK-13 and DK-17. A ternary lithium-aluminum-boron alloy was prepared by electrochemical deposition of lithium in 5 g of AlB₂ contained in a porous iron Retimet structure. The composition of the alloy was assumed to be Li₂AlB₂; on this basis, the theoretical capacity density of the cell was 0.353 A-hr/cm² (0.785 A-hr/cm³). The performance of the ternary alloy as an electrode material was evaluated by cycling the cell at various current densities. Although lithium utilization was reasonably good at a charge rate of 0.032 A/cm² and discharge rates of 0.032 to 0.200 A/cm², cycling at a current density of 0.064 A/cm² produced a rapid decrease in utilization thereby indicating that the electrode has very poor charging characteristics. No further work on this system is planned.

Lithium-Silicon-Boron. An attempt was made in Cell DK-18 to form a ternary lithium alloy from 3.5 g of SiB₄. The SiB₄ was loaded into an electrode structure similar to that of Cell DK-16. The capacity density at ~430°C was <0.040 A-hr/cm² at a current density of 0.016 A/cm². The SiB₄ appears to be nonreactive with lithium under the conditions of interest for cell operation. No further work on this system is planned.

Lithium-Aluminum-Silicon. In Cell DK-15, a ternary Li-Al-Si alloy was electrochemically formed at $\sim 435^{\circ}\text{C}$ from 4.6 g of crystalline Al-50 at. % Si that had been vibrationally loaded into a porous electrode structure. The composition of the active material in the electrode when fully charged was assumed to be Li_4AlSi , which corresponds to a theoretical capacity density of 0.57 A-hr/cm^2 (1.12 A-hr/cm^3). When the cell was cycled at 0.016 A/cm^2 , emf plateaus were observed at about 0.64, 0.35, 0.14 and 0.05 V, and $\sim 8 \text{ A-hr}$ of lithium could be cycled with an ampere-hour efficiency of near 95%. When the cell was operated at a current density of 0.064 A/cm^2 , about 6.5 A-hr of lithium was cycled (0.415 A-hr/cm^2) with an ampere-hour efficiency of near 99%. At a charge rate of 0.064 A/cm^2 and a discharge rate of 0.300 A/cm^2 , approximately 4.8 A-hr of lithium (0.3 A-hr/cm^2) could be cycled with an ampere-hour efficiency of $>95\%$. These results indicate that the Li-Al-Si system shows some promise for use in the negative electrode of high-energy Li/Fe_x cells, but further studies are needed to verify this conclusion.

C. Particulate Loading of Porous Current Collector Structures
(D. R. Vissers, K. E. Anderson, R. Stark,* J. Dorsey)

The proposed use of electrodes with porous current collector structures (e.g., iron or nickel Retimet or vitreous carbon foam)** may require the development of techniques for vibratorily loading the powdered materials (Al, Li-Al, FeS, or FeS_2) into the porous structure. To achieve optimum electrode performance, a specified amount of active material must be distributed uniformly within the structure, and the uniformity must be maintained during both the cell fabrication procedure and subsequent transport of cells and batteries. The latter consideration is particularly important for electrodes that have a vertical orientation. The loading requirements, in terms of volume fractions of active material in the porous matrix, vary considerably with the type of material: 0.60-0.80 for Li-Al, 0.31-0.41 for discharged Li-Al (i.e., Al metal), 0.25-0.35 for FeS, and 0.25-0.30 for FeS_2 . These loading requirements have been determined experimentally and are indicative of electrode systems in which the volume fraction of the electrode occupied by active material changes markedly during cell cycling. In going from the charged state to the discharged state, the volume change is -48% for Li-Al, +186% for FeS, and +258% for FeS_2 .

Experimental studies of vibratory loading techniques, to date, indicate that the loading requirements for Li-Al and aluminum in iron Retimet can be achieved. However, those for the FeS and FeS_2 cannot be achieved by using the powders alone because their physical properties are not suitable. Studies are currently being initiated to determine whether the desired loadings of FeS and FeS_2 can be obtained by blending the materials with LiCl-KCl eutectic salt before loading. Initial results appear promising.

D. Development of Positive Electrodes

A number of positive electrode designs, using both FeS_2 and FeS as the active materials, show promise of meeting the performance goals of cells for off-peak energy storage and electric vehicle propulsion batteries. From a

* Industrial Participant from C & D Batteries, Inc.

** These porous materials have void volumes of 90 to 95%.

consideration of developing batteries with the highest specific energy, FeS_2 is preferred over FeS because the theoretical specific energy is higher (650 W-hr/kg compared with 458 W-hr/kg for FeS , with Li-Al as the negative electrode material). However, FeS continues to be of interest because of the possibility of using much cheaper metallic current collectors in the positive electrode. (Molybdenum is generally used for FeS_2 electrodes.) The lower performance of the FeS electrode may be offset by a lower battery cost, resulting from lower cost materials, reduced corrosion, and/or longer life.

Recent efforts have emphasized the following areas: (1) development of low-cost electrode structures and manufacturing techniques that can be applied to both FeS and FeS_2 electrodes, (2) development of low-cost current collectors, (3) characterization of electrode performance, (4) development of rectangular electrodes that are operated in a vertical configuration, and (5) studies of electrode compositions.

1. Small-Scale Iron Sulfide Electrodes with Porous Current Collector Structures
(E. C. Gay, F. J. Martino)

Performance measurements of small-scale iron sulfide electrodes fabricated by vibrational loading of the active material in porous current collector structures were continued during this reporting period. These structures appear to provide a means of homogeneously distributing the iron sulfide throughout the positive electrode. The present investigations have centered on the development of vitreous carbon foam current collectors for the FeS_2 electrode and porous iron current collectors for the FeS electrode.

FeS_2 Electrodes. In the preceding semiannual report (ANL-75-1, p.63), Cell S-74, which had a positive electrode of carbon foam vibratorily loaded with FeS_2 -15 wt % CoS_2 , demonstrated a performance that met the requirements for off-peak energy storage application. Cell S-74 had cylindrical electrodes with an area of 15.6 cm^2 , and the cell was operated in the horizontal position. On the basis of the high performance of the FeS_2 electrode of this cell, a similar electrode with increased area (46.5 cm^2) was constructed and tested in Cell S-77.

The theoretical capacity for the positive electrode of Cell S-77 was 86.5 A-hr, based on the FeS_2 - CoS_2 mixture. The volume fraction electrolyte in the charged positive electrode was 0.64. The negative electrode consisted of a structure of iron Retimet vibratorily loaded with pyrometallurgical Li-Al powder. The theoretical capacity of the Li-Al electrode was 58.1 A-hr. This cell was designed to operate on the upper plateau ($\text{FeS}_2 \rightarrow \text{FeS}$). It was expected that the Li-Al utilization would be less than 74% of the theoretical Li-Al capacity.

Cell S-77 has been operated for over 4250 hr and 180 cycles at 0.075 A/cm^2 . As shown in Fig. III-8, the high performance achieved in Cell S-74 was sustained in Cell S-77. A conservative charge cutoff voltage, 2.22 V (IR-free) was used in Cell S-77 during the operating period shown in Fig. III-8, to prevent the formation of liquid lithium at the negative electrode and possible subsequent reaction with the boron nitride separator. In Cell S-74, a charge cutoff of 2.32 V (IR-free) had been used. When one

considers the expected decrease in capacity with lower charge cutoff, no loss in performance is seen as a result of the cell scale-up. The Li-Al

Fig. III-8. Comparison of Li-Al Utilizations for Cells S-74 and S-77 (ANL Neg. No. 308-4024)

utilization was slightly greater than 80% at a discharge current density of 0.075 A/cm² (charge cutoff, 2.22 V, IR-free) and decreased to about 20% at 0.33 A/cm². Thus, a slightly greater utilization of the active material in the positive electrode (57% of the FeS₂-CoS₂ theoretical capacity) was achieved at 0.075 A/cm² than was expected for this electrode with an upper plateau design. This performance was sufficient to meet the goals for the off-peak energy storage battery.

Operation of Cell S-77 was continuing at the writing of this report. This cell is presently being used in the lifetime and cycle-life study of Li-Al/FeS₂ cells. Figure III-9 demonstrates the high performance of this cell over the entire operating period and also the good lifetime and cycle-life characteristics of the electrodes. The discharge cutoff voltage was maintained throughout the period at 0.7 V. The maximum charge cutoff was about 2.35 V (IR-free). The cumulative ampere-hour efficiency was greater than 99%.

Operation of Cell S-77 will be continued for 5000 hr or until a significant decline in performance occurs. To date, no indications of performance decline have been observed.

FeS Electrodes. Several cells have also been operated to determine the performance of positive electrodes in which FeS is vibratorily compacted into porous current collector structures. Cells S-75 and S-76, both of which had positive electrodes of FeS-19.8 wt % CoS_2 , were described previously

Fig. III-9. Performance History of Cell S-77

(ANL-75-1 p. 63). The cobalt sulfide was used in an attempt to reduce the large volume increases observed in previous cells with FeS electrodes and to increase the electronic conductivity of the positive electrode. The positive electrode of Cell S-75 had an iron housing, carbon fabric as a particulate retainer, and an iron Retimet current collector (95% porosity), whereas the positive electrode of Cell S-76 had a porous graphite housing, carbon fabric as a particulate retainer, and a vitreous carbon foam as the current collector. The positive electrode of Cell S-78 was very similar to that of Cell S-75, except that no CoS_2 was added to the FeS. The negative electrodes in all three cells consisted of pyrometallurgical Li-Al powder vibratorily compacted into porous iron structures.

These cells, which were operated at 450°C , were charged and discharged at 0.064 A/cm^2 . The discharge cutoff was 0.7 V (IR-included) for all of the cells. For Cells S-75 and S-78, which had iron Retimet current collectors, a charge cutoff of 1.75 V (IR-included) was used to avoid reaction between the iron current collectors and the electrolyte. However, for Cell S-76, with the vitreous carbon current collector, a higher charge cutoff (1.9 V , IR-included) could be used.

Descriptions of the electrodes and a summary of the performance of these cells are given in Table III-3. The highest utilization was achieved

Table III-3. Performance^a of FeS Electrodes
with Porous Current Collectors

Cell No.	Positive Electrode				Charge Cutoff Voltage, V	% of Theor. Capacity Density ^b	Avg. Discharge Voltage, V
	Composition, wt %	Current Collector	Area, cm ²	Thickness, cm			
S-75	FeS-19.8 CoS ₂	Iron Retimet	25.7	0.78	1.75	22.4	1.18
S-76	FeS-19.8 CoS ₂	Vitreous Carbon Foam	15.6	1.3	1.9	48.3	1.16
S-78	FeS	Iron Retimet	25.7	0.78	1.75	29.9	1.08

^a 0.064 A/cm² charge and discharge rate; 0.7 V (IR-included) discharge cutoff; 450°C operating temperature.

^b Based on amount of FeS and CoS₂ in Cells S-75 and S-76 and the amount of FeS in Cell S-78.

with Cell S-76, which had a vitreous carbon foam current collector in the positive electrode. A capacity density of 0.752 A-hr/cm^2 (70% of the Li-Al theoretical capacity density, and 48% of the FeS-CoS_2 theoretical capacity density) was measured at a discharge current density of 0.064 A/cm^2 . In Cell S-78, the utilization of the FeS electrode, which had no CoS_2 additive but had an iron Retimet current collector, was slightly better than that of Cell S-75 with the FeS-CoS_2 mixture and iron Retimet current collector, but the average discharge voltage was lower. For these thick electrodes, 0.78 cm to 1.3 cm, the 1.75-V charge cutoff appears to be too low to completely recharge these cells. Thus, iron Retimet current collectors do not appear to be advantageous for thick, FeS electrodes; they may be suitable, however, for thinner electrodes.

2. Vertical, Rectangular FeS_2 Electrodes with Porous Current Collector Structures (F. J. Martino, E. C. Gay)

The performance of FeS_2 electrodes with porous current collector structures of vitreous carbon foam was evaluated further in two vertical prismatic cells. These cells each had a single positive electrode and two negative electrodes. The electrodes of Cell S-80 were similar to those of a smaller cell (S-74), which had met the performance goals for the off-peak energy storage battery, and the electrodes of Cell S-81 were similar to those of a smaller cell (S-69A) which had met the performance goals for the electric vehicle propulsion battery. (Cells S-74 and S-69A were described in ANL-75-1, pp. 59 and 63). The physical characteristics of Cells S-80 and S-81 are described in Table III-4. The active material in the positive electrodes (FeS_2 -15 wt % CoS_2) was loaded into the vitreous carbon while the electrode

Table III-4. Physical Characteristics of Electrodes of Cells S-80 and S-81

	S-80	S-81
Positive Electrode		
Active Material	FeS_2 -15 wt % CoS_2	FeS_2 -15 wt % CoS_2
Current Collector	Vit. Carbon Foam	Vit. Carbon Foam
Area, ^a cm^2	193.6	193.6
Thickness, cm	2.54	0.94
Vol. % Electrolyte	64	64
Theoretical Capacity		
A-hr	360	133
A-hr/ cm^2	1.86	0.69
Negative Electrodes		
Active Material	$\text{Li}_{1.04}\text{Al}$	$\text{Li}_{1.02}\text{Al}$
Current Collector	Fe Retimet	c
Area, ^b cm^2	193.6	168.4
Thickness, cm	1.6	0.32
Vol. % Electrolyte	45	20
Theoretical Capacity		
A-hr	256	68
A-hr/ cm^2	1.3	0.4

^aArea of both faces.

^bTotal for two electrodes (one face each).

^cElectrode was electrochemically formed with 2 wt % SS current collector.

structures were in a horizontal position, as had been done in the earlier, smaller cells. A schematic of Cell S-80 is shown in Fig. III-10; the configuration of Cell S-81 was similar to this except thinner electrodes were used.

Fig. III-10. Vertically Oriented Prismatic Cell S-80

A major change in the design of cells S-80 and S-81, as compared with the designs of past cells having two negative electrodes and a single positive electrode, was the use of two separate compartments in the positive electrode. This change was made to prevent possible electrode mismatch, which might occur if the cell resistance between one negative electrode and the positive electrode was slightly less than that between the other negative and the positive electrode. With a single-compartment positive electrode, this mismatch might cause excess lithium to be deposited during charge at the negative electrode with the lower resistance. The result would be a lithium-rich composition in one of the negative electrodes, which could cause a deterioration of the BN separator and subsequent short-circuit of the cell. The vitreous carbon foam structure and graphite housing of the positive electrode for Cell S-80 is shown in Fig. III-11. A cross-sectional view of the assembled positive electrode is shown in Fig. III-12.

Cell S-80 is presently operating satisfactorily. The cell has normally been operated at a charge rate of 0.025 A/cm^2 , a charge cutoff voltage of 2.33 V (IR-included), and discharge rates of 0.050 and 0.075 A/cm^2 .

Fig. III-11. Vitreous Carbon Foam and Graphite Housing for Positive Electrode of Cell S-80.

The maximum utilization of the active material in the positive electrode was about 32% of the $\text{FeS} - \text{CoS}$ theoretical capacity at a discharge rate of 0.075 A/cm (about 9-hr rate). This corresponded to a Li-Al utilization of about 45% of theoretical, as compared with 70% of theoretical for Cell S-77 at

Fig. III-12. Cross-Sectional View of Assembled Positive Electrode for Cell S-80.

0.075 A/cm² and a 2.53 V IR-included charge cutoff. The charge cutoff voltage of Cell S-80 will soon be increased to determine the effect on performance.

The present performance of Cell S-80 is considered to be quite good for the first scaled-up, vertical, prismatic cell of this type. Further testing is required to determine if the high performance demonstrated in the smaller, cylindrical electrodes operated in the horizontal position can be sustained in the larger, vertical prismatic cells.

Cell S-81 is also operating satisfactorily at present. This cell has been operated at a charge rate of 0.026 A/cm² and discharge rates of 0.026 to 0.107 A/cm². At a discharge rate of 0.064 A/cm² and a charge cutoff of 2.2 V (IR-included), 32% of the FeS₂-CoS₂ theoretical capacity was obtained. This corresponded to 63% of the Li-Al theoretical capacity density, as compared with about 95% utilization for Cell S-69A at a discharge rate of 0.064 A/cm² and a charge cutoff of 2.35 V (IR-included). At a discharge current density of 0.107 A/cm², 53% of the Li-Al theoretical capacity density was obtained. The operating conditions of Cell S-81 will soon be changed to determine the effect on Li-Al utilization of increasing the charge cutoff to 2.35 V.

Further studies in this area will be directed toward determining the factors that cause the lower performance for vertical, rectangular electrodes, compared with that of the horizontal, cylindrical electrodes operated previously.

The use of FeS₂ as the active material requires inert current collector materials other than common metals such as iron, copper, nickel, stainless steel, etc., which react chemically with FeS₂ at the cell temperature. An integral part of the electrode development studies is the continuing evaluation of current collector materials. In the cells described above, vitreous carbon was the major current collector material used in the FeS₂ electrodes. The cell described below (PR-2) was operated to evaluate (1) a composite structure of molybdenum and vitreous carbon foam as a current collector and (2) a technique for loading the structure with active material while it is a vertical position.

The current collector structure was constructed as follows. A piece of perforated molybdenum sheet (0.25 cm thick) was carbon-cemented between two 0.5-cm-thick sheets of vitreous carbon foam (98% porosity); this structure was then covered with carbon cloth for particulate containment and inserted into a molybdenum housing faced with molybdenum mesh. Difficulty was encountered in fabricating the molybdenum housing: electron beam welding of the thin (0.25 mm) molybdenum resulted in embrittlement of the structure.

An FeS₂ particle size of 180-432 μ m was selected to restrict vibratory loading of the vitreous carbon foam to 60% of its void volume. The material was vibrated into the foam from the top edge. After loading, the electrode was enclosed in a boron nitride cloth, and placed in an open cell with two electrochemically formed Li-Al negative electrodes.

The performance of Cell PR-2 was poor. An electrical short developed early in cell operation. Degassing, which had been a major problem in start-up, was believed to have contributed to the electrical short across the porous boron nitride separator. Post-test examination did not reveal any mechanical shorting. X-ray radiographs of the positive FeS_2 electrode showed considerable slumping and settling of the active material within the vitreous carbon foam structure. A comparison of the performance of Cell PR-2 with that of Cell S-81 described above, indicates that the technique of vertical vibratory loading of the vitreous carbon foam with FeS_2 powder is presently very much inferior to the technique of horizontal vibratory loading. As discussed in Section III. C of this report, considerable effort is being directed to studies of vibratory loading of active powders in porous current collector structures. Results from these investigations are essential to the development of a successful technique for vertical vibratory loading of porous current collectors for positive electrodes

3. Vertical, Rectangular FeS Electrodes Formed by Hot-Pressing
(N. P. Yao, W. G. Howard,* T. D. Kaun, and W. A. Kremsner)

Studies of FeS electrodes formed by hot-pressing are also part of the effort to develop vertical iron sulfide electrodes in which a uniform dispersion of active material is maintained within the electrode structure. Emphasis is placed on attaining a high capacity, in terms of A-hr/cm³ and A-hr/g, and a long cycle life, as well as on developing compact cell designs and fabrication methods that are suitable for manufacturing.

In the present studies, the procedure used for fabricating hot-pressed electrodes is as follows. The active material was FeS containing 13 wt % CoS as an additive. A homogeneous mixture (particle size, <177 μm) of 80 wt % active material and 20 wt % LiCl-KCl (58 vol % active material, 42 vol % electrolyte) was prepared by several cycles of melting the salt and cooling and grinding the mixture. On the basis of past tests of horizontal electrodes, this percentage of electrolyte was near the optimum for electrodes 0.3-0.7 cm thick, with respect to efficient utilization and achievable capacity per unit volume. To form an electrode compact, the mixture of FeS and LiCl-KCl was hot-pressed onto an iron current collector in a rectangular die for about 2 hr at 370°C and 26 kg/cm² pressure. The pressed compacts were generally flat and strong. A compact was then inserted into an iron screen housing having a porous zirconia cloth for particle retention; this assembly was entirely wrapped in a porous boron nitride cloth, which served as the interelectrode separator.

Cell PR-1, the first cell in this series, had prismatic electrodes mounted in a vertical configuration, with one central FeS electrode between two Li-Al electrodes. The two Li-Al electrodes, which were electrochemically prepared, were 12.7 cm high, 7.6 cm thick, and 0.1 cm thick (193 cm² total area, one face of each electrode). The total capacity was 90 A-hr for the two electrodes. The FeS electrode was also 12.7 cm by 7.6 cm (193 cm² area, both faces) and was 0.6 cm thick. The capacity was 58 A-hr.

* An industrial participant from Gould Inc.

The electrical performance of the FeS electrode in Cell PR-1 was generally stable and comparable to that of the horizontal cylindrical electrodes previously investigated. Typical performance data during discharge are shown in Table III-5. The decrease in percent utilization of FeS at 450°C may have been due to temperature gradients in the cell; this possibility is being investigated. However, the data were reproducible over the entire operating period of 1400 hr and 88 cycles, and the coulombic efficiency was generally near 100%, except for temporary electrical shorts between the electrodes in the open cell. For compact sealed cells, total electrical insulation between the electrodes would be a necessary design feature.

Table III-5. Performance of a Hot-Pressed Electrode in a Prismatic Li-Al/FeS Cell^a

Discharge Current, A	% FeS Utilization		Average Cell Voltage, V	
	450°C	530°C	450°C	530°C
5	55	97	1.15	1.16
10	-	83	-	1.10
15	-	77	-	1.00
20	32	68	0.90	0.94

^a Discharge Cutoff Voltage: 0.7 V (IR-included)

From post-test examination (X-ray radiographs and metallographic analysis) of the particle-size distribution in the electrodes, it was concluded that the current (or reaction) distribution was nonuniform, both horizontally and vertically. The most reactive zones corresponded to the interfacial and upper portions of the electrodes. A cross section of the Cell PR-1 is shown in Fig. III-13. Of principal concern was the possible settling or slumping of the positive electrode material, *i.e.*, the particles of FeS or iron in the electrolyte. However, macroscopic and metallographic examinations of the electrode showed no apparent slumping of the active materials. As previously observed in horizontal cylindrical cells, swelling of the electrodes, which often resulted in bulging of the cell housing, was also manifested in the prismatic cell. For example, the FeS electrode swelled considerably--to about one and one-half times its initial thickness. Methods of minimizing electrode swelling by use of steel restraining plates are being investigated.

The results for Cell PR-1 indicate that the hot-pressing technique may be suitable for the fabrication of vertical positive electrodes for prismatic cells. Although excellent electrical performance has been attained, efforts are being continuing to optimize the performance of the FeS electrode by means of modifications in electrode design and assembly procedures.

Fig. III-13. Cross Section of Cell PR-1 after Operation for 1400 hr and 88 Cycles

4. Evaluation of Coated Metal Current Collectors for Iron Sulfide Electrodes
(N. Koura,* J. E. Kincinas, J. P. Yao)

The objective of these investigations is to develop low-cost metal current collectors that are stable in FeS_2 (and also FeS) electrodes. The current collector types that are being studied consist of appropriate forms of iron (or stainless steel) substrates that are coated with nitrides, carbides, or borides of titanium, tantalum, niobium, vanadium, iron, or chromium.

Thermodynamic calculations of the free energy of reactions of these materials with FeS_2 , FeS and Li_2S (see ANL-75-1, p. 74) had indicated that TiN , TiC , TaC , Nb_2C , VC , and FeB would be chemically stable at the cell operating temperature. Subsequent cyclic voltammetric studies had shown that all the materials, with the exception of VC , were stable in the presence of FeS_2 and LiCl-KCl electrolyte (VC appeared to react chemically with FeS_2).

The coating materials TiN and FeB are presently being studied. Evaluations of these current collector materials are being conducted in Li-Al/FeS_2 cells.

TiN -Coated Current Collector. A structure of an Armco iron mesh and rod served as the current collector substrate and was coated with TiN . The coating was prepared** by a commercial vapor-plating technique ($\text{TiCl}_4 + \text{H}_2 + \text{N}_2$, at 1050°C). The coated current collector structure was incorporated

* Resident Research Associate from Tokyo University of Science, Japan.

** By Teledyne Firth Sterling Co., Pittsburgh, PA.

in an FeS_2 electrode and tested in a Li-Al/ FeS_2 cell. A preliminary examination after 200 hr and 8 cycles showed that TiN was stable in the cell test, but because of an inadequate coating (nonuniform coating film, 2-20 μm thick, with some porosity), the iron substrate showed a gradual reaction with FeS_2 . A post-test metallographic examination showed that a substantial amount of iron substrate had been dissolved, while the TiN coating had remained intact. Tests are now under way to evaluate the same type of current collector structure having a thicker TiN coating.

FeB-Coated Current Collector. No commercial method of coating iron (or stainless steel) with FeB is presently available. Consequently, initial efforts were directed toward evaluating a procedure for the deposition of boron on iron in a molten salt bath to form the FeB coating. Both mild steel and Type 304 stainless steel rods served as the substrates and both electrodeless and electrolytic deposition methods were investigated. The molten salt bath was a mixture with the composition (in wt %) BaCl_2 (55.5)- NaCl (23.4)- $\text{Na}_2\text{B}_4\text{O}_7$ (17.8)- B_4C (3.3) maintained at a temperature between 900 and 1000°C.

The variables investigated in the deposition were temperature, plating time, and also, in the case of electrolytic deposition, current density. In the electrolytic deposition, the substrate was the cathode and a cylindrical molybdenum mesh served as the anode. The quality of the deposit was examined metallographically and sometimes identified by X-ray diffraction analysis.

Generally, the type of substrate played an important role in the quality of the deposit. For example, a good quality coating was difficult to obtain with the mild steel substrate by either the electrodeless or electrolytic method or by changes in the variables. The coatings were substantially porous, and the test rods essentially exhibited the oxidation potential of iron, *i.e.*, about 2.1 V *vs.* $\text{Li}^\circ/\text{Li}^+$. The use of Type 304 stainless steel rod as the substrate improved the quality of deposit significantly. Of the two deposition methods, the electrolytic method yielded generally superior deposits, which were both uniform and dense. Investigation of variables in the electrolytic deposition showed that a current density of 40 mA/cm^2 and a deposition time of 20 min at 900°C appeared to be near optimum. The oxidation potential of the FeB-coated rod was about 2.4 *vs.* $\text{Li}^\circ/\text{Li}^+$.

More recently, investigations have been conducted of the deposition of boron on expanded stainless steel mesh, which is the actual form of current collector structure in use. Excellent coatings have been obtained by the electrolytic method, with similar optimum conditions for deposition, namely, 50 mA/cm^2 current density for 20 min at 900°C. A cross section of the FeB-coated mesh is shown in Fig. III-14. Endurance tests of the FeB-coated current collector in actual Li-Al/ FeS_2 cells is now under way.

5. Study of Metal Sulfide Additives for FeS_2 Electrodes (N. P. Yao, N. Koura, J. E. Kincinas)

Preliminary test results on the addition of Co_2S_3 to FeS_2 electrodes and the addition of Cu_2S to FeS electrodes have been encouraging with respect to improving the performance of these electrodes. The effective conductivity

Fig. III-14. Metal Boride Coating Produced on Expanded Stainless Steel Mesh by Electrolytic Technique (deposition conditions: 50 mA/cm², 20 min, 900°C)

of the FeS₂ electrode is improved by the cobalt sulfide additive, with consequent increase in the utilization of the active material. A series of tests was therefore initiated to systematically study the effects of various metal sulfide additives on the performance of FeS₂ electrodes. The screening tests are now nearly complete. These tests were conducted in cells having positive electrodes of FeS₂ plus 15 mol % of the following additives: TiS₂, CoS₂, V₂S₃, Cr₂S₃, MnS, CdS, CaS, ZnS, Ce₂S₃, and NiS. An FeS₂ electrode having no additive was also included in this series to provide a baseline for evaluation of electrode performance.

The test material, FeS₂ and 15 mol % additive, was contained in zirconia fabric supported by a molybdenum-mesh housing. Each electrode had an area of 20 cm² and a thickness of about 0.75 cm. A layer of molybdenum mesh within the electrode served as the current collector. The theoretical capacity of the electrodes (including the capacity of the additives) varied between 10 and 12.5 A-hr. The electrode separator was BN, and the negative electrode was electrochemically formed Li-Al. The Li-Al electrode had an excess capacity, *i.e.*, 20 A-hr, to allow evaluation of the capacity-limited FeS₂ electrode. Each cell was cycled at three current densities (0.05, 0.10, and 0.15 A/cm²) and two temperatures (400 and 450°C). Each variable was tested over several cell cycles to assure reproducibility of capacity and voltage. Generally, each cell was operated for a total of 20 to 40 cycles and 300 to 500 hr.

At 0.05 A/cm² current density, the extent of benefit of an additive on electrode performance varied from nearly none to a significant amount. However, at the higher current density of 0.15 A/cm², all additives improved the electrode performance (primarily the utilization of active material). The results of these tests are summarized in Table III-6, as percent improvement in utilization over an FeS₂ electrode containing no additive. Also given in the table are the resistivities of the additive sulfides.

Table III-6. Effect of Sulfide Additives on the Performance of FeS₂ Electrodes (0.15 A/cm², 450°C)

Additive (15 mol %)	Resistivity of Additive at 450°C, ohm-cm	Percent Improvement in FeS ₂ Utilization
Ce ₂ S ₃	5 x 10 ⁻⁴	65
MnS	10	52
NiS	1.6 x 10 ⁻⁴	52
CoS ₂	2.2 x 10 ⁻⁴	46
Cr ₂ S ₃	0.1	40
V ₂ S ₃	100	37
ZnS	2 x 10 ⁻⁶	33
CdS	10	24
TiS ₂	1.0 x 10 ⁻²	21
CaS	-	18

Of the additives studied, Ce₂S₃, MnS, NiS, and CoS₂ appear to be particularly promising. Discharge curves for the electrodes containing these additives showed stable upper voltage plateaus, and the discharge capacities were insensitive to increases in current. In the absence of additive, the FeS₂ electrode was polarized significantly with increasing current, thereby limiting the discharge capacity of the upper voltage plateau. The resistivity values in Table III-6 indicate that the lower resistivity of an additive, by itself, cannot explain the observed improvement in FeS₂ electrode performance. Generally, the voltage and discharge capacity of the lower voltage plateaus were nearly the same for the FeS₂ electrodes with and without the additives. With the exception of ZnS, the additives produced very little improvement in performance on the lower voltage plateau. The effect of temperature on utilization also varied considerably for the various electrodes.

Further studies are needed to understand the effects of metal sulfide additives on the performance of iron sulfide electrodes. Post-test metallographic examinations of the electrodes from this study have shown the existence

of new intermediate reaction phases, which have not yet been identified. Future efforts will be directed toward the determination of optimum compositions of electrodes containing Ce_2S_3 , MnS , NiS , and CoS_2 and the metallographic identification of the reaction phases in the FeS_2 electrodes containing additives.

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IV. MATERIALS TESTING AND FABRICATION (J. E. Battles, R. O. Ivins)

The fabrication of various cell components such as electrical feedthroughs, insulators, electrode separators, current collectors, and cell housings requires a variety of metallic and ceramic materials. Because of the corrosiveness of the environment of Li-Al/metal sulfide cells and the need for lightweight, low-cost components, extensive evaluations of materials are required for the selection of materials suitable for use in the various cell components. This report discusses not only the corrosion testing of potentially useful materials of construction, but also the fabrication and evaluation of electrical feedthroughs, development of ceramic insulators, studies of electrode separators, and studies of the Li-Al phase diagram.

A. Electrical Feedthrough Development (K. Myles, T. W. Olszanski, W. D. Tuohig*)

The electrical feedthrough required for the Li-Al/metal sulfide cells must be hermetically tight, lightweight, compact, inexpensive, and compatible with the cell environment. Two general types of feedthroughs are under development: (1) a mechanical compression type and (2) a bonded type.

1. Mechanical Compression-Type Feedthrough

The development of the prismatic cell concept has, to some degree, eased the restrictions placed on the design of the mechanical compression-type feedthrough. For example, the internal parts of the feedthrough are no longer in direct contact with the electrolyte, the height and size requirements for the feedthrough are not as stringent, the outside of the feedthrough is surrounded by an inert-gas atmosphere. These modifications allow a reduction in the requirements for leak-tightness and also increase the possibility that a mechanical compression-type feedthrough can be developed to meet these requirements. For these reasons, and because the mechanical feedthrough is expected to have a substantially lower cost and fewer materials-compatibility problems, compared with a bonded-type feedthrough, a renewed effort is being expended to develop a suitable mechanical feedthrough,** and several types of designs are being considered.

On the basis of the satisfactory performance in engineering cells of the Conax-type feedthrough, a compression feedthrough that is similar in many respects to the Conax has been designed; the main objectives of the design changes were to decrease the size and weight and to improve assembly procedures. The internal components are similar to those of the Conax feedthrough, and the BN powder sealant is introduced and compacted in the same manner as described previously (ANL-75-1, p. 76). In this procedure, a pre-weighed charge of BN powder is injected into the feedthrough and compacted in a single step; the apparatus for accomplishing this is shown schematically in Fig. IV-1.

* Materials Science Division, ANL.

** The Materials Group has the overall responsibility for the development of a feedthrough; however, valued assistance has been received from J. E. A. Graae, consultant to the Battery Program, and M. A. Slawicki, of the Installations Group, Chemical Engineering Division, ANL.

Fig. IV-1.

Apparatus for Compacting BN Powder in Compression-Type Feedthrough

In the new feedthrough design, the bulky compacting and retainer nut on the Conax seal has been replaced by a retention plug that is held in position by crimping the housing during assembly of the feedthrough. The housing is designed so that it can be fabricated by an automatic screw machine. A cost savings is realized by the use of AISI 1018 steel instead of the Type 316 stainless steel used in the Conax seal. A schematic drawing of the new feedthrough is presented in Fig. IV-2.

Several prototype feedthroughs of the new design are being fabricated at ANL for testing. In addition, alternative insulators are being developed to replace the BN bottom insulator, which has not shown adequate strength. Methods for producing Y_2O_3 insulators are being studied in-house (see Section IV.B, below), and the Carborundum Corporation is attempting to fabricate bodies of AlN, $2\text{ AlN} \cdot \text{SiC}$, and $\text{AlN} \cdot \text{SiC}$. These latter materials are

Fig. IV-2.

Schematic of Redesigned Compression-Type Feedthrough

particularly attractive because of the potentially low cost of the raw materials. Another attractive ceramic is BeO, and National Beryllia Corporation is producing some BeO parts for our evaluation.

A ram or crunch mechanical-type feedthrough is also being fabricated by the Ceramaseal Corporation for our evaluation. In this design, a metal sleeve is pressed over a ceramic insulator, as shown in Fig. IV-3. One end of the sleeve is plated with a thin layer of soft metal, such as copper, and as the ceramic body moves into the metal sleeve, a portion of the soft metal is smeared onto the ceramic, thereby forming a seal. The metal sleeve, in turn, develops a high hoop stress that holds the ceramic in compression. The selection of the proper metal for the sleeve is critical; it must not undergo stress relief or excessive thermal expansion at temperature. Initially, Type 17-7 precipitation-hardened stainless steel will be used for the sleeve and BeO for the ceramic. Seals of this design have remained leak-tight at 10^{-10} Torr and 450°C ; other advantages are simplicity, compactness, absence of any brazed joints, and the prospect of using a low-cost ceramic such as AlN.

2. Bonded-Type Feedthrough

A feedthrough with a ceramic-to-metal bond will be needed for advanced cell designs. However, limitations in construction materials imposed by the cell environment and the operating temperatures have, thus far, prevented the adaptation of commercially available feedthroughs. As in the case of the mechanical feedthrough, only a limited number of ceramic materials are suitable for use, and none of the commercial brazes by themselves have proved satisfactory. Accordingly, assistance is being sought from industrial concerns that have expertise, often proprietary, in manufacturing brazed feedthroughs. Considerable commercial development work has been carried out with BeO, and this ceramic, in commercial grades of adequate purity, has shown compatibility with the cell environment.

Fig. IV-3. Design of Ram Seal

ILC Technology, Sunnyvale, Calif., is presently attempting to fabricate feedthroughs to our specifications. The feedthroughs, which will be fabricated in the order listed below, will utilize the following components:

<u>Ceramic</u>	<u>Braze</u>	<u>Metal Member</u>
99.5% Al_2O_3	ZrNi	Ni
99.8% Al_2O_3	ZrNi	Ni
99.5% Al_2O_3	NbCu	Nb
99.8% Al_2O_3	NbCu	Nb
99.9% BeO	NbCu	Nb
99.9% BeO	NbNi	Nb
99.9% BeO	NbFe	Nb

Of principal interest are feedthroughs with insulators of BeO, bonded to niobium by a niobium-based braze. However, Al_2O_3 insulators are included so that high-purity Al_2O_3 can be evaluated in the new prismatic cells and ILC can gain experience in the use of the niobium-alloy brazes. All of these metals are reasonably compatible with the FeS-type cell and may also be usable in the FeS_2 -type cell if direct contact with FeS_2 is avoided.

The 3 M Company (American Lava Division) is fabricating test feedthroughs to our specifications, using standard metallizing techniques and titanium-based braze to bond BeO to Kovar. The braze joint is plated with nickel and gold to protect it from the cell environment. National Beryllia is considering the new process, developed by General Electric, that uses the Cu-CuO eutectic to braze BeO bodies. Coors Ceramic has indicated an interest in attempting to find a suitable braze for Y_2O_3 , a ceramic that has shown good compatibility with lithium. Carborundum Corporation has proposed that the nickel and copper brazes developed by them for bonding to SiC might be suitable for bonding SiC·2 AlN and SiC·AlN insulators; the latter two materials are being produced by Carborundum Corp. for use in mechanical feedthroughs. Efforts at ANL will be directed toward testing and evaluating the products of these various programs and also toward development work in areas not already being investigated. Toward this end, a high-temperature (2200°C) brazing and heat-treating furnace is being procured.

Hercules Corporation is attempting to develop a different type of feedthrough--one in which H-resin, a thermosetting polyaromatic resin, is used as a potting material to replace the more conventional ceramic insulator. Several preliminary feedthroughs made by Hercules have been evaluated in a simulated test-cell arrangement. These feedthroughs shorted (across a terminal resistance of less than 30 ohms) after only 118 hr of operation, as a result of severe corrosion of the portion of the resin that had been immersed in the electrolyte. No filler was added in the H-resin feedthroughs and more recent work has centered around the use of purified BN fibers as a filler material. Simulated cell tests of several of these feedthroughs are currently under way.

B. Ceramic Insulator Development
(W. Tuohig, J. Dusek)*

A slip casting process has been developed to fabricate upper insu-

*Materials Science Division, ANL.

lators of Al_2O_3 for the compression-type feedthroughs (ANL-75-1, p. 77). A sufficient number of insulators has been prepared to satisfy the anticipated near-term needs for test cells. The major advantage of fabrication by casting is that design and dimensional changes can be made quickly and easily without changes in die tooling. Multiple molds provide reasonable rates of production in quantities up to 1000.

Attempts to prepare lower insulators of Y_2O_3 by slip casting were not successful, presumably because the powder tends to hydrate. However, Y_2O_3 insulators of the desired configuration have been successfully produced by isostatic-pressing techniques. An effort is now under way to optimize the microstructure and dimensional stability during firing. It was reported previously (ANL-75-1, p. 79) that the fracture strength of sintered Y_2O_3 was lower than most commonly used industrial ceramics. However, a detailed study of the fracture surface in a scanning electron microscope (SEM) has shown the presence of irregular voids such as that shown in Fig. IV-4. These voids are distinctly different from "sinter porosity" and may have their origin in the initial processing of the powder. Greskovich and Woods have described similar fabrication flaws in their doped Y_2O_3 .¹ Clearly, such flaws, if randomly distributed, could reduce fracture strengths by acting as crack initiators. Work is being continued to identify and eliminate the source of these flaws. A substantial improvement in the fracture strength and thermal-shock behavior is anticipated.

C. Electrode Separators

(C. W. Handrich, M. A. McDonnell, J. E. Battles)

Efforts are continuing on the development and evaluation of porous electrode separator materials that are compatible with the Li-Al/metal sulfide

Fig. IV-4. SEM Micrograph of a Defect Intersecting the Fracture Surface in a 96% Dense Y_2O_3 Ceramic (6000X)

cells. Porous papers of boron nitride fibers are being developed by the Carborundum Co. (under contract with ANL) to replace the costly, woven BN fabric that has been successfully used in both test cells and full-scale engineering cells. In a second contract,* emphasis is on the development and evaluation of composite-type separators in which a fine powder is placed between two thin layers of fibers, or a mat-like structure is formed from powders using a binder of fine fibers. The advantage to be gained from this arrangement would be the use of a material that is not presently available as a fiber (*i.e.*, Y_2O_3 , AlN), but which has superior compatibility with the cell environment. Samples of electrode separator materials have been received from both sources, and these are presently being evaluated in in-cell tests to determine their compatibility with the cell constituents and their effect on the electrical performance of the cells. Initial results have been encouraging; however, additional testing is required to complete the evaluation of these samples. Moreover, additional samples are forthcoming, and these will also be evaluated.

D. The Constitution of Lithium-Aluminum Alloys
(J. L. Settle and K. M. Myles)

A knowledge of the phase relationships of the lithium-aluminum alloy system is essential to the optimization of the performance of the Li-Al/FeS (or FeS_2) cells. Accordingly, an investigation of the Li-Al system was undertaken when it became apparent, in the development of the pyrometallurgical process for preparing Li-Al negative electrodes, that the published phase diagram was inaccurate.

Initially studies were concentrated on lithium-rich alloys; the results obtained by differential thermal analysis (DTA) and the experimental techniques were reported in previous semiannual reports (ANL-75-1 and ANL-8109); these results are also included here for completeness. Recent efforts have focused on the more equiatomic and aluminum-rich alloys, in particular, alloys containing the intermetallic compound LiAl_3 .²⁻⁵

The results of the chemical analyses of the Li-Al alloys prepared for this study are given in Table IV-1.[†] The lithium concentrations were determined by dissolving the alloy; separating the lithium from the aluminum and the major metallic impurities by an ion-exchange process; converting the Li to LiI ; vaporizing the LiI ; ionizing the LiI to Li_2I^+ ; and, by means of a mass spectrometer, observing the relative abundances of the ions $^6\text{Li}_2\text{I}^+$, $^6\text{Li}^7\text{LiI}^+$ and $^7\text{Li}_2\text{I}^+$. By comparing these abundances with those from similarly prepared lithium standards, the lithium concentrations were determined to an uncertainty of 0.25 wt % of the total lithium content.

Although the aluminum content has been determined for only one alloy, the sum of the lithium and aluminum analyses for this sample gave a mass balance of $99.73 \pm 0.29\%$. The major metallic impurities of iron and copper were determined by atomic absorption spectroscopy. The minor metallic impurities, determined spectrochemically, were generally less than 200 ppm each for Cr, Ga, Mg, Mn, Mo, Ni, Sn, and Ti. Oxygen was determined by fast-neutron activation analysis, and nitrogen by the Kjeldahl method.

*With Prof. R. D. Walker, Jr., Chemical Engineering Dept., Univ. of Florida.

[†]Analyses performed by members of Analytical Chemistry Laboratory, ANL: Li by D. J. Rokop and A. M. Essling; N, Fe, Cu, and Al by K. J. Jensen, R. E. Telford, and N. L. Johnson; spectrochemical analyses by J. P. Faris.

Table IV-1. Chemical Analysis of Lithium-Aluminum Alloys

O	N	Constituents Found, wt %					Estimated Li Content, at. %
		Fe	Cu	Trace Metals	Li	Al	
0.034		0.472	0.157		1.33		5.0
0.071		0.470	0.152	0.107	2.88		10.4
0.079		0.454	0.141		4.32		12.2
0.156		0.439	0.148		6.25		20.7
0.138		0.457	0.145	0.071	7.96		25.3
0.231		0.432	0.136		10.80		32.1
0.066		0.404	0.136		13.20		37.3
0.160		0.368	0.155		14.81		40.9
0.212	0.036	0.324	0.120	0.194	17.35	81.49	44.9
0.191	0.035	0.415	0.162	0.151	18.95		47.7
0.133	0.018	0.287	0.134	0.104	20.46		50.1
0.168	0.020	0.313	0.128	0.236	21.33		51.5
0.209	0.043	0.288	0.123	0.219	24.30		55.3
0.177	0.040	0.305	0.129	0.175	24.86		56.5
0.254	0.041	0.314	0.120		25.88		57.6
0.384	0.070	0.256	0.112	0.184	27.62		60.3
1.070	0.900	0.238	0.116	0.199	33.68		66.8
0.527	0.320	0.266	0.104	0.175	38.26		71.3
0.280	0.180	0.207	0.086	0.073	46.13		77.2
0.465	0.049	0.163	0.089	0.022	54.02		82.1
0.252	0.026	0.142	0.054	0.010	72.99		91.5

The phase relationship deduced so far is shown in Fig. IV-5 as a tentative phase diagram for the lithium-aluminum system. Twenty-one compositions ranging from 5 to 91.5 at. % lithium were examined by differential thermal analysis (DTA). Between 0 and 45 at. % Li, the liquidus and solidus are in agreement with those determined by Grube, Mohr, and Breuning,⁶ and by Shamray and Saldau.⁷ Our data indicate a melting-point maximum at 50 at. % Li in agreement with the data of Shamray and Saldau,⁷ whereas Grube *et al.*⁶ found that the LiAl phase melted incongruently. The range of composition of the LiAl phase was estimated to be from 50 to 56 at. % Li, whereas Shamray and Saldau⁷ estimated a range of 45 to 56 at. % Li, and our data indicate a range of about 48 to 58 at. % Li. Our estimate of the aluminum-rich phase boundary is supported by the electromotive force measurements of Yao, Heredy, and Saunders,⁸ who measured the emf of lithium-aluminum alloys vs. Li/Li⁺ and found that the transition from two phases to one phase took place somewhere between 46.97 and 48.14 at. % Li. From 60 to 91.5 at. % Li, our results indicate that liquidus temperatures are similar to those of Grube *et al.*⁵

The reaction isotherm shown in Fig. IV-5 at 585°C had not been established prior to this investigation, nor had the peritectic reaction isotherm at 330°C for Li₉Al₄ been detected. The 519°C peritectic reaction isotherm clearly must be associated with Li₃Al₂, instead of Li₉Al₄ (or Li₂Al), as assumed by earlier workers. Our work is in agreement with the work of Grube *et al.*,⁶ in indicating that the Li₉Al₄-Li eutectic melts at about 180°C. However, neither of us have investigated alloys containing more than 91.5 at. % Li. Shamray and Saldau found that the Li₉Al₄ eutectic was at 94 at. % Li

Fig. IV-5.

Tentative Phase Diagram of
Li-Al System (α = Al, β = LiAl,
 γ = LiAl₃, δ = Li₃Al₂,
 ϵ = Li₉Al₄, η = Li)

and at 171°C. This small discrepancy should be resolved by extending our DTA measurements to alloys containing more than 91.5 at. % Li.

Each of the alloys containing more than 69.3 at. % Li (i.e., Li₉Al₄) exhibited an endotherm at about 270°C on heating and an exotherm at about 250°C on cooling. The additional DTA measurements mentioned above, combined with appropriate X-ray diffraction analyses, should allow this reaction to be characterized.

Many of the alloys have been examined metallographically and by X-ray diffraction* and the results have substantiated the conclusions drawn from the DTA data, except in the case of the aluminum-rich alloys. Although a decided peak occurs in the DTA curves at 585°C for several alloys (21 to 41 at. % Li), additional examination of the alloys tends to indicate that the major phases are α -Al and β -LiAl. Several of the alloys have a substantial number of extraneous, low-intensity diffraction lines that are not associated with those of LiAl₃.³ Future effort will be directed toward elucidating the phase relationships in the aluminum-rich alloys, in particular toward establishing the composition range of LiAl₃ and the solid solubility of Li in α -Al.

E. Corrosion Studies (J. A. Smaga, J. E. Battles)

Because of the corrosiveness of the cell environment and the need for lightweight, low-cost materials, an extensive materials-evaluation study of both metals and ceramics is being conducted to provide data for the

* Analyses performed by B.S. Tani and S. Siegel, Analytical Chemistry Laboratory, ANL.

selection of suitable materials for constructing various cell components. Although the performance of materials can be evaluated fully only in operating cells, many candidate materials can be eliminated from further consideration by relatively simple corrosion tests. Generally, materials behavior, as determined in static compatibility tests, has closely paralleled that found upon postoperative examinations of cells. Recent results of postoperative examinations are presented in Section IV.F, below, and corrosion studies are discussed below.

1. Corrosion Studies in the Positive Electrode Environment

The development and evaluation of molybdenum-bearing alloys has been initiated to find materials that would be better suited for current collectors than iron and molybdenum currently used in FeS and FeS₂ positive electrodes, respectively. Corrosion tests were conducted on five molybdenum-bearing alloys in equal volumes of FeS₂ and LiCl-KCl eutectic at 400°C; to simulate the environment of an FeS₂ positive electrode. The alloys and their compositions (in wt %) are as follows: 1) Hastelloy B (Ni-28 Mo-1 Cr-5 Fe), 2) Hastelloy C (Ni-17 Mo-16 Cr-5 Fe), 3) Fe-2.6 Mo, 4) Fe-5.8 Mo and 5) Fe-30.1 Mo.

The planned interval corrosion tests on the two Hastelloys employed time intervals of 250 hr. The results, which are tabulated in Table IV-2, indicate that the higher molybdenum content and the lower chromium content of Hastelloy B provide improved corrosion resistance to the FeS₂/LiCl-KCl. The corrosion rates of both the alloys, as well as the corrosiveness of the environment toward them, decreased with time; however, neither Hastelloy B nor Hastelloy C has the corrosion resistance of molybdenum (2 $\mu\text{m}/\text{yr}$) to this environment. The mode of corrosion attack on these alloys was general over the exposed surface, with isolated areas showing a one-grain-deep intergranular penetration.

Table IV-2 also includes the results of the planned interval corrosion tests on the two solid solution alloys, Fe-2.6 Mo and Fe-5.8 Mo. (The latter composition is near the limit of solid solubility for solid solution in this binary system.) The 750-hr corrosion rates for these two metals are roughly an order of magnitude greater than the rates found for the Hastelloys. As was observed for the Hastelloys, the corrosion rates of these two iron-molybdenum alloys decreased with time. Both of these iron-molybdenum alloys underwent a general corrosion attack which left the surfaces severely roughened. For purposes of comparison, an Armco electromagnet iron coupon

Table IV-2. Planned Interval Corrosion Tests for Molybdenum-Bearing Alloys in FeS₂ and LiCl-KCl Eutectic at 400°C

Time Interval, hr	Corrosion Rate, $\mu\text{m}/\text{yr}$				
	Hastelloy B	Hastelloy C	Fe-2.6 Mo	Fe-5.8 Mo	Fe-30.1 Mo
0-250	156	316	2560	1460	-
0-500	89.0	173	1570	883	-
0-750	76.1	142	1160	602	1100 ^a
500-750	96.2	310	363	114	-

^aActual rate of penetration was somewhat greater due to galvanic attack.

exposed to this environment for 750 hr showed a corrosion rate of 3520 $\mu\text{m}/\text{yr}$, which is a factor of six greater than the corrosion rate for the Fe-5.8 Mo alloy.

The Fe-30.1 Mo alloy contains two phases. Because of the brittleness of the second phase, this material could not be formed easily. As a result only one test was conducted; the calculated corrosion rate was 1100 $\mu\text{m}/\text{yr}$ after 750 hr. Metallographic examination of this alloy indicated that a galvanic couple between the two phases led to a preferential and accelerated attack on the iron-rich phase, which resulted in a mechanically weak surface structure. This form of attack, which produces an actual penetration rate larger than the corrosion rate calculated for this alloy, would be characteristic of any two-phase iron-molybdenum alloy (6 to 44 wt % Mo).

Previous corrosion studies have shown that molybdenum exhibits a very low corrosion rate ($<10 \mu\text{m}/\text{yr}$) in the $\text{FeS}_2/\text{LiCl-KCl}$ environment and in engineering-scale cells; however, the reason for this excellent corrosion resistance is not readily apparent. The molybdenum sulfides, MoS_2 and Mo_2S_3 , are thermodynamically more stable than the iron sulfides, and hence, a reaction would be expected. This lack of reaction has led to the belief that the formation of a thin adherent surface film greatly retards further reaction. However, when the surfaces of molybdenum coupons exposed to $\text{FeS}_2/\text{LiCl-KCl}$ at 400°C were analyzed* by X-ray fluorescence and scanning electron microscopy, the results were inconclusive. Additional tests, using electron scattering chemical analysis* (ESCA), have now been performed on a molybdenum coupon exposed to an equal volume mixture of FeS_2 and LiCl-KCl eutectic for 240 hr at 500°C . The results showed the presence of a sulfide layer containing two sulfur compounds. The exact compounds have not as yet been identified, but are believed to be the two stable sulfides mentioned above. This is the first time that the presence of a sulfide layer has been established on a molybdenum sample from a static corrosion test. Additional evidence of the formation of a sulfide layer on molybdenum has also been obtained recently from postoperative cell examinations (see Section IV.F).

2. Corrosion Studies in the Negative Electrode Environment

Postoperative examinations of Cells W-8 and PR-1 (see Section IV.F), which were operated at or above 500°C for at least part of their lifetime, have shown that extensive reaction occurred between the metal housing and the Li-Al alloy negative electrode to form an Fe-Al intermetallic compound. Corrosion studies were therefore initiated to fully characterize this reaction. In the initial tests, samples of Armco electromagnet iron, AISI-1008, Ni, and Types 304 and 316 stainless steel were immersed in an equal volume mixture of Li-Al alloy and LiCl-KCl eutectic at 400 and 500°C for exposure times of 200, 400, and 600 hr. The Li-Al alloys used in the 400 and 500°C tests contained 47 and 45 at. % Li, respectively. Post test-examination showed no significant weight change in any of the samples. Metallographic examination of the 600 hr samples showed no evidence of reaction, thereby confirming that the Li-Al alloy does not react with these materials under static conditions.

The nonreactivity observed in the above tests indicated that other conditions were necessary for the reaction observed in the postoperative cell examinations; thus, other mechanisms were considered. Near the

*X-ray fluorescence by M. I. Homa, Analytical Chemistry Laboratory, ANL; Scanning electron microscopy, by C. A. Seils, Chemical Engineering Division, ANL; and ESCA by D. Lam, Materials Science Division, ANL.

end of the discharge cycle, the Li-Al alloy is depleted of Li and is in physical contact with the metallic housing materials; moreover, electrochemical contact is provided by the LiCl-KCl electrolyte. These conditions satisfy the requirements for a galvanic couple. The rate of the galvanic reaction would be expected to accelerate as the temperature is increased.

A series of tests was initiated to evaluate this proposed mechanism; in these tests, dissimilar metal couples of Fe-Al and Type 316 SS-Al were immersed in LiCl-KCl at temperatures of 400°C and 525°C. Each member of each couple had an exposed surface area of about 11 cm². The results of these tests are summarized in Table IV-3. At 525°C, the aluminum members of the couples underwent significant weight losses, which were matched by similar weight gains for the corresponding members of the couples. At 400°C, only small weight changes were observed for the individual members of these couples. The rate of aluminum reaction with the cathodic member was 40 times greater at 525°C than at 400°C for the Fe-Al couple and 160 times greater for the 316 SS-Al couple. Metallographic examination of the cathodic members indicated the presence of a brittle reaction layer. Figure IV-6 is a photomicrograph of the reaction layer formed at 525°C on the iron member of the Fe-Al couple. A comparison of this figure with Figs. IV-8 and 11 (photomicrographs of the reaction layers found in Cells W-8 and PR-1, presented later in Section IV.F) illustrates that the reaction layers from the present tests and those found in cells have identical features. Additional tests are being conducted to establish the kinetics of the reaction and to identify housing materials that are less subject to this reaction.

F. Postoperative Cell Examinations
(F. C. Mrazek, J. E. Battles)

Postoperative examinations are conducted on test cells primarily to evaluate the performance of various construction materials, in particular, feedthroughs, current collectors, electrode separators, and cell housings. These postoperative examinations provide important information, not only on the compatibility of cell components with the cell environment, but on the performance and behavior of the lithium-aluminum and metal sulfide electrode materials. The examination procedures were described in a previous semiannual report (ANL-8109, p. 72).

Table IV-3. Reaction of Dissimilar Metal Couples in the LiCl-KCl Electrolyte at 400 and 525°C

	Fe-Al		316 SS-Al	
	400°C	525°C	400°C	525°C
Time, hr	240	240	210	210
Weight Loss of Aluminum Member, mg	27.10	393.20	9.20	52.85
Weight Gain of Cathodic Member, mg	8.90	372.00	0.20	37.20
Rate of Aluminum Pick-up by the Cathodic Member, mg/(cm ²)(hr)	0.0035	0.145	0.00001	0.016

Fig. IV-6. Reaction Layer (top) Formed on Armco Iron Member of Fe-Al Galvanic Couple at 525°C (Nital etch, 400X)

1. Examination of Test Cells

A large number of test cells utilizing a wide variety of test parameters were assembled and operated in the cell development effort (see Section II). The results of the postoperative examinations of these test cells are summarized in Table IV-4. In some cases only the negative or positive electrode was examined from a particular cell. Generally, the metallographic identification of metal sulfide phases present in the positive electrode agrees very well with the results from X-ray diffraction analysis.* Incomplete utilization or reaction of the Li-Al alloy was observed in the examination of the negative electrodes from these cells. The unreacted or incompletely utilized material is located in the portion of the negative electrode that is farthest from the positive electrode. Examination of the positive electrodes for evidence of the additives (Cu_2S , NiS , CoS_2) has been unsuccessful in most cases, perhaps due to the low concentrations and dispersion of the fine particles.

2. Examination of Engineering-Scale Cells

Complete postoperative examinations were conducted on engineering-scale cells W-8, W-9, W-12, and PR-1. The W-series cells are described in Section II. Cell PR-1, which was the first prismatic cell with vertical electrodes, is described in Section III. The results of the postoperative examinations are presented below.

Cell W-8. The two negative electrodes of this cell utilized pyrometallurgically prepared Li-Al alloy; the positive electrode was charged with FeS-16 wt % Cu_2S with a current collector of iron mesh and No. 2 steel wool. The normal operating temperature was about 450°C; however, the last 350-400 hr of operation was at 500°C. After 122 cycles and 3770 hr, cell operation was terminated because of a severe electrical short.

* All X-ray diffraction work on test cells was performed by B. S. Tani, Analytical Chemistry Laboratory, ANL.

Table IV-4. Results of Postoperative Examination of Small Test Cells

Cell No.	Type of Cell ^a	Time of Operation, hr	Phases, ^b X-ray Diffraction Analysis	Remarks
DS-13	Li-Al/FeS-10 wt % Cu ₂ S (Fe). Negative electrode initially charged with 20 wt % electrolyte	1396	Li ₂ S, α-Fe; Cu minor	Homogeneity in the positive electrode was good but the negative electrode was poor with 1/5 unreacted and very low in electrolyte content.
DS-14	Li-Al/FeS-20 wt % Cu ₂ S (Fe). Negative electrode initially charged with 5 wt % electrolyte	736	X _{Cu} , FeS; α-Fe minor	Homogeneity in the positive electrode was good but about 1/3 of the negative electrode was not being utilized even though the electrolyte level was normal.
DS-15	Li-Al/FeS-10 wt % Cu ₂ S (Fe). Negative electrode initially charged with 40 wt % electrolyte	165	X _{Cu} , Li ₂ S, α-Fe; J minor	Both electrodes were nonhomogeneous with the upper 1/3 of the positive electrode being in the charged state and the lower 2/3 in the fully discharged condition. The negative electrode was poorly utilized with 3/5 being unreacted.
DS-19	Li-Al/FeS ₂ + 33 wt % Ni (Fe)	265	Z, J, Josephinite, Ni, α-Fe	In the positive electrode both the iron current collector and the nickel spheres were severely reacted. Approximately 1/3 of the negative electrode was being fully utilized. The Li-Al dispersion in the iron Retimet current collector was very good.
DS-20	Li-Al/FeS ₂ + 11 wt % CoS ₂ (Mo-coated Fe)	355	FeS ₂ , FeS, Z	The positive electrode was nonhomogeneous with the upper 1/6 layer being FeS and the balance a mixture of FeS ₂ + Z. The Mo coating on the current collector was inadequate and the iron substrate was severely attacked. The negative electrode was similar to DS-19.

^aChemical symbols in parentheses denotes positive electrode current collector material.

^bThe phases are listed in decreasing order of intensity and are identified as follows: X phase, Li₂FeS₂; X_{Cu} phase, similar to X phase with some Cu substituted for Fe; Z phase, Li₄Fe₂S₅; J phase, (K,Li)₃Fe₁₂S₁₃ (tentative). Josephinite, an alloy of Ni and Fe (Ni, 77-24%) with small amounts of other elements.

Visual macro observations after sectioning showed that the circumferential space between the positive electrode and the cell housing was void of electrolyte. (All three electrodes contained sufficient electrolyte for particle retention during polishing.) Four parallel cuts were made vertically through the cell dividing it into five separate sections. Resistance measurements between the positive and negative electrodes in four of these sections showed the presence of a direct short and in the fifth, the resistance was 40 ohms, thereby indicating that the electrical shorting was present throughout the entire cell.

Metallographic examination of the positive electrode indicated that the constituents were Li_2S , $\alpha\text{-Fe}$ and Cu. The presence of the Li_2S and $\alpha\text{-Fe}$ was confirmed by X-ray diffraction analysis, but the copper content was apparently too low for detection. Most of the steel wool had reacted because very little of the original "wool" structure was evident.

Samples of the negative electrodes were examined metallographically. Both electrodes appeared to be depleted of lithium, as would be expected in a fully discharged cell. A distinct band of metallic spheres (about 0.4 mm thick), which appeared to have been liquid at some time during the cells operation, were found in both negative electrodes near the positive electrode interface. Figures IV-7a and -7b show the microscopic appearance of the material in this region. From Fig. IV-7a it is also apparent that extensive reaction has occurred with the 325-mesh stainless steel screen used to retain the fine Li-Al alloy particles. The extent of the reaction varied with location along the electrode interface.

Metallographic examination of a section from the bottom of the AISI-1008 steel housing showed evidence of extensive reaction; this reaction is shown in Fig. IV-8. The thickness of the reaction layer ranged from 0.4 to 0.6 mm. Microprobe analysis of other samples that showed this type of reaction, including a sample from Cell PR-1 (discussed below), has indicated that the reaction product is an Fe-Al intermetallic compound. Studies being conducted to determine the mechanism for this reaction were described in a previous section (IV.E.2).

Cell W-9. Cell W-9, a full-scale engineering cell, was terminated in the fully charged state after 76 cycles and 1511 hr of operation. This cell had two electrochemically formed Li-Al alloy negative electrodes and a positive electrode of FeS_2 with molybdenum expanded mesh current collectors. Operation of the cell was terminated voluntarily for postoperative examination. It was believed that examination of this cell, which was still fully operative, would give some indication of the cause(s) of the performance decline that occurs in most cells before complete failure.

Before the cell was cross-sectioned, a resistance of 450 ohms was measured between the positive electrode conductor and the cell housing. After the initial cross-sectioning, the resistance was 7000 ohms in the larger segment, which contained the feedthrough, and 450 ohms in the smaller segment between the positive electrode and the lower negative electrode. The cell was again cross-sectioned to obtain a slab containing the feedthrough and a second segment similar to the first. The resistance across the second segment was 7000 ohms; the feedthrough resistance was 20,000 ohms. These results indicate that a short circuit was developing between the positive and negative electrodes. The feedthrough was in excellent condition.

a.

b.

Fig. IV-7. Typical Photomicrographs of Negative Electrodes in Cell W-8
(a) reacted stainless steel screen (100X)
(b) 0.4-mm band of metallic spheres (500X)

Fig. IV-8. Photomicrograph of Fe-Al Intermetallic Compound (left side) Formed on Inside Surface of Housing in Cell W-8 (Nital etch, 100 X)

Examination of the initial cross section showed that the thickness of the cell was about 0.96 cm greater than the original thickness (~ 4 cm) -- 0.64 cm at the top and 0.32 cm at the bottom. Also, portions of the positive and upper negative electrodes contained little or no electrolyte. Several isolated pockets of pure electrolyte were found in the lower negative electrode, and both negative electrodes showed large areas having a thin layer of electrolyte between the active material and the cell housing, which interferes with electrical contact.

Metallographic examination of the positive electrode showed the presence of four metal sulfide phases: FeS_2 , FeS , and two unidentified sulfide phases. X-ray diffraction analysis showed only FeS_2 and Fe_{1-x}S . Also, microscopic examination showed the first evidence of reaction with the molybdenum current collector (see Fig. IV-9). As shown in the figure, this reaction layer appears dense and adherent in some areas, whereas in other areas, the reaction layer is less dense and has spalled from the surface. This reaction product has been identified by X-ray diffraction analysis as MoS_2 .

Extensive metallographic examinations were conducted on representative sections of both the upper and lower negative electrodes. No evidence was found of the original aluminum wire structure, thereby indicating that the lithium utilization was relatively complete. In most electrochemically formed electrodes, areas of unreacted aluminum wires have been observed. A wide range of particle sizes was found in both electrodes, with the smallest particles occurring at the negative/positive electrode interface. Particle agglomeration or sintering was observed throughout the electrodes, with the

Fig. IV-9. Photomicrograph Showing Formation of Sulfide Layer on the Surface of Molybdenum (as-polished, 500X)

most extensive agglomeration occurring within the lower electrode. Evidence of compositional gradients was found in the larger particles.

Sulfur analysis* of representative samples of the top and bottom negative electrodes yielded 0.076 and 0.080 wt %, respectively. These results indicate that no significant transfer of sulfur had occurred between the positive and negative electrodes. Chemical analysis for molybdenum* in the positive electrode showed the presence of 0.047 wt % Mo, indicating minor dissolution of the molybdenum current collector (the current collector structure was removed before analysis).

A quantitative volume-fraction analysis was conducted on both negative electrodes using an areal analysis method. (This method is described in Section IV.F.3, below.) The volume fractions of Li-Al alloy determined on different samples of the lower electrode were 67.4, 80.6, 63.5 and 26.2 vol %; for the top electrode, the values were 66.2, 48.3 and 39.0 vol %. The lower concentrations of Li-Al occurred near the negative/positive electrode interfaces. These results illustrate the nonuniformity in active-material distribution within the electrodes.

Cell W-12. This cell was constructed and operated to test the use of thin electrodes in high power cells. The negative electrodes were pyrometallurgically prepared Li-Al alloy which had been vibrated into an iron Retimet structure, and the positive electrode was FeS_2 -10 wt % CoS_2 with a molybdenum current collector. The separator and retainer cloths surrounding the positive electrode were sealed by means of two concentric steel hoops. The cell was physically constrained to prevent electrode swelling. Operation

* Sulfur and molybdenum analyses performed by K. J. Jensen, Analytical Chemistry Laboratory, ANL.

of the cell was terminated after 194 hr (10 cycles), because of the beginning of internal electrical shorting.

Macro observation of a vertically cut section of the cell revealed that the upper ZrO_2 retainer cloth had darkened considerably in several places -- near the center of the cell and between the two hoops. A photograph of the vertical cross section is shown in Fig. IV-10. Metallographic examination of the areas where the ZrO_2 had darkened confirmed that a reaction had occurred, probably between lithium and the ZrO_2 . The reaction of lithium with ZrO_2 cloth produces a conductive material and in this cell was a possible cause for the electrical short.

The positive and negative electrodes were analyzed for the volume fraction of active materials by the procedure presented in Section IV.F.3. The volume fraction of sulfide material in the positive electrode was about 75%, which is greater than normally observed. The balance was LiCl-KCl electrolyte. This behavior has been attributed to the mechanical clamping of this cell which prevented the electrode from swelling, as had occurred in unrestrained cells. The sulfide materials were identified by X-ray diffraction as FeS , Li_2FeS_2 (X-phase), and possibly a cobalt compound; the presence of these materials indicates a partially discharged (or charged) electrode.

Analysis of random samples of the negative electrodes showed substantial nonuniformity in the distribution of the Li-Al alloy. For the upper electrode, the volume fraction of Li-Al alloy ranged from 29 to 52% (five different areas analyzed), with an average value of 37%. For the lower electrode, the values ranged from 20 to 40 vol % Li-Al alloy, with an average value of 31%. At this time it is unknown whether the difference in the volume fraction of Li-Al alloy in the two electrodes is an artifact resulting from the nonuniform distribution of material or due to unequal loading or reaction.

Fig. IV-10. Cross Section of Cell W-12. ANL Neg. 308-4059.

Cell PR-1. This cell was a prismatic-type cell with vertical electrodes, which utilized a hot pressed FeS-10 wt % CoS positive electrode and electrochemically formed Li-Al negative electrodes. Cell operation was voluntarily terminated after 1386 hr and 88 cycles for postoperative examination. A cross section of the cell was shown above in Fig. III-14.

Macro examination after sectioning revealed the following information: (1) The electrodes were filled with electrolyte but no excess was observed on the top exposed surface. (2) Considerable swelling of the electrodes was evident, as was the resultant bulging of the cell housing. (3) Severe reaction was observed in one of the mild steel sheets used as a holder for the negative electrode.

Samples were obtained from the top, middle and bottom of one negative electrode for metallographic examination. The Li-Al particle size was smallest in the top sample with the lower two samples being much coarser, even to the extent of retaining some of the original wire-like structure. As is normal, the areas nearest the interface with the positive electrode contained the smallest particles, within a given sample. Some spherical Li-Al particles were found on the outside edge of the bottom sample, indicating that they had been liquid during cell operation.

Metallographic examination of the steel sheet retainer (AISI-1008) for the negative electrodes confirmed that some areas had reacted rather extensively. This reaction is evident in the photomicrograph in Fig. IV-11; also shown in the figure are X-ray scanning images for Fe, Al, and Mg obtained from electron microprobe analysis.* These results show that the reacted material contains Fe, Al, and Mg (from the Al alloy demister mesh). The sample was not analyzed for lithium; however, previous results for a similar reaction with nickel (ANL-8109, p. 73) showed that lithium was present only in the outermost areas. A substantial vertical temperature gradient had existed in the furnace used for testing this cell (see Section III). Our examination confirmed this observation and indicated that a horizontal temperature gradient was also present in this cell test.

An attempt was made to sample the positive electrode in a manner similar to that used for the negative electrode. The topmost area had insufficient electrolyte to hold the sample together; thus, only the middle and bottom specimens could be prepared for examination. The active materials of the positive electrode were identified as FeS and α -Fe (the cobalt sulfide was not detected, apparently because the concentration was too low). Active material loading and particle size distribution was similar to that found in horizontal cells. The iron current collector was centrally located in the electrode and was undergoing the usual level of corrosion.

3. Volume-Fraction Analysis of Electrodes

Information on the volume fraction of active materials and electrolyte within an electrode structure can be used for (1) correlating electrode performance with microstructure, (2) quantitatively determining the active material distribution, and (3) establishing the steady-state volume fraction of active material, compared with the initial loading. These data can then be applied in the design and fabrication of improved electrodes.

* Analysis performed by C. A. Seils, Chemical Engineering Division, ANL.

PHOTOMICROGRAPH 300X AS-POLISHED

SPECIMEN CURRENT IMAGE

Fe K_{α} SCANNING IMAGE Al K_{α} SCANNING IMAGE Mg K_{α} SCANNING IMAGE

Fig. IV-11. Photomicrograph and Electron Microprobe Scanning Images of Li-Al Reaction with Iron (500X)

An *in situ* metallographic method has been devised for obtaining the volume-fraction data. The advantage of this method is that the sample is not subjected to any pretreatment that would alter the structure of the electrode. In this procedure, the area is determined using the lineal analysis method which is a measurement of the fractional line length intercepted by the particular phase of interest. The area determined by this procedure is equivalent to the volume fraction. The lineal analysis may be conducted by manual measurements or by computer scanning of representative photomicrographs such as that shown in Fig. IV-12. The computer scanning method* yields a measurement of the area scanned by line segments, which is directly proportional to the volume, and also displays a reproduction of the area, which can be compared with the original for estimating the accuracy of the measurement.

*Program ALICE, Applied Mathematics Division, ANL.

Fig. IV-12. Typical Microstructure Observed in the Retimet/
Li-Al Negative Electrode from Cell S-63. (The
Li-Al alloy is the white material; 200X.)

The volume fraction of Li-Al alloy as determined from computer scans of Fig. IV-12 (the negative electrode of test Cell S-63) was 46.5 vol %. This electrode was initially loaded with 44 vol % Li-Al alloy (pyrometallurgically prepared). The sponge-like microstructure of this electrode and the initial loading both appear to be advantageous in obtaining a uniform and complete electrochemical reaction during cell operation.

4. Lithium Analysis of Negative Electrodes from Engineering Cell W-9

The distribution of metallic lithium within the negative electrode(s) of operated cells is recognized as an important cell-design parameter. In order to obtain this information, an analytical procedure has been developed for determining the lithium concentration in samples of the negative electrode consisting of Li-Al alloy plus LiCl-KCl electrolyte.

The metallic lithium content of a sample is determined as follows. A weighed sample of the electrode is treated, first with water and then with dilute hydrochloric acid, in a closed system equipped for measurement of the amount of hydrogen evolved.* After the dissolution is completed, the solution is analyzed for aluminum.* The volume of hydrogen evolved from dissolution of metallic lithium is then calculated by subtracting, from the total hydrogen, the amount generated by the aluminum (and by ~5 wt % Mg that was present in the aluminum) and, from this value, the lithium content of the Li-Al alloy is determined.

* Gas collection by M. I. Homa and aluminum analyses by R. E. Telford, Analytical Chemistry Laboratory, ANL.

The analytical results for lithium distribution in the negative electrodes from Cell W-9 are listed in Table IV-5. The trend in the results confirm the metallographic examinations, which have indicated lithium-rich and aluminum-rich areas within the electrodes. Samples of a pyrometallurgically prepared Li-Al alloy of known composition were analyzed to evaluate the accuracy of this method. These samples were from batch Li-Al-13 which was formulated to contain 49 at. % Li. This procedure yielded results of 49 and 55 at. % Li, which are in reasonable agreement with the standard composition.

Table IV-5. Distribution of Metallic Lithium in Li-Al Electrodes of Cell W-9

	Sample Location ^a			
	Upper Electrode		Lower Electrode	
	Top	Bottom ^b	Bottom	Top ^b
Total Sample Wt, g	0.981	0.943	1.237	0.895
Metallic Constituents, g				
Lithium	0.029	0.041	0.054	0.083
Aluminum	0.437	0.240	0.299	0.213
Magnesium	0.022	0.012	0.015	0.011
Total Metals	0.488	0.293	0.368	0.307
At. % Li in Li-Al Alloy	19.7	38.9	40.2	58.9

^aThe samples were ~ 1.3 cm wide and were taken at a distance of ~ 2.5 cm from the circular center point and on the same vertical axis.

^bInterface nearest the positive electrode.

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V. CELL CHEMISTRY (R. K. Steunenbergh)

The objectives of the cell chemistry studies are (1) to provide solutions to specific chemical and electrochemical problems that arise in the electrode and cell development work, (2) to conduct investigations that are expected to lead to innovations and improvements in the electrode and cell designs, and (3) to provide a basic understanding of the processes that occur within the cells.

A. Investigations of Iron Sulfide Electrodes (Z. Tomczuk, A. E. Martin)

Additional laboratory studies have been conducted on FeS, FeS₂, and modified FeS electrodes in support of the engineering development work, which utilizes these types of electrodes. The reactions that occur in the electrode are typically deduced from postoperative metallographic and X-ray examinations* together with the voltage-vs.-time records that are obtained during the discharge-charge cycling of the cells. In addition, cyclic voltammetry studies have been employed in the case of the FeS₂ electrodes.

1. Li/FeS Cell Studies

Several tests were made to obtain additional information on the reactions occurring during the discharge-charge cycling of these cells. The initial discharge of Li/FeS cells is of particular interest because a permanent expansion of the sulfide electrode occurs at this time. The expansion is associated with the formation of the J phase, which is currently estimated to correspond to the following empirical formula: $\text{Li}_{0.4}\text{K}_{2.8}\text{Fe}_{12}\text{S}_{13}$. To better observe the nature of the expansion process, a special electrode was prepared by melting FeS in a graphite mold that was the same diameter as the cavity for the sulfide electrode in the Li/FeS cell. Using this special single-piece FeS electrode, the initial discharge reaction was confined to the upper surface of the electrode. Operation of this cell was terminated after only a 9% discharge. Metallographic examination confirmed that the bulk of the reaction had indeed occurred in the upper portion of the electrode. Vertical expansion of the electrode resulting from the formation of the J phase, which was present as thick layers, was observed. Iron that was formed in the reaction was present as fine particles embedded in the J-phase layers. It was also noted that LiCl had crystallized out as a film at the interface between the electrode and the electrolyte. This effect was presumably the consequence of local depletion of the electrolyte in KCl, which participates in the formation of the J phase.

A second Li/FeS cell was operated at a relatively high temperature, namely, 491°C. At this temperature, a single voltage plateau was observed on charging, instead of the two plateaus observed at lower temperatures. (The two plateaus are known to correspond to the formation of the J phase and its subsequent conversion to FeS.) The cell was cycled three times and the test was then terminated after a 43% charge. X-ray examination of the product electrode showed the presence of the J phase and Li₂FeS₂. The earlier cell test at about the same temperature had been terminated at the end of the plateau, and the product electrode contained FeS. Thus, the combined data

*All X-ray analyses discussed in this section were performed by B. S. Tani, Analytical Chemistry Laboratory, ANL.

from the two cell tests suggest that the single plateau observed at a cell operating temperature of 491°C corresponds to several consecutive reactions, *i.e.*, the formation of J phase and Li_2FeS_2 , followed by the formation of FeS.

2. Li/FeS-Cu₂S Cells Utilizing Copper Mattes

Copper mattes are produced in the molten state as intermediate products in the production of copper from sulfide ores. Copper mattes typically contain from 90 to 95% (FeS + Cu₂S), and they are essentially free of oxide impurities. Such mattes appear to be attractive sources of sulfide materials for the positive electrodes of Li/FeS-Cu₂S type cells. They might be used directly, or if their Cu₂S contents is too high, they could be mixed with FeS, for example on a 1:1 basis, thus supplying all of the Cu₂S and part of the FeS required for the cells. For the purpose of testing their utility in cells, samples of commercial mattes were obtained from Noranda Mines Ltd. and from the Kennecott Copper Corp.

Tests of the Noranda Matte. The sample of Noranda matte contained 44.4 wt % FeS, 48.2 wt % Cu₂S and 7.6 wt % minor constituents (the principal minor constituent in this particular matte was ZnS). The Cu₂S:FeS mole ratio was 0.600, which is considerably higher than the values of 0.2/ for the Kennecott matte and 0.11 to 0.14 for the FeS-Cu₂S mixtures used in Li/FeS-Cu₂S cells that had been tested earlier (ANL-75-1, p.106). Thus, the Noranda matte might be most useful as a mixture with FeS, but in these tests it was used in an undiluted form.

The cell design and size were the same as in earlier laboratory tests.¹ The cell was operated for 12 consecutive discharge-charge cycles at current densities ranging from 0.025 to 0.063 A/cm² and the test was then terminated voluntarily. The voltage-time curves on charging showed a major plateau at about 1.75 V* and an inflection point at 1.85 V, whereas on discharging the curves showed a minor plateau at 1.65 V, a major one at 1.50 V, and a minor one at 1.25 V. The electrochemical behavior of the cell was excellent. The open-circuit voltage was nearly 2.0 V and the short-circuit current density was about 1.2 A/cm². These values are more typical of Li/FeS₂ cells than of Li/FeS cells.

Metallographic examination of the product electrode showed that it was unusually compact and free of porosity. Its X-ray structure, like that of the original matte, was very complex but neither the J phase nor the modified Li₂FeS₂ phase were present. One or both of these phases had been found in the sulfide electrodes of the four Li/FeS-Cu₂S cells that had been operated previously. Thus the results indicated that the formation of the J phase and the modified Li₂FeS₂ phase had been avoided, presumably because the Cu₂S content of the sulfide electrode had been so high that ternary Cu-Fe-S phases had formed instead. (Five ternary phases are known to exist in the Cu-Fe-S system at cell operating temperatures.)

The Noranda matte was tested further in a second cell in which the sulfide electrode consisted of a single piece of matte that had been pre-melted in a graphite crucible having the same diameter as the electrode

* Unless stated otherwise, all voltages reported in this section of the report are relative to elemental lithium and are IR-free.

cavity of the cell. Operation of this cell was terminated after an initial discharge of only 6% of the theoretical capacity. Metallographic examination of the product electrode indicated that the expansion of this electrode was not as extensive as in the similar test with an FeS electrode. The reaction products that had formed on the matte electrode appeared to consist of a number of phases, all present as fine particles, rather than the thick, essentially single-phase layers of J phase observed in the FeS cell.

Tests with the Kennecott Matte. According to the analysis received with the shipment, the Kennecott matte contained 40.6 wt % Fe and 25.4 wt % Cu. The calculated $\text{Cu}_2\text{S}:\text{FeS}$ mole ratio, 0.27, was considerably less than that of the Noranda matte and about twice that of the FeS- Cu_2S mixtures that had been tested previously. Two laboratory cells were operated with the Kennecott matte. The first test was terminated after nine discharge-charge cycles because of dewetting problems that were encountered with the lithium electrode. The second cell operated very well for eleven discharge-charge cycles and the test was then terminated voluntarily. (In retrospect, it seems likely that the problems encountered with the first cell were not caused by the matte but by some other factor, such as impurities in the glovebox atmosphere.) The second cell was operated at current densities from 0.025 to 0.076 A/cm² at temperatures from 415 to 428°C. The characteristics of the discharge-charge voltage-*vs.*-time curves of both cells were quite similar to those of the cells operated with the Noranda matte. On charging, there was a minor plateau at 1.6 V, a major one at 1.75 V, and a minor one at 1.85 V. On discharging, there was a minor plateau at 1.65 V, a major one at 1.50 V, and a minor one at 1.2 V.

As with the Noranda matte, a short test was also made with a single-piece electrode that was formed by premelting some matte in a crucible. The test was terminated when the electrode was 10% discharged. Metallographic examination of the electrode showed that the expansion in the reacted region was less than that of an FeS electrode and was similar to that of the Noranda matte.

The cell tests with mattes indicate that tests of these mattes in larger-scale engineering cells is warranted. In addition to the benefits that are indicated from the successful operation of these cells, the mattes have an advantage over FeS in that they are much less friable. Consequently, cell loading with matte powders would be much easier than with FeS powders.

3. Cells with CoS as an Additive

A few cell tests were performed to determine the possible beneficial effects of CoS as an additive to iron sulfide electrodes.

Li/FeS₂-CoS Cell. An FeS cell was operated with a CoS* additive. The molar and weight ratios of CoS to FeS₂ in this cell were 0.25 and 0.19, respectively. The electrochemical behavior of the cell was excellent. On discharging, the voltage-*vs.*-time curves showed a minor plateau at 2.05 V and a major one at 1.61 V; on charging, the curves showed a major plateau at 1.63

* As discussed in Section V.F.1, below, CoS is not stable at the cell operating temperature; at 400°C, the CoS would be present as Co₉S₈ plus a minor amount of Co₂S₃.

V and a minor one at 1.91 V. The 1.91-V plateau, which is probably associated with the formation of FeS_2 , appeared at a lower voltage than without the CoS additive. The most unusual characteristic of the product electrode was the complete absence of the Z phase (approximate composition, $\text{Li}_4\text{Fe}_2\text{S}_5$), which is a dominant phase produced in cells without the additive. X-ray examination showed the presence of FeS, with a slightly modified lattice parameter, and FeS_2 . Apparently, for some reason not yet identified, the presence of CoS in the electrode prevents the formation of the Z phase so that the progression of phases during charging is (1) Li_2FeS_2 , (2) FeS saturated with CoS, and (3) FeS_2 .

Li/FeS-CoS Cell. An FeS cell was also operated with CoS as an additive. The molar and weight ratios of CoS to FeS in this cell were 0.25 and 0.26, respectively. The electrochemical behavior of the cell was again excellent. On discharging, the cell showed a single plateau at 1.66 V; on charging, it showed a major plateau at 1.68 V and a minor one at 1.93 V. Presumably the plateaus correspond to similar plateaus observed without an additive. Thus, the second plateau on charging probably corresponds to the conversion of J phase to FeS. X-ray examination of the product revealed the J phase and FeS with a slightly modified lattice parameter.

A second Li/FeS cell with CoS as an additive was also operated. The FeS-CoS material used in this cell was melted to form an ingot which was ground to a powder. In this way, an electrode material consisting of a solid solution of FeS and CoS was produced in the hope that the initial deleterious expansion caused by the formation of the J phase could be avoided. The test was terminated after only a 15% discharge and the product was examined. The examination, together with the necessary corroborating tests, showed that upon heating to the cell operating temperature of 405°C , the initial FeS-CoS solid solution had decomposed into FeS-rich and CoS-rich phases. Consequently, during the cell operation, the J phase had formed and the electrode expansion was similar to the expansion of a physical mixture of FeS and CoS. (The available phase data on the FeS-CoS system indicate complete solid solubility of the two phases at temperatures near the melting points, but the system has not been studied at temperatures as low as 400°C .)

The conclusion from the study of the use of CoS as an additive to iron sulfide cells is that it may be a useful additive to the positive electrodes of Li/FeS₂ cells, but that it has little or no beneficial effect on Li/FeS cells.

4. Overcharge Studies of FeS_2 Electrodes (Z. Tomczuk, A. E. Martin)

Cell tests and cyclic voltammetry studies have been conducted to (1) determine the nature of the overcharge products in FeS_2 electrodes, (2) establish the voltages at which these products are formed, and (3) elucidate the reaction mechanism. The cell results and the cyclic voltammetry data are discussed below.

Li/FeS₂ Cell Studies. Five Li/FeS₂ cells were operated through several discharge-charge cycles and charged to successively higher cutoff voltages. Previous cell tests (see ANL-8109, p. 79) had indicated that, upon charging a fully discharged Li/FeS₂ cell, the progression of phases in the

sulfide electrode is as follows:

- I. Fe + Li₂S (fully discharged condition)
- II. X phase (Li₂FeS₂)
- III. Z phase (approximately Li₄Fe₂S₅) + FeS
- IV. FeS₂ (fully charged condition)

In these earlier studies, the maximum charge cutoff voltage was 2.50 V. The purpose of the present work was to investigate the effects of extending the charge cutoff voltage to 2.88 V. The results, presented in Table V-1, indicate that the increase in charge cutoff voltage caused increased porosity of the sulfide electrode and a decrease in the current efficiency. X-ray diffraction data on the positive electrodes indicated that FeS₂ was the only sulfide phase present, as had been observed at the lower cutoff voltage, but there was evidence that FeCl₂ had formed at voltages above 2.65 V and reacted with KCl in the electrolyte to produce KFeCl₃ (or K₂FeCl₄):

The fact that a higher porosity than usual was observed in the sulfide electrode suggested very strongly that a gaseous product was being formed (this product was later identified as sulfur, as discussed below).

The discharge-charge curves, such as those shown in Fig. V-1 for Cell RU-6, for these cells are very similar to those obtained at lower charge cutoff voltages, except that a marked upswing of the charge curve occurs as the charge cutoff voltage is increased.

Cyclic Voltammetry Studies. As indicated above, a gaseous product appeared to be formed in the FeS₂ electrodes at charge cutoff voltages >2.65 V. Cyclic voltammetry studies were therefore undertaken to define the product and also to elucidate the reaction mechanism.

Table V-1. Results of Charging Li/FeS₂ Cells to Successively Higher Cutoff Voltages

Cell No.	Charge Cutoff Voltage, V	Average Coulombic Efficiency, %	Porosity of Sulfide Electrode	FeS ₂ Phases Found by X-ray
RU-1	2.52	92	Very low	FeS ₂
RU-2	2.65	91	Low	FeS ₂ , Z phase
RU-3	2.74	87	Medium	FeS ₂ , KFeCl ₃ or K ₂ FeCl ₄
RU-5	2.79	84	High	FeS ₂ , KFeCl ₃ or K ₂ FeCl ₄
RU-6	2.88	83	Medium-high	FeS ₂ , KFeCl ₃ or K ₂ FeCl ₄

Fig. V-1. Typical Discharge-Charge Curve for Cell RU-6

The experiments were performed in a cell having a positive electrode of single-crystal FeS_2 embedded in an ATJ graphite container, counter and reference electrodes of 40 at. % Li-Al alloy, and an electrolyte of LiCl-KCl. The measurements were made with a Wenking potentiostat and voltage scan generator. Experimental variables examined were the effects of scan rate (3-20 mV/sec), voltage range (1.70-2.70 V), and cell temperature (372-453°C) on peak position. The voltage range was selected to cover those voltages at which both the normal charge reactions and overcharge reactions occur in the FeS_2 electrode.

A typical voltammogram is shown in Fig. V-2. These data, which were taken at 372°C, show the presence of three anodic (oxidation) peaks and four cathodic (reduction) peaks. As the temperature was increased above 400°C only three cathodic peaks were observed; the minor peak near 2.15 V had completely disappeared. This result suggests strongly that there is at least one chemical reaction occurring at the higher temperature.

The first cathodic peak results from a reversal of the major anodic peak, starting near 2.4 V vs. Li-Al. For a cell temperature of 372°C, this peak was not observed until an anodic potential of 2.5 V was used. The cell test data, plus data from an additional constant-voltage charging experiment, indicated that the products of the anodic reaction were FeCl_2 and sulfur.

The second cathodic peak, observed only at temperatures between 372 and 391°C, probably involves the reduction of free sulfur to S_2^{2-} by the reaction

The third cathodic peak involves the formation of S^{2-} by the reaction

Fig. V-2. Typical Voltammogram at 372°C

This reaction path was confirmed by examining the effect of the addition of Li_2S on the peaks. As the amount of Li_2S in the electrolyte was increased, the third cathodic peak as well as the anodic peak near 1.85 V also increased. It was concluded that the species formed on the cathodic side must be sulfide, S^{2-} , because it is the only species present that is capable of being oxidized near 1.85 V.

The last cathodic peak is not included in consideration of the overcharge reactions because it results from the onset of the cell reaction

This is the first electrochemical reaction observed during the discharge of Li/FeS_2 cells.

On the basis of the observed cathodic and anodic peaks, the conclusion is that the observed peaks are caused by the onset of the major reaction of FeS_2 close to 2.4 V. Therefore, the overcharge mechanism is simply the oxidation of FeS_2 to form FeCl_2 and free sulfur by the following reaction:

The remaining peaks involve free sulfur. A possible reduction mechanism for this sulfur is as indicated by Reactions 2 and 3. The oxidation mechanism would be the reverse of Reactions 2 and 3. Reactions 2, 3, and 5 are all electrochemical. An inability to obtain meaningful data at scan rates >10 mV/sec made it almost impossible to identify the chemical reaction(s) that must be taking place at the higher temperatures. The reaction obviously cannot involve the reaction of sulfide with free sulfur because there is no additional source of sulfide. The observation that the electrolyte melt, after cycling was completed, had turned yellowish suggests strongly that a more complex sulfur species, perhaps a polysulfide greater than S_2^{2-} , had formed. Out-of-cell tests with FeS_2 in the LiCl-KCl electrolyte failed to give the same coloration.

B. Electrochemical Characteristics of Lithium-Aluminum Electrodes

1. Diffusional Overpotential of Li-Al Electrodes (M. F. Roche, D. R. Vissers, K. E. Anderson)

Current-interruption measurements, at about 700 K, on Li/LiCl-KCl/Li-Al cells and $\text{Li-Al/LiCl-KCl/iron sulfide}$ cells have shown that diffusional overpotentials play a major role in determining the extent of utilization of the Li-Al and iron sulfide electrodes (see ANL-75-1, p. 109). The diffusional overpotential, which arises from the concentration gradient in Li-Al during its discharge, is treated here.

As fully charged particles of Li-Al are discharged, the volume of beta phase (approx. 50 at. % Li)³ in the particles decreases as the volume of alpha phase, which is aluminum containing 8.7 at. % Li at saturation,³ increases. In this approximate treatment, the alpha phase is treated as a uniformly thick, void-free shell growing on the surface of the beta phase (which is shrinking in volume) as discharge proceeds, thus providing an increasingly thick diffusion barrier. In addition, the solid Li-Al structure is treated as a collection of parallel wires of constant length and extending from front to back of the electrode. (A treatment based on particles rather than wires gives similar results, but the wire model is more readily adapted to later, more detailed analysis.) The wire radius is adjusted to fit diffusional data, and is approximately 10^{-3} cm for well-cycled Li-Al . The current is assumed to flow equally to all regions of the electrode. This is equivalent to setting the electrolyte resistance and the wire electronic resistance equal to zero.

Because of this uniform-current approximation, the equations to be given here are restricted to modeling electrode characteristics near the end of discharge, when the solid-state diffusional overpotential overwhelms the other electrode overpotentials. Solutions to the coupled, nonlinear partial differential equations that describe the entire discharge have not yet been obtained. However, approximate treatments have shown that it is essential to include the effects of limited current penetration into the electrode in order to adequately model the diffusional resistance early in the discharge.

The concentration of lithium in the alpha phase is low enough to permit this phase to be treated simply as a diffusion barrier, and the lithium

concentration profile in the alpha phase is, therefore, that for steady-state radial diffusion through a cylindrical shell:⁴

$$C_{\alpha} = \rho_{\alpha} w_{\alpha} \left[1 - (1 - a_s) \frac{\ln(r_{\beta}/r)}{\ln(r_{\beta}/r_{\beta + \alpha})} \right] \quad (6)$$

where

C_{α} = concentration of Li in alpha phase

r = radius measured from wire axis

r_{β} = radius of beta phase (decreases from initial radius, r_{β}^0 , with discharge)

$r_{\beta + \alpha}$ = total wire radius (decreases with discharge)

ρ_{α} = density of alpha phase, 2.7 g cm^{-3}

w_{α} = weight fraction lithium in saturated alpha = 0.024

a_s = activity of lithium at electrolyte/alpha phase interface. (The lithium activity of saturated alpha phase is defined as unity.)

The rate of beta-phase utilization per unit area of beta phase and the Fick's second-law flux in the alpha phase at r_{β} are equated:

$$\frac{\rho_{\beta} w_{\beta}}{A_{\beta}} \left(\frac{dV_{\beta}}{dt} \right) = \frac{D \rho_{\alpha} w_{\alpha} (1 - a_s)}{r_{\beta} \ln(r_{\beta}/r_{\beta + \alpha})} \quad (7)$$

where

D = diffusivity of lithium in alpha phase

= $1.8 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$ at 700 K^5

ρ_{β} = density of β -Li-Al = 1.75 g cm^{-3}

w_{β} = weight fraction Li in Li-Al = 0.20

V_{β} = volume of beta phase (decreases from initial volume, V_{β}^0 , with discharge).

A_{β} = area of beta phase (decreases with discharge)

The total current to the electrode is set equal to the rate of beta phase utilization:

$$I = FM^{-1} \rho_{\beta} w_{\beta} \left(dV_{\beta}/dt \right) \quad (8)$$

where

I = current

F = Faraday

M = atomic weight of Li

The geometric constraints on the radii and, through them, on the volumes and areas of the phases, are satisfied by the following:

$$\begin{aligned}
 r_{\beta} &= r_{\beta}^{\circ} (1 - U) \\
 r_{\beta} + \alpha &= r_{\beta}^{\circ} + \alpha [1 - kU] \\
 k &= 1 - \frac{\rho_{\beta} (1 - w_{\beta})}{\rho_{\alpha} (1 - w_{\alpha})}
 \end{aligned}
 \tag{9}$$

where U is the fraction of the electrode discharged. Combination of the above equations results in the following equation for the solid-state diffusion overpotential, η_D :

$$\begin{aligned}
 \eta_D &= -\frac{RT}{F} \ln a_s \\
 &= -\frac{RT}{F} \ln \left[1 - \frac{MI (r_{\beta}^{\circ})}{4FD \rho_{\alpha} w_{\alpha} V_{\beta}^{\circ}} \ln \left(\frac{1 - kU}{1 - U} \right) \right]
 \end{aligned}
 \tag{10}$$

The curve for discharge capacity density vs. current density for a high, IR-free discharge-cutoff potential is obtained from Eq. 10 by holding η_D at the appropriate value and solving for fractional utilization as a function of current density. This type of plot is shown in Fig. V-3 for Cell DK-19 (see Section III.B.1) discharged to 700 mV (IR-free) vs. lithium. (A 700 mV IR-free cutoff corresponds to $\eta_D = 400$ mV, since $\alpha + \beta$ Li-Al has an emf of approximately 300 mV with respect to lithium.) The model is seen to fit the data reasonably well. Cell DK-19 was constructed and operated in such a way that it met the conditions required by the diffusion model. Good electronic current collection was insured through the use of a Retimet current collector,

Fig. V-3. Discharge Capacity Density Data for Cell DK-19 and Curve Calculated from Solid-State Diffusion Model

and the result was a high lithium utilization, namely, about 97% of theoretical at low current densities. The measurements are now being extended to higher current densities and to a range of cell temperatures, and the model is being refined in order to treat a wider variety of conditions.

2. Nonuniformity of the Electrochemical Reaction in Li-Al Electrodes (J. R. Selman)

The distribution of particle sizes observed in cross sections of electrochemically formed Li-Al electrodes indicates that the reaction does not occur uniformly throughout the electrode. Such nonuniformity might occur in the absence of diffusional polarization in the Li-Al alloy and in the electrolyte; for this to be the case, the ohmic resistance in the electrolyte path must be far greater than the kinetic resistance associated with the charge-transfer reaction

The dimensionless number that expresses the ratio of these resistances

$$\nu^2 = i_0 a F L^2 / R T \kappa$$

where

i_0 = exchange-current density of Reaction 11, A/cm²

a = specific area, cm²/cm³

L = electrode thickness, cm

κ = ionic conductivity, ohm⁻¹ cm⁻¹

was estimated to be $>10^6$. From this result, it follows that the reaction is distributed very nonuniformly, at least initially; that is, the reaction zone is concentrated at the electrode-electrolyte interface (penetration depth, $\sim 10^{-3}$ cm). If the reaction is assumed to remain concentrated in a narrow zone that advances into the porous electrode, the optimization of electrode thickness and volume percentage of electrolyte in the fully charged electrode is relatively simple. The optimum thickness (for a fixed cutoff resistance of the electrode) is 0.56 cm. The optimum volume of electrolyte, 20%, agrees well with experimental results, which indicate an optimum electrolyte volume of 20-30% for 0.32- and 0.64-cm-thick electrochemically prepared Li-Al electrodes.

This result was unexpected, since the assumption of a narrow reaction zone that was made in the model is plausible only in the beginning of the discharge. The reaction zone broadens rapidly as solid-state diffusional resistance builds up; a model based on a uniform distribution of the reaction fits the polarization measured at the end of a discharge fairly well (see preceding subsection B.1).

Optimization of the volume percent electrolyte in the electrode involved maximization of the product of the capacity per unit volume of the electrode and the effective electrolyte conductivity. The applicability of this approach may be general; this possibility is being investigated.

C. Investigations of Other Cell Systems
(S. J. Preto, M. F. Roche, A. E. Martin)

The use of calcium as the active material in the negative electrodes of molten-salt secondary cells is attractive for several reasons: its salts are abundant and low in cost, and the metal has a low equivalent weight, high reactivity, and high melting point (839°C). Because of its high melting point, solid calcium can be used in cell geometries that preclude the use of liquid metals such as lithium and sodium. The objective of this study is to develop cells having calcium electrodes and evaluate their use for off-peak energy storage and electric-vehicle propulsion. Both molten-salt and low-temperature (organic solvent) cells are under consideration, but the initial studies have been focused on molten-salt-electrolyte cells.

A 1.4-V $\text{CaAl}_4/\text{NaCl-CaCl}_2/\text{FeS}$ cell of 3 A-hr capacity (limited by the negative electrode) was operated successfully for 14 discharge-charge cycles at 550-560°C with a coulombic efficiency and a negative electrode utilization of nearly 100%. The charge and discharge current densities in the 7-cm² negative electrode were 43 and 86 mA/cm², respectively. The NaCl-CaCl_2 eutectic (mp, 506°C) used in this cell is the same as that employed in Downs cells for sodium metal production. Sodium reduction must be avoided in the present cell, however, so that an invariant salt composition can be maintained. (Calcium sulfide, which has a free energy of formation⁶ that is 30 kcal/mol more negative than that of sodium sulfide, will be precipitated in the positive electrode structure.) Aluminum, which forms compounds with calcium but not with sodium,³ was added to the negative electrode to lower the calcium reduction potential and thereby eliminate reduction of sodium. The emf of the (CaAl_4 , Al) electrode measured with respect to a Na-5 wt % Ca pool in the NaCl-CaCl_2 electrolyte was approximately 0.4 V at 550°C throughout charge and discharge.

Compounds more rich in calcium than CaAl_4 are desired for use in the cell negative electrode. Calcium silicides such as Ca_2Si and calcium aluminum silicides are being prepared pyrometallurgically and electrochemically for this purpose. Lower melting electrolytes are also being sought. An electrolyte with a melting point of 407°C and a composition of 54 mol % LiCl , 29 mol % CaCl_2 , 4 mol % CaF_2 and 13 mol % KBr has been prepared; calcium metal has remained a stable solid in this electrolyte at temperatures up to at least 475°C. The electrolyte will be tested in Ca/FeS and Ca/FeS_2 cells.

The current collector in the positive electrode of the CaAl_4/FeS cell described above was molybdenum screen. Metallographic examination revealed that two unidentified reaction layers had formed on the molybdenum: an adherent, highly reflecting phase, and a gray, anisotropic phase present both as needles and as a poorly adherent layer. These observations suggest that molybdenum may not be a suitable current collector in these cells. However, in cells with lower operating temperatures, molybdenum may exhibit reduced corrosion rates.

D. Wetting and Creeping Characteristics of LiCl-KCl Electrolyte

1. Wetting Studies

As indicated in the preceding semiannual report (ANL-75-1, p. 111), the wetting characteristics of various cell components by the molten LiCl-KCl electrolyte are important factors in achieving optimum performance and longevity of high-temperature cells. The electrolyte must wet the porous separator material in the cell to permit the passage of lithium ions between the electrodes, and the proper wetting relationship must be maintained between the electrolyte, active material, and current collector in both electrodes. On the other hand, it would be desirable, if possible, to avoid the wetting of certain components, such as electrical feedthroughs, by the electrolyte.

Additional wetting measurements were made to assess the effect of various electrolyte additives and the type and pretreatment of the solid surface. The tests were performed in a helium atmosphere at temperatures near 400°C. In one experiment, the effect of moisture that is taken up by LiCl-KCl eutectic as it is stored in a helium-atmosphere glovebox for long periods of time was determined by wetting tests on porous BN surfaces that had been fired at 1650°C in a nitrogen atmosphere. A fresh batch of the salt had an advancing contact angle of $145 \pm 2^\circ$, whereas salt that had been stored in a sealed jar for four months gave a value of $128 \pm 3^\circ$. Since this electrolyte is known to pick up significant amounts of moisture when stored under these conditions, these results suggest that its wetting of BN is enhanced by the presence of moisture. The difference in the two values for the contact angle is considered more significant than the individual values.

Moisture in the LiCl-KCl electrolyte is thought to be converted to oxide ion over a period of time (see Section V.E, below). Thus, the addition of moisture was simulated by saturating the salt with Li₂O. On a porous BN surface, the advancing contact angle was $127 \pm 8^\circ$ for electrolyte without Li₂O and $106 \pm 1^\circ$ after the Li₂O addition. Thus, wetting was improved by the oxide addition. On a polished iron surface, the effect was much more striking. In the absence of Li₂O, the advancing contact angle decreased from $83 \pm 1^\circ$ to $77 \pm 1^\circ$ over a period of about 2 hr. With the oxide-saturated salt, the contact angle, which was initially about $96 \pm 2^\circ$, decreased to a constant value of $17 \pm 1^\circ$ after about 3 hr. The change of contact angle with time is shown in Fig. V-4. Although the oxide addition appeared to have only a small (or insignificant) effect initially, it greatly increased the ultimate wettability of the iron surface by the LiCl-KCl eutectic.

The effect of fluoride ion on wetting was studied with a 3.5 mol % LiF addition to the LiCl-KCl eutectic. On a BN surface, the difference is not significant; the advancing contact angle was $145 \pm 2^\circ$ without fluoride and $142 \pm 2^\circ$ with fluoride. On a polished iron surface, a significant but rather modest improvement in wettability was obtained; the wetting angle was $86 \pm 4^\circ$ without fluoride and $73 \pm 4^\circ$ with fluoride.

Studies were also undertaken to evaluate a chemical plasma treatment of BN surfaces as a possible alternative to nitrogen-firing at 1650°C. A low-temperature plasma produced by a radio-frequency generator has a high concentration of very reactive free radicals that can change the surface chemistry of solids that are exposed to the plasma.⁷ Some BN specimens were treated in

Fig. V-4. Variation in Wettability of Polished Iron by Li_2O -Saturated LiCl-KCl Eutectic at 440°C in a Helium Atmosphere

this fashion at the International Plasma Corp. (Hayward, Calif.). On a BN surface with the usual nitrogen-firing, the salt had an advancing contact angle of $126 \pm 2^\circ$. On a BN surface that was nitrogen-fired and later treated with a $\text{H}_2\text{-N}_2$ plasma essentially at room temperature, the angle was $109 \pm 2^\circ$. On a BN surface that was not nitrogen-fired, but was treated with an NH_3 plasma, the angle was $118 \pm 2^\circ$. These plasma treatments, like the nitrogen-firing, are intended to reduce B_2O_3 that may be on the surface of the BN specimen. These results suggest that, on the basis of wettability only, the low-temperature plasma treatment is at least as effective as the high-temperature nitrogen treatment.

2. Electrolyte Creeping Studies

Creeping of the molten LiCl-KCl electrolyte over various surfaces has been observed both in laboratory experiments and in the operation of cells. A relationship exists between wettability and the tendency of a liquid film to creep on a solid surface; that is, a necessary condition for creeping is that the liquid spread on the solid. However, there appears to be an additional requirement of a driving force involving a gradient in the liquid surface tension. This liquid film movement, which is known as the Marangoni effect,⁸ is a convection process that causes the liquid to move from regions of lower surface tension to those of higher surface tension. Such gradients can result from differences in temperature, concentration, surface electric charge, or extent of chemical reactions.⁹ Studies have been reported on surface movement induced by chemical reactions at liquid metal surfaces.¹⁰

An alternative theoretical framework for creeping is provided by the concept of the film disjoining pressure.¹¹ For a thin, planar liquid film, the surface tension is a function of the thickness, and the film disjoining pressure is used to characterize the difference between the surface

tension of the thin film and the ordinary surface tension of the liquid. This effect can cause a thin liquid film to climb up a vertical solid surface to a much greater distance than that predicted from classical meniscus-shape calculations.¹²

Very preliminary calculations on the dependence of surface tension on layer thickness for a liquid metal (a much simpler case than molten salts) showed that thin layers have a higher surface tension than the bulk liquid. This result relates the film disjoining pressure concept to the Marangoni effect because the surface tension gradient of a thin, climbing film is in the upward direction. Moreover, an increase in surface tension with decreasing film thickness relates creeping and wetting effects, since the thin film will exist only at the leading edge of a liquid that advances with a contact angle near zero.

Experimental tests were conducted on the creeping characteristics of molten salts in various types of crucibles under helium atmosphere at temperatures from 380 to 500°C. The initial tests were performed with the LiCl-KCl eutectic in crucibles or beakers of stainless steel, nickel, borosilicate glass, alumina, or molybdenum. An alumina crucible that had been presoaked in electrolyte was also used. The tests were of 3 to 14 days duration. No liquid film was observed on the surfaces of the containers, and no weight loss could be detected. Tests were also performed with LiCl-KCl eutectic that contained various additives. Lithium-saturated salt was tested in an alumina crucible, and salt containing 3.5 mol % LiF was tested in an alumina crucible and a stainless steel beaker. Again, no films of molten salt were observed and there were no measurable weight losses.

Because of the pronounced effect of oxide addition on wetting of iron by LiCl-KCl, a test was performed on the wetting of a molybdenum cup at 500°C by LiCl-KCl eutectic saturated with Li₂O. During the first few days, a film of the molten salt gradually crept up the inside surface of the cup, and after about eight days the entire inner and outer surfaces had a shiny, wet appearance. This condition was maintained for 13 days, but the cup showed no overall loss of weight. Throughout the test the cup was well wet by the molten salt meniscus. The results of this test suggest that creeping of the electrolyte may be enhanced by the presence of impurities such as moisture or oxide.

In experimental work, it has often been a practice to support a vessel containing molten electrolyte on a porous ceramic block. Under these conditions a large amount of the electrolyte may be lost by creeping out of the vessel and into the porous ceramic. This possibility is being examined as a mechanism of electrolyte loss.

E. Electrochemical Studies of Impurities in LiCl-KCl Electrolyte (C. A. Melendres)

A major cost consideration in the development of Li-Al/iron sulfide batteries for commercial-scale applications has been that of the LiCl-KCl eutectic electrolyte. The laboratory and engineering cells to date have been operated with research-grade electrolyte costing about \$250/kg. To make Li-Al/iron sulfide batteries economically viable, this cost must be lowered markedly, either through the development of less expensive purification methods, the

tolerance of higher impurity levels, or both. In any case, analytical methods are needed to detect impurities in the electrolyte so that acceptable levels can be specified. Electrochemical techniques that are being developed in the present program appear promising in this regard.

1. Determination of Impurities in LiCl-KCl Electrolyte

Cyclic voltammetry has been explored to detect water contamination in the LiCl-KCl eutectic. In this technique, the potential of a working electrode is varied continuously over the range in which the substances of interest undergo electrochemical reactions. These reactions occur at definite characteristic potentials and give rise to current peaks that are proportional to the concentration of the species involved. However, the results are affected by a number of variables, such as potential scan rate, type of electrodes (and design), nature of the electrode surface, temperature, purity of the helium atmosphere, etc., and these must be optimized for the analytical method to be reliable. The proportionality between peak current and concentration can be affected by the presence of chemical reactions coupled to the electron-transfer process and by adsorption phenomena which therefore need to be considered in using this technique as an analytical procedure.

Previous work had established the utility of ($\alpha + \beta$) Li-Al alloy (with compositions in the range 5-45 at. % Li) as a reference electrode and tungsten and vitreous carbon as working electrodes in the voltammetric study of LiCl-KCl melts. The difficulty in sealing tungsten in glass to obtain electrodes of well-defined area has led to the use of platinum as a working electrode. Platinum is also sufficiently noble to allow the study of most redox systems (with a potential range of over 3 V). To ensure utmost "cleanliness," all components of the present voltammetric cell system were made of platinum. A platinum dish was used as a container for the electrolyte and at the same time as the counter electrode. The thermocouple was sheathed in platinum tubing. The reference electrode compartment consisted of an alumina crucible placed inside a platinum crucible. Borosilicate or quartz containers were found to be unsuitable for the melt, especially in the presence of O^{2-} ion; etching of these materials introduces electroactive impurities into the melt. The working electrode consisted of platinum tubing attached to a lead of platinum wire sealed in glass.

At the present stage of this work, it is possible to conduct routine analyses by linear sweep voltammetry for the presence of O^{2-} , OH^- and H_2O in the electrolyte. Contamination of the LiCl-KCl eutectic by water was found to introduce electroactive species such as H^+ , OH^- , O^{2-} , H_2O , HCl and H into the melt through the dissociation of H_2O and its hydrolytic reactions with the salt. Detection of one or more of these species may therefore provide the basis for an analytical method. By standard-addition procedures using known quantities of Li_2O and KOH , the potential ranges for reversible redox reactions involving O^{2-} , OH^- and H_2O were determined. These results are summarized in Table V-2. Calibration curves of peak currents and concentrations were also constructed. Diffusivity values for O^{2-} and OH^- were obtained from these data and the variation of peak current with scan rate, as given by the Randles-Sevcik^{13,14} equation for a reversible process at 400°C:

$$i_p = 1.80996 \times 10^5 n^{3/2} A D^{1/2} C_o v^{1/2} \quad (12)$$

where

- i_p = peak current, A
- n = number of electrons transferred
- A = electrode area, cm^2
- D = diffusivity, $\text{cm}^2 \text{sec}^{-1}$
- C_o = concentration, mol cm^{-3}
- v = scan rate, V sec^{-1}

The diffusivity of H_2O is currently being determined. The value for OH^- ion appears to be rather high, possibly because of some kinetic complications related to coupling with the Lewis acid-base reaction

The equilibrium for this reaction appears to be farther to the left than previously thought. The low solubility of water in the melt ($\sim 2.4 \text{ ppm Torr}^{-1}$) shifts the reaction to the right, but at a very low rate. In determining the proportionality between peak current and concentration, it was necessary to take into account changes in the concentration of the substance of interest brought about by the above equilibrium. Other complications resulting from Reaction 13 are therefore being examined.

At the present stage of development of the voltammetric sweep method for the determination of initial moisture contamination in LiCl-KCl eutectic, detection sensitivities of about 10 ppm each for O^{2-} , OH^- and H_2O appear attainable. The O^{2-} concentration in highly purified and lithium-contacted LiCl-KCl from the Anderson Physics Laboratories varied between 10 and 50 ppm, but the value was typically less than 20 ppm, and one sample that was analyzed for OH^- showed a level of 20 ppm. Significantly higher concentrations of H_2O and O^{2-} were found in Anderson salt that had not been treated with chlorine or contacted with lithium, and in LiCl-KCl that had been prepared in this laboratory by drying the individual constituents in a fluidized bed. When the latter material was filtered and purified further by electrolysis, however, the H_2O and O^{2-} concentrations were both less than 10 ppm. A sample of LiCl-KCl that was obtained from the Lithcoa Corp. had as low a concentration of H_2O as the lithium-contacted Anderson salt, but the O^{2-} content was higher.

Table V-2. Potential Ranges for Reversible Redox Reactions of O^{2-} , OH^- , and H_2O

Electrode Reaction	Potential Range, ^a V	$E_{1/2}$, ^a V	Diffusivity, $\text{cm}^2 \text{sec}^{-1}$
$\text{O}^{2-} \rightleftharpoons \text{O} + 2e^-$	2.2-2.65	2.465	$4.3 \times 10^{-6} (\text{O}^{2-})$
$\text{OH}^- + e^- \rightleftharpoons \text{H} + \text{O}^{2-}$	0.3-0.8	0.508	$1.3 \times 10^{-4} (\text{OH}^-)$
$\text{H}_2\text{O} + e^- \rightleftharpoons \text{H} + \text{OH}^-$	1.4-1.8	1.573	-

^aVersus Li-Al.

Plans are being made to check the accuracy of the sweep voltammetric method by a comparison of the total oxygen in O^{2-} , OH^- , and H_2O observed by this method with the results of neutron activation analysis for oxygen. The voltammetric technique is not being extended to other electrolyte impurities at present because the metallic elements can be determined more easily by emission spectral analysis. In addition, Prof. H. A. Laitinen at the University of Florida is investigating more sensitive electrochemical methods for the measurement of metallic impurities. Meanwhile, the voltammetric method appears to be adequate for the routine analysis of electrolyte impurities that are of greatest concern in the cell development work.

As an adjunct to the above studies, the kinetics of O^{2-} discharge at platinum, gold, and glassy carbon electrodes were examined to investigate the possible use of electrolysis as an electrolyte purification procedure. The O^{2-} ion appears to be oxidized reversibly in molten $LiCl-KCl$ at platinum and gold electrodes *via* a two-step mechanism:

Oxidation at the glassy carbon electrode occurs irreversibly, giving three voltammetric waves with peak potentials in the regions of 1.6, 2.8, and 3.1 V *vs.* Li-Al. The first diffusion-controlled peak at ~ 1.6 V is attributed to the reaction

which has a theoretical potential of 1.57 V *vs.* Li-Al. Initial results indicate that $\alpha n_a = 1.34$, where α = the transfer coefficient, and n_a = the number of electrons involved in the rate-determining step. Assuming n_a to have a value of 2, α would then be 0.67. The waves at 2.8 and 3.1 V appear to correspond to two consecutive irreversible electron transfers. Further studies of the reaction mechanism, including chronopotentiometric measurements, are planned.

2. Effect of Electrolyte Impurities on Cell Performance

To specify the level of impurities that can be tolerated in the electrolyte for Li-Al/iron sulfide cells, their effects on the performance of each cell component and the cell lifetime must be investigated. Laboratory cells show an increasing difficulty in charging close to the end of their lifetime. It is possible that the buildup of impurities such as corrosion products plays a significant role. Experiments have therefore been planned to examine the performance of the Li-Al electrode initially using electrolyte with known levels of O^{2-} , OH^- and metallic impurities.

F. Related Physical Research*

1. Phase Studies of Metal Sulfide Systems

The Li-Fe-S System at 400°C. A knowledge of the Li-Fe-S phase diagram at 400°C is important in understanding the reactions that occur in FeS

*This work was supported by the ERDA Division of Physical Research.

and FeS_2 electrodes as they are charged and discharged. As mentioned earlier (ANL-75-1, p. 120) the investigation of this system was suspended because a suitable inert-atmosphere metallographic facility was not yet available. However, some metallographic samples of preparations that had been made in an earlier study of the system were reexamined. Evidence was obtained for the existence of a third ternary phase, designated "Y", which had not been distinguished previously from the Z phase. The Y and Z phases both have a composition near $\text{Li}_4\text{Fe}_2\text{S}_5$, but the Y phase is slightly richer in sulfur. (The other ternary phase, the X phase, was established previously as having the composition Li_2FeS_2 .) Samples of sulfide electrodes from Li/ FeS_2 cells were then reexamined, but the Y phase was not detected. Presumably the Y phase would form only when the sulfur:iron ratio is greater than two, an unusual situation that could occur if Li_2S was added to the sulfide electrode.

The Li-Co-Fe-S System at 400°C. Cobalt sulfide is one of the sulfides that has been added to the positive electrodes of Li/ FeS and Li/ FeS_2 cells to obtain improved performance. A study of selected portions of the Li-Co-Fe-S system at 400°C was made to assist in the understanding of the effect of cobalt sulfide additions on the reactions in these cells.

Three cobalt sulfide materials were available for study. They were labeled by their suppliers as CoS (Rocky Mountain Research, Inc.), Co_2S_3 and CoS_2 (Cerac-Pure, Inc.). From the cobalt-sulfur phase diagram,³ CoS₂ is the only one of these sulfides that is stable at 400°C, the normal cell operating temperature. The phase diagram indicates that at 400°C, the CoS and Co_2S_3 materials would consist of (a) Co_9S_8 plus a minor amount of Co_3S_4 and (b) Co_9S_8 and Co_3S_4 , respectively. (The CoS phase is not indicated as being stable below 460°C, and Co_2S_3 is not indicated as a stable phase at any temperature.)

Mixtures of Li_2S with each of the three cobalt sulfide materials were pressed into pellets and heated as follows: Li_2S -CoS, for 19 days at 400°C; Li_2S - Co_2S_3 , for 1 hr at 950°C plus 0.5 hr at 400°C; and Li_2S -CoS₂, for 16 hr at 620°C plus 16 hr at 400°C. Metallographic examination of the products indicated that no reactions had occurred. An X-ray diffraction examination of the products confirmed that no compounds had formed. Furthermore, in each case, the Li_2S phase had its normal lattice parameter. This information indicated that none of the cobalt sulfides were significantly soluble in Li_2S at 400°C.

In addition, pellets of Li_2S -CoS-FeS in a mole ratio of 50:10:40 were heated for 1 hr at 950°C and 0.5 hr at 400°C. Metallographic and X-ray examination showed Li_2FeS_2 as the major phase in the product. The X-ray lattice parameter of the Li_2FeS_2 phase had its normal value; hence, a significant solubility of cobalt sulfide in Li_2FeS_2 at 400°C was not indicated.

Formation of the J Phase. The J phase is a Li-K-Fe-S phase that usually forms in the sulfide electrodes of Li/LiCl-KCl/ FeS cells. The formation of this phase has been observed during the initial discharge of the cells and also subsequently during each charging operation. The KCl of the electrolyte obviously must participate in the formation of the J phase because the electrolyte is the only source of potassium in the cell system.

The exact composition of the J phase has not yet been established. Based on the analyses of J-phase material recovered from engineering cells, the J-phase composition has been estimated as $K_{2.8}Li_{0.4}Fe_{12}S_{13}$ (ANL-75-1, p. 100). (Although X-ray examination indicated that this material consisted only of the J phase, metallographic examination showed the presence of iron as a minor phase.)

Attempts are being made to form the J phase by out-of-cell reactions in the hope of obtaining a purer material than that recovered from cells. The composition and stability relations of the J phase might then be determined more exactly.

Three methods that have been used to form the J phase by out-of-cell reactions were described in ANL-75-1, p. 119. A modification of the first of these methods, a two-stage process, is currently being used. In the first step, Li_2FeS_2 is formed by melting mixtures of FeS and Li_2S powders in a graphite crucible at about $1200^{\circ}C$. An excess of Li_2S is used so that the product will not contain an excess of FeS, which is difficult to separate from J phase. In the second stage, the Li_2FeS_2 - Li_2S product is mixed with LiCl-KCl eutectic salt and heated with iron at $400^{\circ}C$ for about a week. The iron is in the form of powder, wire, or sheet. The advantage of using wire or sheet rather than powder is that the excess iron can be quantitatively removed from the product by crushing the product and physically removing the iron. The remaining product is dissolved in water, leaving the J phase undissolved. A single-phase J material, based on X-ray analysis, was produced by this process using iron wire. Larger preparations using iron sheet are currently being made.

2. Electrochemical Studies (J. R. Selman, C. J. Cagigas)

Emf Studies of Lithium-Rich Lithium-Aluminum Alloys. Further emf measurements have been made on the lithium-rich half of the lithium-aluminum system. Measurements at constant composition and varying temperature have been completed. Emf data were obtained at seven compositions ranging from 49.3 to 82.3 at. % lithium. The results at $427^{\circ}C$ (700 K) were presented earlier (ANL-75-1, p. 115). The potential difference between the alloy and liquid lithium, which is 296 mV in the two-phase $\alpha + \beta$ region, decreases to 24 mV in the composition range from 48 to 56 at. % lithium (the single β -phase region). Figure V-5 shows that this steep increase of the lithium activity in the β phase is also accompanied by a reversal of the temperature dependence of the emf on going from the ($\alpha + \beta$) two-phase region to the ($Li_3Al_2 + liquid$) two-phase region.

These results indicate that the use of lithium-aluminum electrodes containing more than 50 at. % lithium may not be feasible in practical cells because of the high lithium activity at these concentrations. Moreover, the solid-liquid two-phase region apparently extends from the compound Li_3Al_2 to the lithium-rich liquidus; the range of solid alloys is therefore limited to 60 at. % lithium.

To determine the lithium-rich liquidus more accurately, coulometric emf measurements were made by discharging lithium from alloy samples containing approximately 90 at. % lithium. In these measurements, the earlier cell

Fig. V-5. Temperature Dependence of the Emf for Alloy Compositions in Three Different Regions of the Li-Al Phase Diagram

arrangement was reversed, that is, the alloy sample was a pool in which was immersed the porous BeO crucible containing the electrolyte and the lithium reference electrode. The reference electrode was a porous metal plaque saturated with lithium. Only with a large amount of alloy sample was the long-term stability of the emf satisfactory. At 470°C the liquidus was found at 82.8 ± 0.3 at. % (Fig. V-6). This value agrees more closely with the data of Grube *et al.*¹⁵ than with those of Shamray and Saldau¹⁶ (80 at. %). which were adopted by Hansen.³ The lithium activity coefficient was 0.94, which is in agreement with a negative deviation from ideality recently reported¹⁷ for the whole composition range at temperatures between 630 and 820°C. Coulometric emf measurements are continuing at temperatures of 400, 510, and 550°C.

Electrochemistry of Lithium Carbide. This work was prompted by the observation of an apparent interaction of lithium and carbon in molten LiCl-KCl eutectic electrolyte; this observation had been made in studies of the overdischarge of cells with porous graphite current collectors in the positive electrodes, and also in various basic research studies in which carbon electrodes were used. The possibility that carbide might be formed in this interaction made it desirable to investigate the electrochemistry of carbide in molten LiCl-KCl eutectic. Only exploratory methods were used, since commercially available Li_2C_2^* contained substantial amounts of metallic lithium, elemental carbon, and Li_2O (see ANL-75-1, p. 117).

The potentials of spectrographic-grade graphite immersed in molten LiCl-KCl eutectic saturated with Li_2C_2 were measured at various temperatures. The original measurements were made relative to a liquid lithium electrode,

* Alfa Products, Ventron Corp., Beverly, Mass. 01915.

Fig. V-6. Coulometric Emf Measurement of the Lithium-Rich Liquidus at 470°C

but this procedure was not satisfactory because of rather rapid self-discharge of the cell. Subsequent measurements with respect to a Li-Al reference electrode (in the two-phase $\alpha + \beta$ region of the system) gave stable potentials over periods of several hours.

The potentials that were measured in this manner were fairly reproducible (± 50 mV); these are shown, relative to the potential of liquid lithium, in Fig. V-7. These potentials would yield the standard free energy of formation of Li_2C_2 at the various temperatures, provided that the reaction

occurs reversibly at the positive electrode. Estimates of ΔG_f° found in the literature¹⁸⁻²⁰ show sizable discrepancies (see Table V-3; also Fig. V-7).

Table V-3. Values^a for ΔG_f° of Li_2C_2 (kcal/mol)

	298 K	700 K	1000 K
JANAF ¹⁸	-13.41	-11.92	-10.71
Beskorovainyi <i>et al.</i> ¹⁹ (estimate)	-10.86	-5.7	-1.4
Long ²⁰			-21.5
This Work		-26.0	

^aOf the literature values cited, only the JANAF value at 298 K is an experimental value; all others are estimates. Also, the value obtained in this study should be considered tentative, owing to the uncertainty in the reversibility of the cell reaction.

Fig. V-7. Potentials of Graphite in Molten LiCl-KCl Saturated with Li_2C_2

The present data suggest that the free energy of formation of Li_2C_2 is approximately -26 kcal/mol at 700 K. However, there is as yet no evidence that Reaction 17 is reversible; therefore, the observed potential cannot be ascribed unambiguously to Li_2C_2 formation.

Reaction 19 was explored subsequently by cyclic voltammetry. Figure V-8 shows a voltammogram obtained at a graphite electrode in LiCl-KCl without Li_2C_2 addition; Fig. V-9 was obtained after the addition of Li_2C_2 to give a concentration of $0.05M$ (the numbers in Fig. V-9 represent successive cycles). The current surge at $+1$ V vs. $\text{Li}^+/\text{Li}^\circ$, which results from an undefined interaction with graphite, as well as the subsequent oxidation peak were unchanged by the addition of Li_2C_2 . However, an oxidation peak occurred at $+2.8$ V, which decayed in time but reappeared when more Li_2C_2 was added. Oxidation of C^{2-} ions apparently takes place at $+2.8$ V, which is surprisingly high and very close to the potential of O^{2-} ion oxidation in LiCl-KCl.

The reduction maxima at $+1.7$ V probably do not result from carbon reduction but rather from the reduction of adsorbed oxygen and an abrupt change of the graphite equilibrium potential as O^{2-} ions are occluded in the finely divided carbon adhering to the graphite.

Confirmation of the oxidation potential for C^{2-} ions is being sought by chronopotentiometry.

Fig. V-8. Cyclic Voltammogram of a Graphite Electrode in Molten LiCl-KCl Eutectic

Fig. V-9. Cyclic Voltammogram of a Graphite Electrode in Molten LiCl-KCl Eutectic Saturated with Li₂C₂. (The numbers indicate successive cycles.)

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VI. DESIGN, TESTING, AND COMMERCIAL DEVELOPMENT OF BATTERIES

(R. O. Ivins, A. A. Chilenskas)

The battery design and development group provides the engineering support necessary to develop present laboratory- and engineering-scale cells into technically and economically attractive high-performance batteries. The work of the group is primarily concerned with cell and battery design, component development, battery testing, systems and cost analysis, and commercial development. Commercial development is being pursued by contracting with various industrial firms to develop and produce components such as electrical feed-throughs and ceramic separators, as well as electrodes and cells.

A. Design of a 42 kW-hr Battery for an Electric Automobile (V. M. Kolba, M. A. Slawewski,* W. W. Lark, E. C. Berrill, A. A. Chilenskas)

A design study was undertaken in cooperation with Linear Alpha, Inc., to determine whether a Li-Al/iron sulfide battery meeting certain performance goals could be installed under the hood of a compact American car. The selection and redesign of the car for electric propulsion, size and output of the battery, selection of the electrical components, and calculation of the performance characteristics of the car were subcontracted to Linear Alpha, Inc., Skokie, Illinois, with the work carried out primarily by Dr. G. J. Murphy. The work at ANL consisted of scoping the battery hardware requirements, *i.e.*, the cell design, battery case design, cell layout, insulation, heating and cooling system, and bus and connector design. In addition, calculations describing battery performance during power pulses and at constant power discharges were carried out.

The car that was selected for this design study was a 1975 Ford Mustang II. Iterative calculations resulted in a loaded car weight (two passengers) of 1568 kg (3450 lb); this weight included a 383 kg Li-Al/FeS battery or a 292-kg Li-Al/FeS₂ battery. The calculations involved estimation of the car weight, calculation of the required battery power and energy capacity, design of the battery cells, and calculation of the battery weight. Performance specifications selected were an acceleration of 0 to 50 mph in 15 sec, and a driving range of greater than 100 miles. The calculated battery characteristics that are required are shown in Table VI-1.

1. Design of a Cell for the Electric Vehicle Battery

The cell design selected for the electric vehicle battery is a cylindrical multiplate cell with central positive plates faced by negative plates; the design is based on an extension of the engineering-scale cells being tested by the Cell Development Group. The design specifications of cells employing either FeS or FeS₂ as the active material in the positive electrode are shown in Table VI-2. The values of specific energy given in the table for the two cell types (FeS and FeS₂) are 132 W-hr/kg and 173 W-hr/kg, respectively; these values represent a significant but achievable improvement over present-day engineering scale cells. The best specific energy achieved for an FeS cell is 84 W-hr/kg at the 20-hr rate and 140 W-hr/kg for an FeS₂ cell at the 10-hr rate.

*Installations Group, Chemical Engineering Division, ANL.

Table VI-1. Li-Al/Iron Sulfide Battery Specifications
for Electric Car

Basis: Converted 1975 Ford Mustang II, loaded weight of 1568 kg (3450 lb)		
Power		
Peak		60 kW ^a
Sustained Power at 55 mph		18 kW
Specific Energy		
Li-Al/FeS		110 W-hr/kg
Li-Al/FeS ₂		144 W-hr/kg
Energy Output		42 kW-hr
Battery Weight ^b		
130 Li-Al/FeS Cells		383 kg
110 Li-Al/FeS ₂ Cells		292 kg
Discharge Time		2 hr
Charge Time		5 hr
Watt-hr Efficiency (urban driving)		70%
Battery Life		
Number of Cycles		1000
Years		4
Cost of Capacity		
\$/kW-hr		20-30
\$/Battery		840-1260
Heat Loss Through Insulation		150-200 W

^aProvides 0-50 mph acceleration in 15 sec.

^bThe ratio of cell weight to battery weight is 0.83, as determined by the design study. The specific energy of Li-Al/FeS cells is 132 W-hr/kg; that of Li-Al/FeS₂ cells is 173 W-hr/kg.

A cell design employing a cylindrical multiplate configuration is shown in Fig. VI-1. To achieve this compact configuration, significant improvements in component design and electrode performance must be achieved. In the area of design, the compact feedthrough and the thin paper or cloth separator are under intensive development but are not yet available for present-day cells.

2. Design of the Battery System

In the battery design, cells are assembled in a series arrangement within an oxygen resistant container (jacket) to provide a module. The module, which is the basic building block of the battery, is the smallest unit of the battery that is easily replaceable.

Table VI-2. Design Specifications for Multiplate Cells

Design Specification	Li-Al/ FeS	Li-Al/ FeS ₂
<u>Cell</u>		
Number of Cells/Battery	130	110
Diameter, cm	15.0	15.0
Height, cm	5.23	4.63
Average Voltage, V	1.10	1.30
Theoretical Capacity, A-hr	392	392
% Utilization at End of Discharge	75	75
Energy Output, W-hr	323	382
Specific Energy, W-hr/kg	132	173
<u>Component Weights, g</u>		
Li-Al	497	497
FeS or FeS ₂	644	435
Separator	56	53
LiCl-KCl	700	691
Housing	227	217
Current Collector	219	218
Plate Hardware	27	20
Feedthrough	75	75
Total Weight	2445	2206
<u>Power and Specific Power</u>		
Peak		
W	462	546
W/kg	189	248
Normal		
W	138	164
W/kg	56	74
<u>Current and Current Density</u>		
Peak		
A		420
A/cm ²		0.430
Normal		
A		126
A/cm ²		0.129

The module design is shown in Fig. VI-2. The module consists of eleven Li-Al/FeS₂ or thirteen Li-Al/FeS cells in a series arrangement. In this module, the cell housings are insulated from each other and from the module jacket. The module jacket, which is a hermetically sealed oxidation-resistant container,* provides additional protection to the cells from the atmosphere. The cells are stacked in series by connection of the positive terminal of each cell to the housing (at negative potential) of the cell above. For charging control, a voltage lead from each cell is connected to a multiple conductor

*Nickel-plated steel is a candidate material of construction.

Fig. VI-1. Conceptual Design of a Multiplate Cell

feedthrough in the wall of the module jacket. It is possible to monitor the voltage of each cell and to adjust the charge of the cells by means of solid-state circuitry. Efforts in this area are under way (see Section VI.B.1, below) to develop charging circuits that are capable of correcting cell mismatch resulting from varying self-discharge rates, without exceeding voltage limits imposed on the system by the oxidation potentials of the cell materials. A preliminary analysis has indicated that such a charging unit would contain parts costing several hundred dollars, but that the cost might be considerably less as a mass-produced item.

The battery consists of 10 hermetically sealed modules with each module containing eleven Li-Al/FeS₂ cells or thirteen Li-Al/FeS cells. The battery design showing the space requirements for both types of cells is shown in Fig. VI-3. The space that was made available for the battery under

Fig. VI-2. Conceptual Battery Module

Fig. VI-3. Conceptual Battery for Electric Vehicle Propulsion

the hood of a Mustang II, by removing the gasoline engine (as shown by the Linear Alpha study), is a parallelepiped 50.8 by 61.0 by 91.4 cm. As shown in Fig. VI-3, the space requirements for the Li-Al/FeS battery may necessitate some repackaging of the cells and/or possible relocation of an additional component presently under the hood of the Mustang II. Repackaging the Li-Al/FeS₂ cells using a smaller diameter cell with a larger number of plates will clearly permit the Li-Al/FeS₂ battery to fit the available space. The weights of the battery and components are shown in Table VI-3.

Table VI-3. Battery and Component Weights

	Weight, kg	
	Li-Al/FeS	Li-Al/FeS ₂
Cells	318	242
Battery Hardware		
Cases	39.2	30.0
Insulation	12.7	9.7
Heaters	2.3	1.9
Bus and Connectors	5.9	4.6
Cooling Ducts	4.9	3.8
(Total)	(65)	(50)
Total Battery Weight	383	292
Ratio of Cell Weight to Battery Weight	0.83	0.83

The battery is insulated with a vacuum jacket containing multifoil insulation. This insulation, with allowance for heat losses through the battery terminals, would meet the requirements of the 150 to 200 W heat loss specified in Table VI-1. Heater tapes are provided for battery start-up and for maintaining battery operating temperature during extended periods of vehicle inactivity. When the car is operated continuously for more than half an hour of highway driving, the temperature in the battery will build up, as a result of heat generation from resistance and diffusion losses within the battery. Both liquid cooling and air cooling were considered for removal of this heat. It was concluded that air cooling would be the less expensive and more efficient method. The air flow is provided by a scoop at the front of the car, since only 15 to 20 cfm air flow is required. The incoming air is heated by countercurrent heat exchange within the battery pack before it comes in direct contact with the battery modules; this air can be used to heat the car interior during winter months.

3. Design of Battery Bus and Connectors

In the design of a Li-Al/iron sulfide battery for automobile use, careful attention must be given to the expected total internal resistance of the battery. This resistance is very important in the prediction of power losses and voltage drops during normal automobile operation and especially during peak power operation.

The internal resistance of a battery is a series combination of all resistance of the cells, cell feedthroughs, cell connections, and bus connections. In a high-temperature battery such as the Li-Al/iron sulfide battery, the resistances of the current carrying leads and connections are a more important consideration than in a battery operating at ambient temperature, because of the increases in materials resistivities and contact resistances at the higher temperatures.

Calculations were made of the resistance values of each of the components on the basis of the materials proposed for use and power loss, voltage drop, and weight considerations. Connection resistances were estimated on the basis of information available in the literature. These resistance values are summarized in Table VI-4.

Table VI-4. Battery Resistances

	Resistance, milliohms	
	Li-Al/FeS ^a	Li-Al/FeS ₂ ^b
Cell Resistance	65	60
Cell Feedthroughs	9.3	7.9
Module Hardware	34.4	30.2
Battery Case Hardware	8.3	7.9
Total Battery Resistance	117	106

^a130 cells in series.

^b110 cells in series.

The calculations showed that using conventional materials, *i.e.*, nickel- or iron-clad copper conductors, the current-carrying circuit for the 42 kW battery would weigh about 5 kg and would have a resistance, for the entire battery, about twice as great as the sum of the cell resistances.

4. Battery and Automobile Performance

The voltage-current relationship of the battery as a function of utilization of the active materials was derived from tests made on a Li-Al/FeS laboratory cell (Cell Y-2).¹ In these calculations, some allowance was made for improvements in the cell design, particularly with regard to reduction in the electrolyte fraction in the FeS electrode; however, the calculations are based on actual current densities (A/cm²) and voltages obtained in Cell Y-2. Shown in Fig. VI-4 is a plot of the calculated voltage-current relationship for various stages of battery discharge. The battery is considered fully discharged when 75% of the theoretical capacity has been used. Lines of constant power are shown for the power ranges of interest at constant-speed driving conditions. A second plot, shown in Fig. VI-5, was derived from Fig. VI-4 to show the effect of the extent of discharge upon the power capability of this battery. As is shown for a 500-A current, which can be readily handled by the solid-state motor-control system, the design peak power output of 60 kW is available until the battery reaches two-thirds of full discharge. At the end of discharge, about 48 kW is still available. Because 22 kW is required to maintain a 60 mph speed, as is shown in Fig. VI-6, the car would still be capable of a constant speed well in excess of 60 mph and would have reasonable acceleration at the end of discharge. The expected range at a constant speed of 60 mph would be about 120 miles, and the range at 20 mph would be about 300 miles (see Fig. VI-6).

Fig. VI-4. Battery Voltage as a Function of Current and Stage of Battery Discharge (100% discharge = 75% utilization). ANL Neg. No. 308-7525.

Fig. VI-5. Peak Battery Power as a Function of Current and State of Discharge. ANL Neg. No. 308-7528

5. Vehicle Design Considerations

The design features for the conversion of a conventional, gasoline-powered Mustang II to an electric vehicle with a Li-Al/iron sulfide battery has been described by Dr. G. J. Murphy of Linear Alpha, Inc.² A brief summary of the main design features follows.

Fig. VI-6. Driving Range of a 1568-kg Electric Vehicle at Constant Speed. ANL Neg. No. 308-7524

The battery is mounted under the hood, firmly attached to the chassis of the vehicle for safety, and as close to the firewall as possible, for good weight distribution.

A heat exchange system is mounted near the battery. Air is passed through the battery and the heat exchanger, with provision to circulate heated air through a conventional automobile heater to heat the passenger compartment.

A small, high-speed motor is mounted at the rear of the vehicle and is coupled through a two-speed automatic transmission to the differential. The original rear axle is replaced with an independent suspension system, to accommodate this type of drive. The motor, which was designed on the basis of proprietary work incorporated in the design of the Linear Alpha electric vehicles, has a top speed of approximately 10,000 rpm.

The controller for the motor is a Linear Alpha, Inc. Model 101 electric vehicle controller. This is an silicon-controlled rectifier (SCR) chopper with foot pedal control, operated by the original accelerator pedal in the Mustang II. The controller is mounted in the drive-shaft tunnel, which is no longer required for its original purpose since the motor is now mounted behind the rear axle.

An on-board battery charger is provided, to make the car independent of its base location. The charger is mounted in the trunk of the automobile. The resulting loss of luggage space is not significant, because the compact electric car is not intended for long trips, and there should be no need to carry luggage. The axles can be strengthened to provide the capability for carrying a payload other than the driver and passengers.

Both the steering and the braking is done without power assistance. The braking capability will be improved, however, by changing the cylinder diameter and the stroke.

An artist's conception of this compact electric car, in a cutaway view illustrating the major components of the propulsion system, is shown in Fig. VI-7.

6. Safety Considerations

The program to develop a battery for electric vehicles includes a study of the safety aspects of the battery. The principal safety considerations are (a) to evaluate the hazards associated with inadvertent contact of the active materials in a Li-Al/iron sulfide battery with each other or with the atmosphere, and (b) to provide for safe operation for stationary and vehicular use. A cell consists of solid electrodes, *i.e.*, Li-Al alloy as the negative electrode and FeS or FeS₂ powder in a metal matrix as the positive electrode. These electrodes are separated by a flexible cloth (boron nitride) and are immersed in a molten salt held at about 50°C above its melting point. The active materials in the cells in the present design are doubly encapsulated, *i.e.*, the cells are individually sealed in a mild steel or iron cell housing within a secondary container of some oxidation-resistant metal.

A preliminary safety analysis conducted early in the test program suggested that the solid electrodes would limit the extent of reaction even

Fig. VI-7. Conceptual Drawing of Electric Car. ANL Neg. No. 301-563 R1

if the negative electrode was forced into direct contact with the positive electrode, because of the surface reaction products formed. Such an experiment was carried out using FeS_2 and Li-Al alloy; temperature monitoring showed that indeed only a small degree of reaction occurred.³

A preliminary analysis has been made of the consequences of the rupture of both containment housings and the resulting direct exposure of the active materials to the circulating air coolant or air environment. The analysis suggests that, in this case also, a limited reaction of the active materials (Li-Al, Li_2S , FeS_2 , FeS) will occur, because of the protective nature of the molten salt. Safety tests to determine the type and extent of reactions that occur owing to exposure of active materials to air are to be included in the engineering safety program.

B. Development of Battery Components

1. Charge Equalization Circuit (E. C. Berrill, W. W. Lark)

Three methods are being considered for equalizing the charge in a series-connected string of unequally charged cells; these are as follows:

(1) Charge-current bypass method. A device would be provided to bypass a fixed charging current around fully charged cells and force the current to flow through undercharged cells. The devices would be connected in parallel with the cells using small tap wires capable of carrying up to 5 A.

(2) Separate cell-voltage sensing method. The addition of small voltage-sensing leads to each cell would eliminate undesirable feedback between the current-carrying tap wires and the voltage-sensing input of any device used.

(3) Constant-voltage method. This method provides each cell with a constant voltage source, which is set to the charge cutoff voltage. As the cell voltage rises, the charging current is proportionally reduced and becomes zero when the cell voltage matches the source.

These methods have been evaluated in two ways, namely, by constructing circuits using lead-acid batteries to simulate cell operating conditions and by analysis using a computer program that models the nonlinear circuit elements.

A preliminary version of the constant-voltage charging circuit was assembled and a series of initial tests indicated the following: (a) differential charging was observed, that is, low cells received a higher charging current than cells that were closer to full charge; (b) the system was stable and capable of unattended operation; (c) the charging rates were much lower than anticipated (hundredths of an ampere instead of amperes). Work on refining this system is being continued.

Because of the need for a simulation program to analyze the various battery and charger interconnections, as well as a means for predicting battery behavior under load and fault* conditions, an electronic circuit-analysis

* Fault conditions are those conditions that occur in practice due to cell shorting, cell-capacity mismatch, current surge in the load due to lightning strikes, etc.

computer program was sought. The program selected is called SPICE (Simulation Program with Integrated Circuit Emphasis).⁴

SPICE is a general-purpose circuit-simulation program for nonlinear dc, nonlinear transient, and linear ac analysis. Circuits may contain resistors, capacitors, self-inductors, mutual inductors; independent voltage and current sources, voltage-dependent current sources, and the four most common semiconductor devices; the latter are bipolar junction transistors, diodes, and junction field-effect and metal-oxide-semiconductor field-effect transistors. SPICE has built-in models for the semiconductor devices and the user specifies only the pertinent model parameter values.

The circuit to be analyzed is described to SPICE by a set of element cards, which define the circuit topology and element values, and a set of control cards, which define the model parameters and the run controls.

SPICE will accept external element models (comprising resistors, capacitors, inductors and the four common semiconductor devices aforementioned) with up to 20 external nodes (junctions). This feature will allow us to plug in a model of our Li/S cell and pursue an analytical approach in determining battery performance under charge, load, and fault conditions.

2. Bus and Connector Components (M. A. Slawicki, G. W. Redding)

One of the current-carrying components of both electric vehicle and off-peak energy storage cells is the conductor from the positive-electrode current collector of the cell. A proposed conductor design involves the shrink-fitting of either aluminum or copper rod (for high conductivity) into a cylinder of iron or stainless steel (for corrosion resistance). Because of the possibility that a high-resistance intermetallic bond might form at an operating temperature of 400-450°C, several experiments were conducted to measure bond resistances at cell operating temperatures for extended periods of time. The first tests performed (see ANL-75-1, p. 139) were the bond resistance of aluminum clad with or shrink-fitted into iron or steel, which could be used as the positive pole of a Li-Al/FeS cell. Similar tests have now been performed to measure the bond resistance of copper clad with or shrink-fitted into iron or steel; the results of both sets of tests are shown in Fig. VI-8.

The bond resistance of copper clad with Type 304 stainless steel sheet is slightly lower than that of aluminum clad with stainless steel; moreover, the resistance value shown in the figure for copper clad with stainless steel remained constant after 500 hr at 400-450°C. The lower curve for the sample of copper rod in Armco iron shows the bond resistance found during the first heat-up of the sample. After about 150 hr between 400-450°C, the sample was removed from the furnace because of shorting of the voltage sensing leads. Upon reheating the sample and operating for 1000 hr at 400-450°C, the upper curve shown for the sample of copper rod in Armco iron was obtained. The resistance at temperature was about 60% greater than the resistance after the initial heat-up. This increase in resistance is attributed to creep of the copper in iron during the first heat-up, which resulted in a weaker bond between the copper and the iron upon cycling of the sample to room temperature and back to 400-450°C. The sample will be subjected to further tempera-

Fig. VI-8. Intermetallic Bond Resistances at 400-450°C

ture cycling to determine whether the bond resistance continues to increase with cycling.

Based on the results of the tests to date, an iron-clad copper conductor would be usable for a cell positive pole, and the resistance, as calculated, would increase by about 25% due to the increase in bond resistance. However, this increase in bond resistance would produce an increase in the total resistance of the battery of only about 2%.

3. Development of a Mobile Gas Chromatographic (GC) Unit for the Measurement of Water Vapor (M. I. Homa,* G. W. Redding)

Most of the test cells operated at ANL have been assembled in helium-atmosphere gloveboxes, and nonwelded (open) cells have also been operated in a helium atmosphere. However, in the development of economical fabrications methods for cells, *e.g.*, assembly in a dry room, a knowledge of the effect of small amounts of moisture on the cell constituents has become an increasingly important consideration. Commercially available instruments for measuring water vapor have been found to be unreliable, and have required frequent checking and calibration against a reliable, accurate standard. Accordingly, a portable gas-chromatographic monitoring device has been developed to sample the atmospheres of gloveboxes and/or dry rooms and determine the water vapor content. A schematic of this unit is shown in Fig. VI-9.

To obtain a sample, the Carle metal valve is positioned so that a known amount of atmosphere is drawn from the glovebox, by means of a nonpulsating pump, and through a loop (containing Porapak**) that is immersed in

* Analytical Chemistry Laboratory, ANL.

** A product of Waters Associates, Milford, Mass.

Fig. VI-9. Schematic of Portable Gas Chromatographic Unit for Analysis of Water Vapor in Helium Glovebox Atmospheres

Freon-11/dry ice bath; under these conditions, the water vapor is trapped on the Porapak. With the Porapak trap still immersed in the dry ice bath, the Carle valve is positioned so that residual amounts of air are swept out of the trap loop by the helium carrier gas and through the GC column, and are detected by the thermal conductivity (TC) cell and recorder. The dry ice bath is now withdrawn and the Porapak trap is immediately immersed in an oil bath at $\sim 150^{\circ}\text{C}$. The water is flash-evaporated off the trap (along with any CO_2 from the glovebox) and sent through the GC column, where it is separated from any CO_2 and is detected by the TC cell.

The unit has been constructed and standardized with aliquots of helium saturated with water vapor at room temperature. A standard curve of gas chromatographic peak height vs. water vapor content is linear from 1 to $0.3 \mu\text{mol H}_2\text{O}$; the limit of detection is $0.05 \mu\text{mol H}_2\text{O}$. For a glovebox containing about 10 ppm water vapor, a sample size of 250-300 ml is required to yield $\sim 0.1 \mu\text{mol}$ water vapor. The approximate limits of accuracy for varying water levels are as follows: 1-10 ppm, 100-50%; 10-25 ppm, 50-10%; and 25-100 ppm, 10-5%. This unit is providing very useful information on the water-vapor content of the many gloveboxes in use in the program.

C. Materials and Manufacturing Costs
(W. L. Towle,* J. E. A. Graae**)

An estimate has been made of the cost of commercially manufacturing Li-Al/FeS cells for load-leveling in utility networks. The first process selected for this study was based on assembly of cells in the discharged state, that is, a negative electrode structure of aluminum (containing no lithium) and a positive electrode of Li_2S and iron. The latter is made up initially as a charged positive electrode containing an equimolar mixture of Fe and FeS_2 , and the discharged electrode is formed by the electrochemical addition of lithium in a molten salt bath. The purpose of this procedure was to minimize the need for inert-atmosphere protection in the handling of lithium. In this it succeeded. However, the cost of the electrolysis equipment was higher than anticipated; thus, this approach may not be the most economical.

The cell design chosen was that of the 0.92 kW-hr cell proposed for the BEST Facility (see ANL-75-1, p. 126). A few changes were made in the design in the interest of facilitating construction and lowering materials costs. A detailed flowsheet was then worked out, in which the conceptualized steps in manufacture were carefully planned. Included in this study were conceptual designs of machinery needed to carry out these operations on a highly automated basis, so that labor costs were held to a low level. An estimate was then made of the cost of the equipment, based primarily on the authors' knowledge and experience with machinery of a similar nature. Labor requirements were similarly estimated.

The manufacturing plant was sized to produce 5000 0.92-kW-hr cells per day. This corresponds approximately to the daily energy storage capacity produced in a typical automotive lead-acid battery plant. These cells are assembled for sale in battery cases, or submodules, 24 cells to a case. A schedule of materials costs based primarily on up-to-date information from vendors is shown in Table VI-5. Labor cost was based on a \$6/hr rate plus 30% for fringe benefits. Supervision, indirect labor, and indirect operating costs (e.g., power) were included at 200% of direct labor. Depreciation was calculated on a straight line basis. To the sum of the above (\$3.70/kW-hr for labor and overhead) were added the basic materials cost (\$19.02/kW-hr) plus a 5% allowance for plant materials losses (\$0.95/kW-hr). The sum of these costs represents factory cost, to which was added 11% for general and administrative costs, and 11% for profit. The total is \$29.16/kW-hr, yielding a return of just over 25% on the total plant investment of \$12,500,000.

When a recycle salvage allowance was justified, a 25% credit was estimated; this was done for lithium plus LiCl values in the basic materials cost. The amount of this credit is \$1.83, bringing the net selling price to \$27.33/kW-hr. The manufacturing costs are summarized in Table VI-6.

The principal conclusion from this study is that cost of labor and overhead is low in relation to the materials cost. Secondly, the overall cost is in the same range as that of the lead-acid battery.

* Industrial Participant, Globe-Union Inc.

** Consultant to Chemical Engineering Division, ANL.

Table VI-5. Costs of Materials for Off-Peak Energy Storage Cells and Submodules in a Full-Scale Manufacturing Plant

	\$/kW-hr	\$/Unit
<u>Electrolyte</u>		
LiCl	2.49	2.49/kg
KCl	0.27	0.22/kg
<u>Negative Electrode</u>		
Lithium	4.21	17.05/kg
Aluminum	1.21	1.10/kg
Steel Wool	0.42	2.20/kg
Iron Screen	1.08	1.10/kg
<u>Positive Electrode</u>		
FeS	0.35 ^a	-
Cu ₂ S	0.53	1.28/kg
Steel Wool	0.36	2.20/kg
<u>Separators</u>		
BN Paper	2.72	10.75/m ²
<u>Cell Components</u>		
Steel Sheet	1.48	0.73/kg
Steel Rod	0.09	1.19/kg
Feedthrough	1.08	1.00 ea ^b
Subtotal Cells	16.99	
<u>Submodule Components</u>		
SS Sheet	1.41	26.87/m ²
Conductors	0.54	1.76/kg
Feedthrough	0.18	4.00 ea ^b
TOTAL	19.02	

^aBased on FeS₂ at \$0.11/kg and Fe powder at \$0.40/kg

^bCost goal for mass-produced unit.

Thirdly, automated manufacturing operations of the type considered in this study are highly sophisticated. An extensive and expensive program of development engineering will be required to bring a factory of such a type into being. Needless to say, the cost per unit product in a pilot plant will be much higher than in the manufacturing plant described here. Indeed, even the cost of the first full-scale plant will be considerably higher, because it will represent a "first" for much of the engineering work. The figures given here should be taken as representative of the second or third plant that is operated.

D. Commercial Development (R. O. Ivins)

To achieve the highly significant impact on the energy crisis that the commercial availability of lithium-aluminum/iron sulfide batteries will

Table VI-6. Manufacturing Cost Summary for Li-Al/FeS Batteries (in dollars)

<u>Labor and Overhead (basis, annual)</u>	
Direct Labor	1,080,000
Overhead	
Fringe Benefits (30%)	324,000
Supervisor, Indirect Labor (2 x direct labor)	2,160,000
Depreciation	<u>692,000</u>
Total Labor and Overhead	4,256,000
<u>Factory Cost (basis, 1 kW-hr)</u>	
Labor and Overhead	3.70
Materials	19.02
Plant Losses at 5% of Materials	<u>0.95</u>
Total Factory Cost	23.67
<u>Battery Price (basis, 1 kW-hr)</u>	
Factory Cost	23.67
G & A at 11%	<u>2.60</u>
Subtotal	26.27
Profit at 11%	<u>2.89</u>
Battery Price per kW-hr	29.16 ^a

^a Recycle of lithium values would give a net figure of \$27.33/kW-hr.

represent requires a rapid and efficient transfer of technology to industry. Toward this end, the participation of industrial firms capable of manufacturing components, cells, and batteries has been sought at an early stage in the development program. Commercial development is being further pursued by contracting with industrial firms to develop (1) components such as electrical feedthroughs and ceramic separators and (2) manufacturing techniques for electrodes and cells.

1. Industrial Participation in ANL Program

A program is being carried out in which chemists and engineers from industrial firms spend from six months to a year working in the ANL battery program. This program is bringing industrial experience in battery design and manufacture to the laboratory cell development efforts. This direct participation has also provided the participating firms with the knowledge that they need in bidding on contracts to develop manufacturing techniques for electrodes and cells. Requests for proposals to develop manufacturing techniques for electrodes and cells were issued in January 1975, and the first contract was initiated on April 1, 1975.

To date, five industrial firms have assigned highly qualified personnel to ANL. These are Gould Inc., Globe-Union Inc., C & D Batteries, Inc., Catalyst Research Corp., and Eagle-Picher Industries, Inc. In addition,

negotiations were started with an electronics firm for a participant who would work on cell charging equipment.

2. Component Development

a. Electrode Separators

The development of a low-cost porous electrode separator is essential to the commercial development of lithium-aluminum/iron sulfide batteries. Boron nitride fabric, woven from fibers produced by the Carborundum Co. has been successfully used in both small-scale cells and full-scale engineering cells. In order to obtain an improved separator and, at the same time, a reduction in cost, a contract was instituted with the Carborundum Co. to develop the technology of fabricating a porous paper separator from BN fibers. As part of this contract, Carborundum has supplied to ANL, for in-cell evaluation, samples of test papers. Because BN fibers are not ideally suited for paper making, development efforts have been directed toward the use of organic binders (Resole, H-Resin, PVA, etc.) and inorganic binders (Si_2O , Al_2O_3 , and nitrided B_2O_3). The organic binders have been unsuccessful owing to decomposition at cell operating temperatures ($\sim 450^\circ\text{C}$). Marginal success has been obtained with the nitrided B_2O_3 binder. The Al_2O_3 and SiO_2 binders are rapidly attacked by lithium. The initial test papers were very thin (~ 15 mils) and had porosities of 94-96%. Carborundum is now preparing thicker papers (30 and 60 mils) with porosities of about 85%. Also, the fabrication process using BN fibers with nitrided B_2O_3 binder is being refined. During the second year of the two-year development effort, emphasis will be on the optimization of physical properties and of the fabrication process for cost reductions.

A separate program at the University of Florida (funded directly by ERDA) is now under way to develop ceramic paper separators. The major emphasis of this development program is on the fabrication of composite-type separators using various combinations of fibers and ceramic powders. Initial efforts with BN and asbestos fibers indicated that the addition of a small amount of asbestos substantially improves the strength of the BN papers. Future efforts will be directed toward fabricating ceramic papers using combinations of ceramic fibers (BN, LiAlO_2 , Y_2O_3) and ceramic powders (Y_2O_3 , AlN).

Ceramic fibers of LiAlO_2 were produced for our evaluation by Horizons, Inc. These fibers have been forwarded to the University of Florida to determine if they can be fabricated into a suitable separator. Also, Zircar, Inc. is attempting to prepare fibers of Y_2O_3 (under purchase order). If they are successful, these fibers will also be forwarded to the University of Florida to be fabricated into paper separators. Sources for AlN fibers are also being sought.

Also, contacts have been made with a number of companies that are interested in producing separators (W. R. Grace, Eagle-Picher, Herty Foundation, and Kimberly-Clark) on a commercial basis from a developed process or are willing to develop a process under contract.

b. Electrical Feedthroughs

The effort to develop an electrical feedthrough has been expanded to include work by several commercial manufacturers of ceramic

bodies and feedthroughs. It is anticipated that additional manufacturers will be asked to participate as the development effort continues.

The materials of construction being evaluated as components were chosen on the basis of expected compatibility with the cell environment and present commercial availability. Accordingly, only Al_2O_3 , BeO , and Y_2O_3 ceramic bodies are being evaluated at the present time. Restrictions on materials costs have been deemphasized for the present, but designs that minimize the quantity of expensive materials are being encouraged. A brief description of the present programs is given below.

Ceramaseal, Inc. is developing a ram-type mechanical seal wherein BeO parts are forced into a ductile hoop to produce a seal; no braze is required. National Beryllia is producing the lower insulator for the mechanical Conax-type feedthrough from pressed-and-sintered BeO . The 3M Company is supplying feedthroughs with three different, more or less conventional, types of brazes; these are subsequently plated for corrosion protection. ILC Technology is producing feedthroughs with Al_2O_3 , Lucalox, and BeO components and a number of niobium-base brazes, including Nb-Cu, Nb-Ni, Nb-Au, and Nb-Ag. They are also designing feedthrough concepts that are uniquely suited to the ANL battery program. Coors Porcelain Co. is developing brazes for Y_2O_3 ; the latter material promises to be a nontoxic competitor to BeO .

An in-house effort is under way to evaluate these various feedthroughs to identify those that show promise for continued development.

3. Cell and Battery Procurement (R. F. Malecha, V. M. Kolba)

Development contracts have been made with industrial firms to fabricate test electrodes and cells. The purposes of these contracts are to (1) transfer ANL technology on lithium-aluminum/iron sulfide cells to industrial firms, (2) provide industrial capability to manufacture test electrodes and individual cells in the quantity necessary for the ANL battery development program, and (3) develop manufacturing techniques and procedures applicable to mass-manufacture of cells and batteries.

The cells to be fabricated in the vendor contracts are a prismatic type having a positive center electrode with a negative electrode at each face (see Fig. VI-10). Two thicknesses of electrodes and cells will be fabricated. The thin type (A) is applicable for use in electric vehicles, whereas the thick type (B) is applicable for use in utility off-peak energy storage systems. For each application, several techniques will be used to prepare Li-Al, the active material for the negative electrodes. Moreover, several techniques will be investigated for fabricating positive electrodes; the positive electrode materials to be used are $\text{FeS-Cu}_2\text{S}$ and $\text{FeS}_2\text{-CoS}_2$.

During this reporting period, the design and specification package was completed and the bid packages were prepared. Bids were solicited, and five firms responded in February 1975 to the bid request. A board established to review the bids selected three firms for the contracts. A precontract award meeting was held with the potential contractors to review the bid with regard to the scope of work and to reach a mutual understanding of the work to be performed by the contractor.

Fig. VI-10. Prismatic Test Cell (dimensions in inches)

The first contract -- with Gould Inc. -- had an effective date of April 1, 1975. This contract covers the development of electrodes having porous current collector structures into which the active material, as a powder, is loaded. In addition, some negative electrodes will be prepared electrochemically. Twenty-four aluminum plaques, eighteen negative electrodes, twelve positive electrodes, and twelve cells, six each of types A and B, will be fabricated.

The second contract was signed with Eagle-Picher Industries, Inc., with an effective date of May 1, 1975. In this contract, cold pressing of powders (mixtures of active material and electrolyte) will be used as the method of electrode fabrication. Nine negative electrodes, twelve positive electrodes, and twelve cells each of types A and B will be fabricated.

The area of effort for the third contract -- with Catalyst Research Corp. -- is being reviewed with the contractor, and a contract date in the first quarter of FY 1976 is anticipated.

A steering committee has been formed at ANL to provide technical direction for the contracts. This committee reviews the contracts in progress, identifies necessary development work in support of the contracts, informs the appropriate ANL groups of the need for this support work, and when necessary recommends changes to the contracts.

Technology-transfer and progress-report meetings are held with the contractors at intervals of about six weeks to review the work. Day-to-day contact is maintained with the contractors by the technical representative for the contracts and by the specific technical monitor assigned to the given contract.

The status of the work, at the end of the reporting period, under the Gould and Eagle-Picher contracts is summarized below.

Gould Contract. Installation of the glovebox purification system was begun, and a Varian Trace-Gas Analyzer was ordered. Development of a technique for fabricating aluminum plaques is under way. Work on techniques for vertical loading of FeS_2 into positive current collector structures is in progress. The quality assurance (QA) program policy and procedures are being prepared.

Eagle-Picher Contract. The gloveboxes and purification system have been ordered. After preliminary tests on cold-pressing of powders, pressing requirements were established and a press was ordered. A QA program, including a management plan, is being prepared.

4. Battery Energy Storage Test (BEST) Facility

A study has been performed on the design and cost of a facility to test advanced battery systems and power conditioning equipment for energy storage on a utility network. This effort was carried out cooperatively between ERDA and the Electric Power Research Institute (EPRI). This facility has three purposes: (1) to test advanced batteries and their subsystems, (2) to test converter systems, and (3) to evaluate battery energy storage systems on a utility network. The objectives of the design and cost study were to

develop (1) definition of the requirements for the facility, (2) technical justification of the facility, (3) criteria for the conceptual design of a satisfactory facility, and (4) preliminary cost estimates and schedules.

A planning group made up of representatives from ERDA, EPRI, utility firms, and ANL directs this effort. Staff members from utility firms, EPRI, and ANL having experience in utility power systems, battery technology, and power conditioning technology were selected to form a working group. This group, designated the project team, gathered information and conducted the initial study to establish the justification, requirements, and the design concept. Bechtel, as the Architect/Engineer under contract to ANL and EPRI, performed detailed design and cost studies.

The planning group directs the activities of the study groups and formulates plans for funding, siting, and construction of the facility. As currently envisioned, the facility would be a national test bed funded equally by ERDA and EPRI. Utilities interested in acting as hosts for the facility are being sought. The host utility would be expected to provide the site and intertie.

The project team completed its assigned study in June 1975. The results of the project study are reported in two joint EPRI-ERDA reports.^{5,6} The recommended facility is a building (160 by 180 ft) of reinforced concrete structure. It includes three battery rooms, three staff offices, a control room, a conference room, an inverter area, and a general shop area. The battery rooms are of adequate size (60 ft by 80 ft each) to accommodate the advanced batteries (≤ 1 MW-10 MW-hr) under test, spare modules, and work area. The building layout is shown in Fig. VI-11. A data analysis room is adjacent to each battery room. No additions to the building will be necessary to accommodate added equipment. It would be possible to expand the building in the future to accommodate more than three battery systems, if required.

Initially the equipment installed in the building will include a lead-acid battery, a 2.5-MW converter, the associated electrical and control hardware, and a synthetic load. A single-line diagram of the electrical systems is shown in Fig. VI-12. Additional electrical and control hardware and instrumentation will be added as the specific advanced battery systems to be tested are identified. The estimated cost of this baseline facility is 6.4 million dollars (in 1975 dollars).

Fig. VI-11. BEST Facility Layout

Fig. VI-12. BEST Facility Electrical System

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