ADVANCED CELL TECHNOLOGY FOR HIGH PERFORMANCE Li-Al/FeS₂ SECONDARY BATTERIES

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ABSTRACT

In early 1993, Argonne National Laboratory (ANL) initiated a major R&D effort to develop bipolar Li-Al/LiCl-LiBr-KBr/FeS₂ batteries for electric vehicles, targeting the USABC Long-Term Goals. Significant advancements were achieved in the areas of (i) chemical purity, (ii) electrode and electrolyte additives, and (iii) peripheral seals. It was determined that key chemical constituents contained undesirable impurities. ANL developed new chemical processes for preparing Li₂S, FeS, and CoS₂ that were >98.5% pure. We evaluated a large variety of electrode and electrolyte additives for reducing cell area specific impedance (ASI). Candidate positive electrode additives offered increased electronic conductivity, enhanced reaction kinetics, and/or improved porous electrode morphology. CoS₂, CuFeS₂, MgO, and graphite (fibers) were identified as the most beneficial impedance-reducing positive electrode additives. Although electronically conductive carbon and graphite additives produced measurable ASI reductions in the negative electrode, they degraded its structural integrity and were deemed impractical. LiI and LiF were identified as beneficial electrolyte additives, that enhance positive electrode kinetics. ANL refined its baseline metal/ceramic peripheral seal and increased its strength by a factor of three (achieving a safety factor >10). In parallel, ANL developed a high-strength advanced metal/ceramic seal that offers appreciable cost reductions.

INTRODUCTION & BACKGROUND

Lithium-alloy/metal sulfide secondary cells and batteries have been under development at Argonne National Laboratory (ANL) since 1973. The Li-Al alloy negative and FeS or FeS₂ positive electrode materials were selected for electric vehicle (EV) and stationary energy storage (SES) applications, primarily for cost reasons. In the late 1980s, ANL began emphasizing its bipolar Li-Al/FeS₂ cell technology that employs a LiCl-LiBr-KBr electrolyte, after demonstrating >1000 cycles of life in a flooded-electrolyte laboratory cell. This achievement and the subsequent development of a bipolar stack technology, which uses an off-eutectic LiCl-rich electrolyte, are described in detail elsewhere (1,2).
An artist's rendition of a bipolar lithium/iron sulfide battery is provided in Figure 1. The cylindrical bipolar battery stack is housed in a vacuum-insulated thermal enclosure to maintain its operating temperature in the range of 400-450°C. This shape allows the use of a light-weight thermal enclosure consisting of alternating layers of glass fiber and aluminum foil packaged between an inner and an outer steel case.

The design of ANL's baseline bipolar stack is illustrated in Figure 2. The anode, cathode, and electrolyte/sePARATOR plaques are pressed powder pellets. The plaques are packaged inside a ceramic-to-metal seal assembly and metal bipolar plates. Baseline cells of this technology were 8-mm thick and approximately 15-cm diameter. They employed molybdenum bipolar plates and baseline seals that used molybdenum metal rings. Final stack assembly was accomplished by welding the molybdenum metal bipolar plates to the molybdenum metal rings of the seal assembly.

The overall electrochemical reaction for this cell operating on the upper voltage plateau of the FeS₂ electrode is:

$$2\text{Li-Al} + \text{FeS}_2 \rightarrow \text{Li}_2\text{FeS}_2 + 2\text{Al}$$  \[1\]

However, the electrodes and electrolyte/sePARATOR are actually blends of chemicals, as shown for baseline cells in Table I.

| Cell Component         | Constituents                                      |
|------------------------|--------------------------------------------------|
| Negative Electrode     | Li-Al, Al₆Fe₂, MgO, electrolyte                  |
| Positive Electrode     | FeS₂, Co₃S₂, LiS₂, Li₂FeS₂, electrolyte          |
| Electrolyte/SEPARATOR  | LiCl-LiBr-KBr (34-32.5-33.5 mol %)/MgO           |

During the early 1990s numerous technical advances were achieved at ANL, under a project aimed at refining this technology to meet the U.S. Advanced Battery Consortium (USABC) Long-Term performance goals for EVs in full-size prototype bipolar cells and stacks. This paper discusses three key areas of technological advancement:

- chemical synthesis and purification procedures (to produce high-purity chemicals)
- electrolyte and electrode additives (to enhance specific power)
- advanced chalcogenide ceramic-to-metal seal (to reduce cost).
CHEMICAL SYNTHESSES & PURIFICATION

A key element in the successful development of any battery system is chemical purity and the electrochemical characteristics of the active materials. Commercial battery manufacturers spend millions of dollars in qualifying the materials used in their cells. The qualification process is ongoing, because the use of an off-specification batch of active material can be costly to a manufacturer because of reject cells.

Since the qualification process involves both chemical purity and electrochemical activity, the process can be time consuming and expensive to implement. Because the lithium/iron disulfide battery system evolved out of a low-level R&D project during the 1989-92 time frame, these qualification processes for the electrode active materials were not yet established. Also, without an established market for these materials, vendors were not interested in participating in such a qualification process.

When the project expanded dramatically in early 1993, we worked with our industrial development partner (Saft America) to procure “high-purity” chemicals to replenish ANL’s dwindling inventory. Cell performance and life were diminished when baseline cells were built and tested with these newly procured chemicals, that contained deleterious impurities. Together with Saft, we evaluated commercially available high-purity chemicals from alternative suppliers, but were unable to identify suitable sources for some of the chemicals needed for our joint R&D projects. Therefore, ANL developed chemical syntheses and/or purification procedures for Li$_2$S, FeS$_2$, FeS, CoS$_2$, and MgO. The Li$_2$S and FeS are reacted together to form the Li$_2$FeS$_2$ used in the positive electrode mix (see Equation 2).

\[
\text{Li}_2\text{S} + \text{FeS} \rightarrow \text{Li}_2\text{FeS}_2
\]  

Lithium Sulfide (Li$_2$S)

ANL’s baseline cells were built in a partially charged state and this required the use of Li$_2$FeS$_2$ as an additive to the positive electrode, as shown in Table I. The reason for starting the cells in the partially charged state was to develop a high-activity lithium type lithium-aluminum alloy which contained 22.4 wt% lithium needed for overcharge protection. In the “as-fabricated” cell, the lithium-aluminum alloy contained about 20 wt% lithium. In the latter stages of our program, it was decided to go to a “fully charged” cell using 100 mol% FeS$_2$ in the positive electrode and 22.4 wt% lithium in the lithium-aluminum alloy negative electrode.

Previously, ANL obtained its lithium sulfide from Eagle Picher Industries, Inc. and from Cyprus Foote, both of whom terminated production of this material prior to 1993. In seeking a new supplier of lithium sulfide, Saft identified Cerac, Inc., who...
was willing to prepare bulk quantities (kilograms) of lithium sulfide. Analytical work on the material by both Cerac and ANL indicated that the material contained a significant quantity of lithium sulfate (2-3%). Cerac prepared the lithium sulfide by reacting hydrogen sulfide and lithium hydroxide, see equation [3]. Because the LiOH and Li₂S form a low melting eutectic, it is very difficult to drive this reaction to completion, and usually requires several grind steps during the preparation process. To avoid this problem, ANL recommended preparing the lithium sulfide by reacting lithium carbonate with hydrogen sulfide, because there are no low melting eutectics that can form, see equation [4]. ANL developed this preparative process earlier and found it to be an excellent way of preparing the lithium sulfide.

\[
2\text{LiOH} + \text{H}_2\text{S} \rightarrow \text{Li}_2\text{S} + 2\text{H}_2\text{O} \quad [3]
\]

\[
\text{Li}_2\text{CO}_3 + \text{H}_2\text{S} \rightarrow \text{Li}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \quad [4]
\]

Cerac used the process and found that their product material was >98.5% pure and we were able to qualify a high-purity material for use in the battery.

**Iron Disulfide (FeS₂)**

Early work at ANL, in the late 1970s, on developing a source of high-purity FeS₂ focused on using American Mineral FeS₂ as a source material. This material was upgraded using a flotation process at the University of Minnesota to produce a material which was ~98.5 percent pure, with its principal impurity being silicon dioxide (SiO₂). Thus, in the present program, Saft and ANL again used the American mineral FeS₂ as their source material. However, to develop a higher purity FeS₂ product, Saft used an acid wash (~6 N HCl). It was hoped that any iron oxide materials present in the FeS₂ would be solubilized, see equation [5].

\[
\text{Fe}_3\text{O}_4 + 8\text{HCl} \rightarrow \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O} \quad [5]
\]

Analysis of this material again indicated a product purity of approximately 98.5 percent FeS₂, with the major impurity being silicon dioxide or silica (SiO₂). However, in examining the material more carefully under a microscope, we found that a portion of the FeS₂ material was strongly magnetic. Separation and analysis of this material indicated the presence of traces of iron particulate and some residual magnetite (Fe₃O₄), a material which could cause formation of iron particulate in the separator and premature cell failure. To resolve this problem, ANL utilized a solenoid device to magnetically separate the one percent Fe₃O₄ and the small traces of iron particulate materials present from the FeS₂ material.

Cells using this highly purified material tended to have significantly longer cycle life, as well as many fewer premature failures, again indicating the critical importance of high purity material for the fabrication of lithium/iron disulfide.
batteries. Future studies need to be carried out to determine the exact role played by sink flotation in the purification of the FeS$_2$ material and the removal of metal oxides such as magnetite.

**Iron Monosulfide (FeS)**

Initial efforts to prepare high-purity iron monosulfide by direct reaction of elemental sulfur with elemental iron were unsuccessful. The product always seemed to contain residual iron. To overcome this problem, we decided to prepare the iron monosulfide from the purified iron disulfide by thermal decomposition at 650°C, see equation [6].

\[
\text{FeS}_2 \rightarrow \text{FeS} + \text{S} \\
[6]
\]

This preparative method was carried out successfully for Saft at Great Western Inorganic in Golden, Colorado, and yielded a product which was >98 percent pure. Having produced both pure lithium sulfide and iron monosulfide, it was possible to prepare high purity X-phase (Li$_2$FeS$_2$) for the partially charged cells, via equation [2].

**Cobalt Disulfide (CoS$_2$)**

Cobalt disulfide (CoS$_2$) is another critical material, where about 15 mol% CoS$_2$ was added to the positive electrode to enhance the power characteristics of the electrode. Because our baseline cells were fabricated in a partially charged state, the cobalt sulfide material used in these cells was Co$_3$S$_2$, along with Li$_2$FeS$_2$, FeS$_2$, and Li$_2$S. Thus, during the first charge, these materials were converted to CoS$_2$ and FeS$_2$. Thus, as the technology moved from a partially charged cell concept to a fully charged cell concept, it was necessary to acquire a source of high purity cobalt disulfide. Attempts to acquire high-purity CoS$_2$ material from various sources revealed that the best material available was that marketed by Cerac, but this material tended to be deficient in sulfur and contained a sufficient amount (2-3 wt%) of cobalt sulfate, an impurity that could result in cobalt metal deposition in the separator with resultant cell failure.

To eliminate the impurities in the cobalt disulfide, ANL discussed and reviewed the process that Cerac used for producing their material, which was prepared by reacting sulfur with cobalt oxide (CoO), see equation [7].

\[
2\text{CoO} + 5\text{S} \rightarrow 2\text{CoS}_2 + \text{SO}_2 \\
[7]
\]

In examining the process, we found that the sulfur dioxide (SO$_2$) formed in the reaction could react with the CoO to form a stable cobalt sulfite, which when exposed to air could be converted to cobalt sulfate.
To avoid this problem, ANL suggested to Cerac that they prepare the cobalt disulfide by reacting cobalt metal instead of cobalt oxide with sulfur at about 500-600°C. That is a direct synthesis from the elements, see equation [8].

\[
\text{Co} + 2\text{S} \rightarrow \text{CoS}_2
\]  

[8]

In attempting to prepare the cobalt disulfide by this process, Cerac found that they could prepare essentially pure cobalt disulfide by this process (>99 percent pure material). Thus, through the efforts of ANL, Saft, and Cerac a new processing approach was developed for this material.

**ELECTRODE & ELECTROLYTE ADDITIVES**

During the last year of this project, increased priority was placed on improving cell performance, primarily in the area of power density at higher depths of discharge, without detrimentally affecting cycle or calendar life. Prior work at ANL had shown that a key factor in achieving long life was to keep the operating temperature below 450°C. Therefore, ANL’s approach was to retain its existing cell chemistry and to evaluate the use of electrode and electrolyte additives that would reduce cell ASI. With the aid of reference electrodes and half-cell tests, we established that the positive electrode was the major contributor to cell ASI. So emphasis was placed on identifying additives that would decrease the ASI of the positive electrode. Table II lists the most beneficial positive electrode additives identified in this study.

### Table II. Most Beneficial Positive Electrode Additives

| Additive       | ASI Reduction Mechanism | Conductivity | Chemistry | Morphology |
|----------------|-------------------------|--------------|-----------|------------|
| CoS₂           |                         | X            | X         |            |
| CuFeS₂         |                         | X            | X         |            |
| MgO            |                         |              |           | X          |
| Graphite Fibers|                         | X            |           | X          |

These additives alter the ASI of the positive electrode via several mechanisms: they increase the electronic conductivity, modify the chemistry, and/or alter the morphology of the porous electrode. Figure 3 provides ASI vs. depth-of-discharge (DOD) data for a cell that does not utilize positive electrode additives. The ASI measurements were obtained during 30-sec current interruptions at several current densities and during a 30-sec peak power pulse. The peak power ASI is the most meaningful in terms of the cell’s ability to deliver power during a 30-sec vehicle
acceleration. This cell's peak power ASI remains between 0.6 and 1.0 ohm-cm² over the first half of its discharge, but continues to increase beyond 50% DOD, with a dramatic increase at about 70% DOD.

Figure 4 provides ASI vs. DOD data for a cell that utilizes 12 mol% CoS₂ as a positive electrode additive. This level of CoS₂ additive keeps the cell's peak power ASI below 1.0 ohm-cm² out to 70% DOD, but it continuously rises and reaches 1.2 ohm-cm² at 80% DOD. CoS₂ was used as a positive electrode additive in our baseline cell technology at about the 15 mol% level. We examined various levels of this additive and the peak power ASI values at 80% DOD for these cells are shown in Figure 5. The 15 mol% level is an optimum in terms of reducing cell peak power ASI at 80% DOD.

Figure 6 provides ASI vs. DOD data for a cell that utilizes 18 mol% CuFeS₂ as a positive electrode additive. This is the most effective positive electrode additive identified in our study and it offers a major cost benefit over CoS₂. It possesses significant electronic conductivity and is believed to eliminate the formation of high-impedance intermediate compounds in the positive electrode during discharge. It keeps the peak power ASI below 0.5 ohm-cm² for half of the discharge and below 0.9 ohm-cm² even at 100% DOD. At 80% DOD the peak power ASI was less than 0.7 ohm-cm². In a manner similar to what was done for the CoS₂ additive, we examined various levels of CuFeS₂ and found the 12-18 mol% level to be optimum. It should be noted that deposition of metallic Cu in the electrolyte/separator was a concern with this additive. A cell with 25 mol% CuFeS₂ in the positive electrode was subjected to more than 1000 C-rate charge/discharge cycles and its coulombic efficiency remained >99% over these 1000+ cycles. Post-test examination of this cell showed some metallic Cu in the separator, but it was in the form of small particles and quite dispersed.

Although MgO is an electronic insulator, it acts like a sponge for the electrolyte and was found to have a favorable effect on reducing ASI when used as a low-level expander additive in the positive electrode. This beneficial effect became more pronounced after accumulating 10-20 cycles on cells. It apparently increases the solid/liquid interfacial area within the electrode and helps retain electrolyte within the electrode during cycling. Post-test analyses of cells without the MgO additive in the positive electrode, which had undergone several hundred cycles, indicated a tendency for the positive electrode to become starved of electrolyte with cycling. This was at least partially responsible for their increased ASI and reduced high-rate capacity as a function of cycling.

Graphite fibers are electronic conductors and function as an electrode expander to enhance interfacial surface area. Low levels of graphite fiber additives to the positive electrode were found to reduce cell ASI. Graphite fibers do not appear to do as good a job of holding and retaining electrolyte as MgO and may not
have the same ability as MgO to prevent the positive electrode from becoming starved of electrolyte with extended cycling.

Additives to the negative electrode and the electrolyte were examined as well. Table III lists the most beneficial impedance-reducing additives identified for these two cell components. Several forms of graphite and carbon were partially substituted for MgO, as a negative electrode expander. Although they provided some reduction in peak power ASI, via their electronic conductivity, they degraded the structural integrity of the electrode. Also, MgO is known to provide other benefits in the areas of anti-agglomeration and anti-sintering, thereby preserving negative electrode capacity with cycle testing. Although they provided some reduction in cell ASI, the carbons and graphites are not deemed to be practical negative electrode additives.

The LiI and LiF additives to the electrolyte were effective and deemed practical in low concentrations (3). They both increase the Li\(^+\) content of the electrolyte and enhance the kinetics of the positive electrode. Lithium iodide’s effect on enhancing the positive electrode kinetics more than offsets the slight detrimental reduction in electrolyte ionic conductivity it produces. In the case of LiF, this additive remains primarily in the solid phase (less than 1 mol% solubilizes in our standard electrolyte) and was most effective when dispersed directly in the positive electrode. By improving the positive electrode kinetics, these two electrolyte additives reduce overpotential and enhance the active material utilization of the positive electrode.

![Table III. Most Beneficial Additives for the Negative Electrode and Electrolyte](image)

| Location        | Additive       | Mechanism                          |
|-----------------|----------------|------------------------------------|
| Negative Electrode | Graphite, Carbon | Increase electronic conductivity   |
| Electrolyte     | LiI, LiF       | Increase Li\(^+\) content & improve positive electrode kinetics |

Figure 7 illustrates the performance enhancements that were achieved through the use of these electrode and electrolyte additives in full-size prototype EV cells. The dashed line shows the impact of increasing the constant-power discharge rate on the specific energy output of a cell without additives. The solid line illustrates the enhanced performance demonstrated in a cell that incorporates most of these beneficial electrode and electrolyte additives. Both types of cells employ high-purity chemical constituents, so any impact of deleterious impurities is minimal.

ADVANCED CHALCOGENIDE SEAL
A key element in the successful development of bipolar battery stacks is a viable high-strength low-cost peripheral seal technology. This molten salt battery requires a ceramic-to-metal seal that is compatible with the cell operating environment. Figure 8 compares the baseline seal and the advanced seal design concepts. The baseline seal employs a Mo-ring/ceramic-ring/Mo-ring construction. A separate ceramic locator ring is used to establish the proper positioning of the three seal components. The advanced seal replaces the two Mo metal rings with steel rings and buries the lip of a Mo cup between two ceramic seal rings. Again, a separate ceramic locator ring is used to position the seal components. Since the baseline cell design employs a separate Mo cup, for positioning the positive electrode, and a Mo bipolar plate, the advanced seal reduces the number of Mo parts per cell from four to one.

The ceramic seal rings developed by ANL employ mixed metal sulfide and ceramic filler materials. Many of the candidate metal sulfides and ceramic fillers are listed in Table IV. The metal sulfides offer low fusion temperatures (in the range of 850-1050°C) to minimize grain boundary growth and embrittlement of Mo during the seal bonding/formation process. The ceramic filler materials are selected to tailor the coefficient of thermal expansion (CTE) of the structural ceramic to match that of the metal seal components. The CTE for iron is double that for Mo (12x10⁻⁶ vs. 6x10⁻⁶). These ceramics are stable to alkali metals and to our baseline molten salt electrolyte. Also, they form high-strength reaction bonds with metals, ceramics, and graphite (4).

Table IV. Candidate Metal Sulfides and Ceramic Filler Materials

| Metal Sulfides | Ceramic Fillers |
|----------------|-----------------|
| Ca₃Al₂S₄, Li₂CaAl₂S₆, YAlS₃, Ca₂Al₂SiS₇, LiAlS₂, CaY₂S₄ | CaO, MgO, Al₂O₃, AlN, BN |

During the course of this R&D effort, ANL refined its baseline seal and developed the advanced seal technology. Figure 9 illustrates the progressive improvements made in the strength of these two seal technologies. For the baseline seal technology, a high-density AlN-filled chalcogenide ceramic material was developed to replace the less-dense CaO-filled baseline ceramic material. This new ceramic was responsible for achieving the high-strength Mo/Mo bonded seal assembly in 1994. This ceramic is less porous than the CaO-filled ceramic material and possesses a CTE that is closer to that of Mo; both factors contribute to the higher strength properties of this seal assembly. Modeling calculations of the internal stresses and imposed mechanical forces in the baseline seal were compared to the measured physical properties of seal assemblies to predict a safety factor of >10 for this seal technology.
The steel/ceramic/Mo/ceramic/steel advanced seal technology incorporates a mixed oxide filler material to produce a new ceramic, whose thermal expansion coefficient lies between those for Mo and steel. These two ceramic seal rings bond two steel rings to a central Mo cup. In addition to reducing the quantity of Mo used in the cell, this seal technology facilitates final stack assembly by replacing a Mo/Mo weld with a steel/steel weld. The strength of this seal assembly is close to that of the refined baseline seal, with a corresponding cost reduction.

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FIGURES

Figure 1. Artist’s Rendition of Bipolar Lithium-Aluminum/Iron Disulfide Battery Module.
Figure 2. Exploded View of Baseline Bipolar Stack Design.

Figure 3. ASI vs. DOD for a Cell without Positive Electrode Additives.
Figure 4. ASI vs. DOD for a Cell with 12 Mol% CoS$_2$ Additive in the Positive Electrode.

Figure 5. Peak Power ASI (at 80% DOD) vs. Mol% CoS$_2$ Additive.
Figure 6. ASI vs. DOD for a Cell with 18 Mol% CuFeS$_2$ Additive in the Positive Electrode.

Figure 7. Cell Specific Energy as a function of Constant Power Discharge Rate.
Figure 8. Baseline and Advanced Seal Design Concepts.

Figure 9. Improvements in Seal Strength.