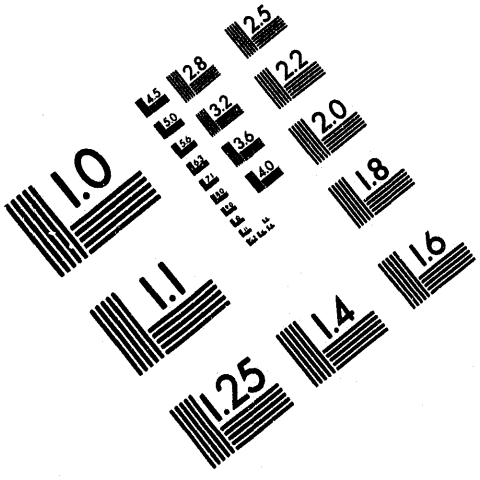

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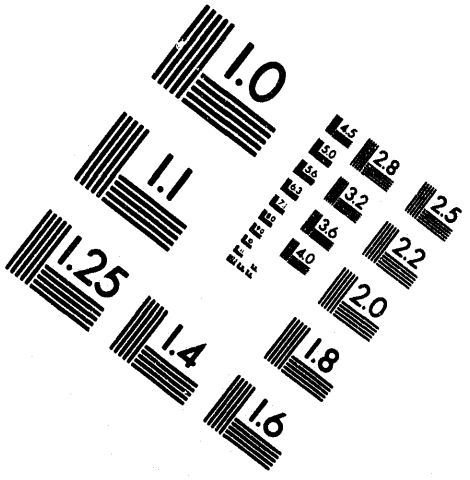

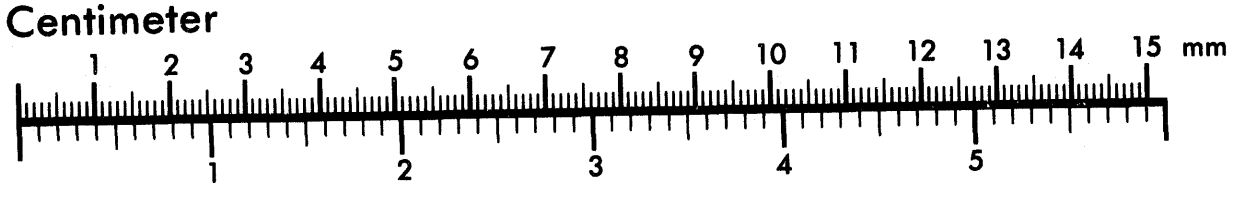

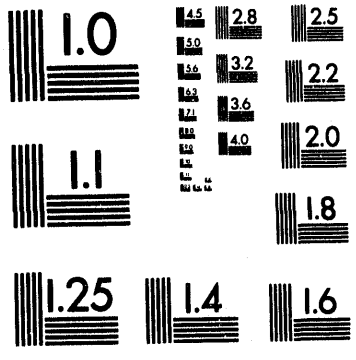

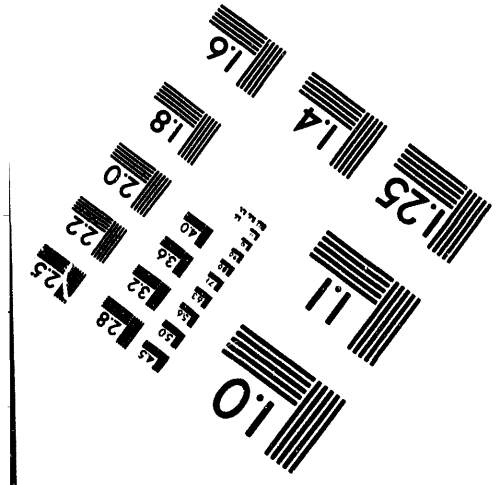

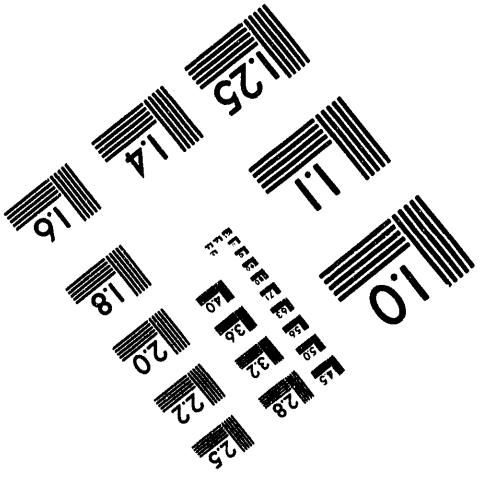

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SAFETY CHARACTERISTICS OF LITHIUM-ALLOY/METAL SULFIDE BATTERIES

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1. INTRODUCTION

The development of high temperature cells containing lithium and sulfur electrodes was initiated at Argonne National Laboratory in the late 1960s [1, 2] and has continued at Argonne and at several industrial laboratories. Early emphasis was placed on the development of a prismatic LiAl/FeS cell targeted to batteries for the electric van market. This technology has been superseded by a more powerful system, which employs a two-phase Li-alloy negative electrode, a LiCl-rich LiCl-LiBr-KBr molten salt electrolyte with lower melting point than the LiCl-KCl used earlier, and either an upper-plateau (U.P.) FeS_2 or an FeS positive electrode assembled into an "electrolyte-starved" bipolar cell configuration [3]. Use of $Li_5Al_5Fe_2$ with the two-phase Li alloy (α + β)-Li-Al negative electrode material provides *in situ* overcharge tolerance that renders the bipolar design viable. The combination of dense U.P. FeS_2 electrodes and low-melting electrolyte produces a stable and reversible electrochemical couple with high power capabilities, capable of achieving over 1000 cycles. In addition, a family of stable chalcogenide-based ceramic sealants was developed that produce high-strength bonds between a variety of metals and ceramics, which renders lithium/iron sulfide bipolar stacks practical. Full-size bipolar Li-Al/FeS and Li-Al/FeS_2 cells (13-cm dia) and four-cell stacks using these seals are being built and tested for the electric-vehicle (EV) application.

The overall electrochemical reaction for the Li-Al/FeS and Li-Al/FeS_2 cells can be written as:

$$2Li\text{-}Al + FeS = Li_2S + 2Al + Fe$$
$$2Li\text{-}Al + FeS_2 = Li_2FeS_2 + 2Al$$

The theoretical specific energies for the FeS and U.P. FeS_2 cells are approximately 450 and 490 Wh/kg, respectively. The open-circuit voltage plateaus of these cells are about 1.34 V for the FeS and 1.76 V for the FeS_2.

Thermal management of these batteries requires a containment vessel that employs high-efficiency thermal insulation to maintain the cells at the

operating temperature (normally ~450°C) and does not impose excessive weight, volume, or thermal loss penalties.

2. CHEMICAL HAZARDS AND TOXICITY

The use and/or formation of chemically hazardous or toxic chemicals in the lithium-alloy/iron sulfide battery is limited by the intrinsically safe nature of the chemistry and electrochemistry of the system. The chemically and electrochemically active elements, lithium and sulfur, are not present in their elemental form but are combined with other elements to form alloys or compounds, e.g., lithium is alloyed with aluminum and iron, while sulfur may exist in the form of several compounds (FeS, FeS_2, Li_2FeS_2 or Li_2S). Combining the active elements with these other elements significantly reduces their chemical activity. Further, these materials are dispersed and coated with a noncombustible molten salt electrolyte. Thus, an important inherent safety mechanism is provided by the molten salt electrolyte, which coats the surfaces of all the active materials.

In a severe vehicle collision, it may be possible to rupture the battery containment vessel, as well as the containment vessels of cells in the battery. Even in this scenario, the resulting chemical hazards will be minimal and somewhat dependent on environmental factors. Under dry weather conditions, no direct chemical hazards are posed by the exposed cell chemicals, because the active chemicals are coated by the protective layer of alkali halide electrolyte. Under wet weather conditions, water could gradually dissolve the protective salt layer and react with active chemicals to form alkaline lithium compounds, H_2, and/or SO_2. Although these compounds pose several types of hazards, their levels will be lower than those posed by other types of EV batteries, because they are not available for immediate release. Many of the other types of EV batteries contain significant quantities of toxic chemicals, such as the highly alkaline or acid electrolytes, that are released immediately when the battery case is ruptured.

3. THERMAL HAZARDS

The cells are sealed and contained within a gas-tight double walled battery case [4] that uses a vacuum-multifoil insulation for heat retention. During normal operation, the cells are kept at about 425°C. However, due to the high efficiency of the insulation, the outer case temperature remains within 10°C of ambient temperature. This system provides triple containment for the active materials of the cell, i.e., the sealed cell backed up by the double wall of the battery case, which is further reinforced by mutiple layers of aluminum foil and glass fiber paper.

If an accidental puncture or rupture of the battery case results in the loss of the vacuum, the outer surface temperature of the battery case will rise slowly to 100-150°C, while the inside temperature will fall, resulting in the solidification of the molten salt electrolyte and loss of battery power. This

results in no special hazard other than the possibility of a skin burn should the battery case be touched.

4. HAZARDS POSED UNDER ELECTRICAL ABUSE

The normal charge and discharge reactions in Li-Al/FeS_x systems form solid products without gaseous side reactions, thereby permitting these cells to be sealed and eliminating the need for electrolyte replacement or maintenance.

With the Li-Al/(U.P.)FeS_2 cell, the normal charge cutoff voltage (IR-included) is 2.01 V, and the reversible (IR-free) voltage is approximately 1.76 V. When the cell is driven into overcharge beyond its overcharge tolerance capability, the first reaction occurs at about 2.4 V (IR-free) and is

$$2LiCl + FeS_2 + 2Al \rightarrow 2LiAl + FeCl_2 + 2S$$

This reaction involves (1) the anodic oxidation of the FeS_2 to $FeCl_2$ and sulfur in the positive electrode and (2) the deposition of additional lithium in the Li-alloy electrode. Similar to a life-limiting mechanism in FeS cells, lithium and $FeCl_2$ become dissolved in the electrolyte and react chemically with the dissolved lithium in the electrolyte to form deposits of metallic iron in the separator. This results in a partially or totally shorted cell.

When the lithium-limited U.P. FeS_2 cell is discharged, a cutoff voltage of 1.35 V is normally used. Should the cell be driven into overdischarge, the sequential reactions are:

$$2\,Al + 3\,Li_2FeS_2 \rightarrow Al_2S_3 + 3\,Li_2S + 3Fe$$
$$Al_{(anode)} \rightarrow Al_{(cathode)}$$

For both FeS and U.P. FeS_2 batteries, the overcharge and overdischarge reactions result in the formation of short circuits in the cell, with an accompanying loss of columbic efficiency. No pressure buildup due to gas generation occurs.

5. SAFETY TESTS AND EXPERIENCE

The historical safety record of the Li-alloy/metal sulfide battery during its development has been excellent. Hundreds of prismatic laboratory and engineering-size cells have been built and tested at ANL and at several industrial firms without a safety problem. This record clearly reflects the intrinsically nonhazardous nature of the chemistry and electrochemistry of the system.

The earliest safety test conducted at ANL simulated the effect of a short circuit caused by a ruptured separator. In this study, a negative electrode and a positive electrode were heated to operating temperature and then

physically contacted to examine the effects of this extreme condition. Although the temperature rose slightly, full discharge of the electrodes via a direct short circuit was prevented by the reaction product, Li_2S, which formed an insulating layer on the positive electrode surface.

Another experiment was conducted in which a cell was operated in an air environment rather than the normal argon cover gas. The only observed effect was the slight oxidation of cell components.

Simulated crash safety tests were conducted at the Budd Technical Center in 1977 [5]. Several unprotected full-scale Li-Al/FeS prismatic EV cells at full charge were subjected to drop tower tests at operating temperature (~450°C) to simulate the impact of a 30 mph (48 km/h) barrier crash in an air environment. Although the cell cans ruptured, no explosion, fire, or release of noxious gas was noted. A small amount of electrolyte was, however, released from these electrolyte-flooded cells.

In 1979, two 20-kWh batteries, consisting of full-scale LiAl/FeS prismatic EV cells, were constructed. During startup testing, short circuits developed and propagated within one of the batteries so that most of the stored energy of the battery discharged in about 20 min [6]. The failure was later determined to be caused by either electrolyte leakage or electrical arcing between the cells and adjacent battery hardware. Although internal spot temperatures rose to ~1000°C, the outer battery case temperature only reached 130°C, and no external breach of the battery case occurred. Even under these extreme conditions, the individual cell cases were not breached. An additional safety characteristic of the Li-Al/FeS_2 cell is the entropic cooling associated with the discharge reactions, which helps counter the I^2R heating and thereby suppresses the tendency for excess temperature rise under an internal or external short-circuit condition.

A preliminary assessment of possible hazards associated with battery operation is summarized in Table 1.

6. CONCLUSIONS

Although extensive safety tests on Li-alloy/FeS_x battery systems have not been conducted, those that have been reaffirm our collective development experience, which indicates that these batteries are inherently safe. This could be a significant advantage in the commercial development of this battery for EV applications. It is unlikely that any elaborate safety features will have to be engineered into Li-alloy/FeS_x batteries to meet the safety requirements for EV applications. This alleviates concerns with system complexity and cost, which often accompany the incorporation of safety-related design features. More extensive safety tests will be conducted as part of the ongoing development program to validate this conclusion.

TABLE 1. PRELIMINARY HAZARD ASSESSMENT

Component	Failure Mode	Consequences/Hazard Assessment
Cell	Short Circuit (internal)	Cell heating. Controllable with cooling subsystem sized to handle maximum charging rate. Further evaluation planned.
	Electrolyte Leak	Cell-to-cell or cell-to-case electrolyte bridging. Gradual loss of capacity associated with affected cells. Contained by battery case. Further evaluation planned.
	Feedthrough Short Circuit (prismatic)	Cell heating. Loss of cell voltage and capacity but battery remains operational. Little or no hazard.
Insulated Case	Loss of Insulating Quality (vacuum)	Outer case temperature rises to 100-150°C. Electrolyte freezes and encapsulates the active materials. Skin burn hazard if contact made with battery case.
	Loss of Containment (Rupture of case)	Cells at about 425°C are exposed to air. Electrolyte freezes. Slow oxidation of cell components, e.g., copper intercell connectors. Little or no hazard except for skin burn if contact made with cells.
Assembled Battery	Short Circuit	Temperature rise of cells controlled by cooling subsystem. Temperature rise could cause irreversible damage to cells. Safely contained within battery case. Further evaluation planned.
	Thermal Management System	Overheating of cells may cause premature cell failure. Allowing cells to freeze cuts off battery power. Cells can be reheated back to operating temperature when management system is corrected.
Charger	Overcharge Cells	Cells damaged (shorted) irreversibly. Cell temperature rise controlled by cooling subsystem.

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