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## Thermal Batteries Session

# REVIEW OF CHLOROALUMINATE SYSTEMS FOR THERMAL BATTERY APPLICATIONS

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### Introduction

Production thermal batteries conventionally use LiCl—KCl electrolyte and therefore operate only at very high temperatures (400°–600° C). Use of this highly conductive, high temperature electrolyte maximizes available current densities but imposes a severe thermal stress on surrounding components. Excellent insulation is required to insure an active life of more than a few minutes.

We have found the equimolar NaCl—AlCl<sub>3</sub> mixture to be a reasonable electrolyte at much lower operating temperatures where low to moderate current densities can be tolerated. Single cell studies made over a temperature range of 175°–275° C and a current density range of 15–150 mA/cm<sup>2</sup> showed that LiAl was a suitable anode material, and chlorides of copper(II), iron(III), and molybdenum(V) were suitable cathode materials. The Eureka Company, under Air Force contract, has successfully built and tested thermal batteries based on chloroaluminate electrolytes.

This paper reviews relevant characteristics of chloroaluminate electrolytes, summarizes single cell research, describes present status of battery development, and indicates areas of current research.

### Properties of Chloroaluminate Electrolytes

Aluminum chloride reacts exothermally with alkali metal chlorides to form the ionic chloroaluminates, AlCl<sub>4</sub><sup>-</sup> and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>. The relative amounts of AlCl<sub>4</sub><sup>-</sup> and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> present depend upon the initial ratio of AlCl<sub>3</sub> to MCl, and, in fact, appreciable unreacted AlCl<sub>3</sub> remains (as Al<sub>2</sub>Cl<sub>6</sub><sup>\*</sup>) at very high initial AlCl<sub>3</sub>:MCl ratios (1).

At all reasonable melt temperatures, the concentrations of Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> and Al<sub>2</sub>Cl<sub>6</sub> are negligibly small when AlCl<sub>3</sub> and MCl are reacted in equal molar amounts. For example, at 175° C,  $X_{Al_2Cl_7} = X_{Cl^-} = 1.4 \times 10^{-4}$  and  $X_{Al_2Cl_6} = 3.6 \times 10^{-9}$  when MCl is NaCl (1). When MCl is LiCl,  $X_{Al_2Cl_7} = X_{Cl^-} = 7 \times 10^{-3}$  (2);  $X_{Al_2Cl_6}$  is also very small in the AlCl<sub>3</sub>—LiCl system (3). Vapor pressures of the equimolar mixtures are very low (4,5), and may be neglected in the thermal battery environment.

The electric conductivities of NaCl—AlCl<sub>3</sub> and LiCl—AlCl<sub>3</sub> mixtures are the greatest at or very near the equimolar composition. At 175° C, for example,  $\kappa = 0.378$  (6) and 0.325 ohm<sup>-1</sup> cm<sup>-1</sup> (7), respectively for the two systems. Viscosities of the equimolar mixtures also are low [ $\eta = 2.827$  (8) and 3.834 mPas (9), respectively, at 175° C] and rise as the AlCl<sub>3</sub>:MCl ratio becomes greater than one. The two equimolar mixtures melt at 152° and 142° C, respectively.

\*At pressures and temperatures encountered with thermal batteries, unreacted AlCl<sub>3</sub> is virtually completely dimerized and exists in liquid and gas phases and in solutions as Al<sub>2</sub>Cl<sub>6</sub>.

In practice, the electrolytes are not exactly NaAlCl<sub>4</sub> and LiAlCl<sub>4</sub>, for it is convenient to saturate the melts with NaCl and LiCl, respectively. The solubility limits are very near the equimolar compositions, and all of the properties cited above differ negligibly in saturated solutions and equimolar solutions. The solubilities are slightly temperature dependent; at 175° C  $X_{AlCl_3} = 0.4975$  for NaCl(satd)—AlCl<sub>3</sub> (10), and 0.4925 for LiCl(satd)—AlCl<sub>3</sub> (11). Unless specifically stated otherwise, all following references to electrolytes will assume alkali-saturated mixtures.

Limited study has been made in our laboratory of mixed NaAlCl<sub>4</sub>—LiAlCl<sub>4</sub> electrolytes. All of the desirable properties cited appear to be retained in such mixtures, except melting point. In fact, the melting point drops rather sharply to slightly over 100° C for the eutectic composition (5) which would be even more advantageous for long life applications.

### Single Cell Studies

The experimental work on anode and cathode materials was performed using single cells of the same type that would be expected to be used (in stacks) in an actual battery. This approach allowed us to quantitatively recognize the interdependence of anode-electrolyte-cathode in cell optimization.

## EXPERIMENTAL

Detailed discussions on electrolyte preparation, cell fabrications, and discharge experiments have been presented earlier (12–14).

Single cells were fabricated as three-layer pellets consisting of an anode layer, a cathode layer, and a separating electrolyte layer. The separating electrolyte layer consisted entirely of electrolyte-binder mixture (EBM) which was composed of 90 weight percent (w/o) electrolyte and 10 w/o SiO<sub>2</sub> binder. The cathode layer was a mixture of EBM, graphite, and active cathode material. The anode layer usually contained in addition to the active anode material, a small amount of EBM to facilitate pelletizing. Single cell configuration is shown schematically in Figure 1.

Single cells were discharged at constant current between heated platens. Cell performance was measured by calculating the energy density at 80% of initial closed circuit voltage and based on cell weight.

## ANODE STUDIES

Materials initially investigated for use as anodes included aluminum, lithium, and LiAl alloys of various compositions. As shown in Figure 2, the discharge behaviors of lithium and LiAl were superior to that of aluminum; however, the lithium-containing anodes experienced a high voltage "spike" during cell activation, as seen in Figure 3. Two features of these

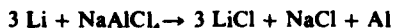
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**ANODE:** | Li Alloy Foil  
 or  
 Li Alloy Powder and EBM\*  
**SEPARATOR:** | EBM\*  
**CATHODE:** | CuCl<sub>2</sub> or FeCl<sub>3</sub> or MoCl<sub>5</sub>  
 Graphite Flakes  
 EBM\*

\*EBM: | 90 wt% Electrolyte  
 10 wt% Silica

Figure 1. Single cell configuration

activation plots bear special notice. First is that the spike appears below the electrolyte melting point, then sharply decays to the aluminum potential at the melting point. The second important characteristic is the much smaller cell polarization during discharge noted for cells containing lithium-aluminum alloy. The superior performance of LiAl seen in Figure 2 is a reflection, at least in part, of the low cell polarization characteristics of LiAl. The high voltage spike has been attributed to a displacement reaction between lithium in the anode and the molten electrolyte (15)



Several lithium-aluminum alloy compositions were investigated (14,15). The best performance was given by the alloy 60.2 atomic percent (a/o) (28 w/o) lithium. This alloy was used in subsequent optimization studies of other cell components.

The actual role of the lithium in the anode is not clear, but there is indirect evidence that it is the lithium itself that is actually reacting during cell discharge, perhaps by the reaction above. Total energy output of single cells was proportional to the amount of lithium initially present in the anode. Furthermore, the melting point of the electrolyte in discharged cells

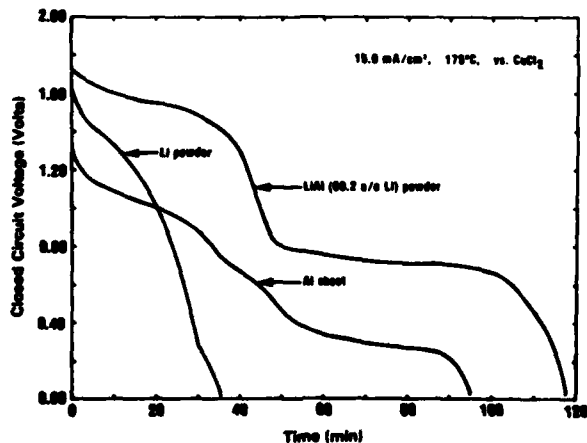


Figure 2. Discharge curves for aluminum, lithium, and lithium-aluminum anodes.

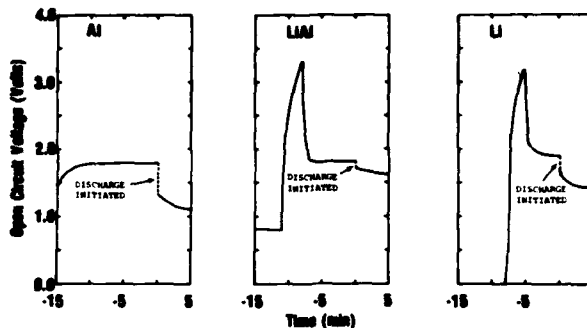


Figure 3. Activation voltage behavior for aluminum and lithium-containing anodes.

was substantially lowered, as much as 30° C in some cases, implying the addition of some foreign component, e.g., Li<sup>+</sup>. Carpio and King (16) have shown that lithium can be electrochemically removed from LiAl into a LiCl(satd)—AlCl<sub>3</sub> electrolyte.

Recently, LiSi and LiB have been tested and their performance compared with LiAl. The energy densities obtained from LiSi/CuCl<sub>2</sub> cells were essentially the same as for LiAl/CuCl<sub>2</sub> cells at all operating conditions. These data are shown in Figure 4 for high and low current densities. Internal resistances determined from cell polarization data are given in Table I.

Experiments with LiB anodes were limited to a single temperature (200° C) and to current densities of 15–100 mA/cm<sup>2</sup> because of limited availability of LiB. Figure 5 shows that energy densities for LiB/CuCl<sub>2</sub> cells were slightly higher than for LiAl/CuCl<sub>2</sub> cells at most current densities. This was due in part to the weight difference between the two cell types. The LiB was supplied as finished anodes of about 0.16g LiB pressed on to a stainless steel substrate, whereas the lightest LiAl anode we could fabricate contained 0.27g LiAl. However, at 100 mA/cm<sup>2</sup>, the LiB/CuCl<sub>2</sub> cell energy density is significantly higher than the LiAl/CuCl<sub>2</sub> cell. Insufficient data were available to calculate LiB/CuCl<sub>2</sub> cell resistances.

While our study indicates that LiB may be the superior anode for chloroaluminate thermal batteries, additional work is needed to fully explore this possibility.

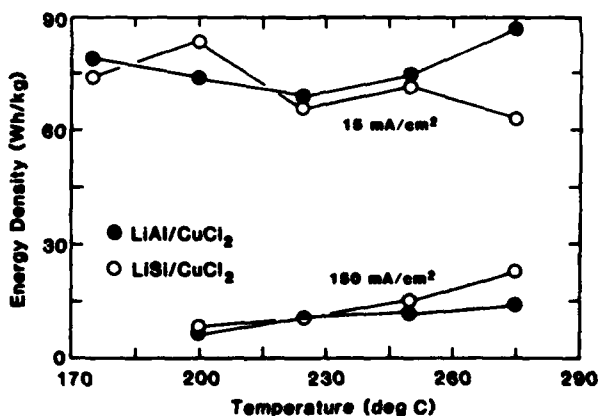


Figure 4. Comparison of LiSi/CuCl<sub>2</sub> and LiAl/CuCl<sub>2</sub> cells at 15 and 150 mA/cm<sup>2</sup>.

TABLE I  
SINGLE CELL INTERNAL RESISTANCES

Temperature (°C)	Internal Resistance ( $\Omega$ )	
	LiAl/CuCl <sub>2</sub>	LiSi/CuCl <sub>2</sub>
175	0.89	0.96
200	0.32	0.35
225	0.32	0.34
250	0.31	0.28
275	0.29	0.28

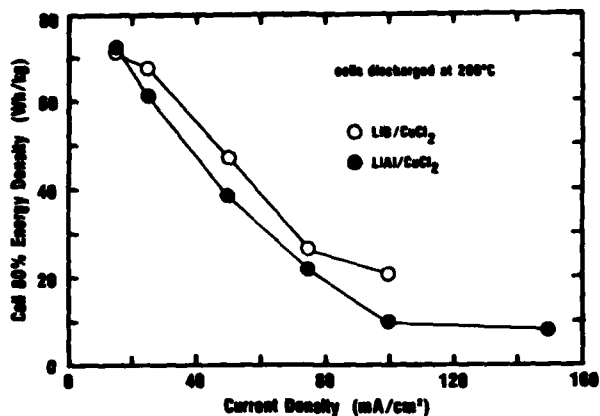


Figure 5. Comparison of LiB/CuCl<sub>2</sub> and LiAl/CuCl<sub>2</sub> cells

#### CATHODE STUDIES

In studies of over 40 inorganic sulfides, oxides, and halides, MoCl<sub>5</sub>, CuCl<sub>2</sub>, and FeCl<sub>3</sub> were identified as good cathode materials for chloroaluminate thermal cells (13,17). Consequently, these three materials were studied extensively in optimized single cells (14,15,18).

The open-circuit potentials were 2.4, 2.3, and 1.8V, respectively, for LiAl/MoCl<sub>5</sub>, LiAl/FeCl<sub>3</sub>, and LiAl/CuCl<sub>2</sub> cells. Internal resistances of the three cells types were similar; at 200°C, for example, single cell resistances were 0.63, 0.5, and 0.42  $\Omega$ , respectively.

Even though CuCl<sub>2</sub> produced the lowest potential, it pro-

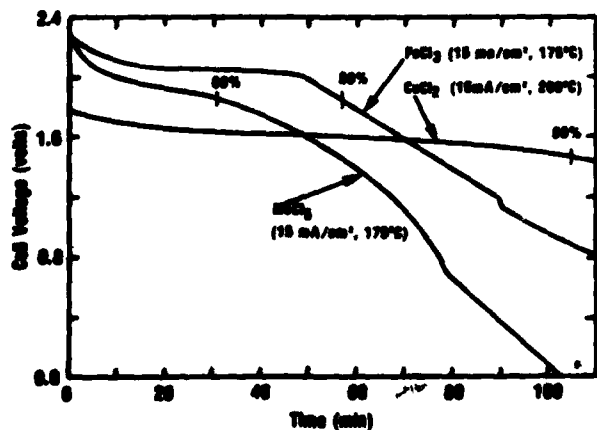


Figure 6. Comparison of discharge curves for the best cell of each of the three cell types.

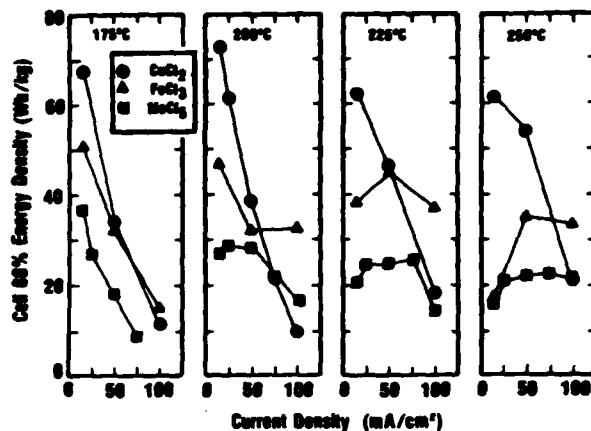


Figure 7. Energy densities of LiAl/CuCl<sub>2</sub>, LiAl/FeCl<sub>3</sub>, and LiAl/MoCl<sub>5</sub> cells.

duced the highest energy density, over 80 W-hr/kg, due to a much longer lifetime (110m at 15 mA/cm<sup>2</sup>). The discharge curves and operating conditions for the best cell of each type are compared in Figure 6. Figure 7 shows the energy densities for the three cell types over the complete range of operating conditions. At low current density, CuCl<sub>2</sub> clearly showed greater energy densities than the other two cathodes. At high current density, FeCl<sub>3</sub> was the superior cathode while CuCl<sub>2</sub> and MoCl<sub>5</sub> were similar in performance.

Another performance criterion examined was the temperature tolerance of the different cells. The ideally temperature tolerant cell would be one in which the energy density did not change over the operating temperature range. As a measure of the performance change over the temperature range, we defined the percent change in performance, at a given current density, as

$$\frac{\text{maximum energy density} - \text{minimum energy density}}{\text{maximum energy density}} \times 100$$

A comparison of the three cell types in this way is shown in Figure 8. At low current density, CuCl<sub>2</sub> was the cathode most tolerant to temperature changes (smallest percent change

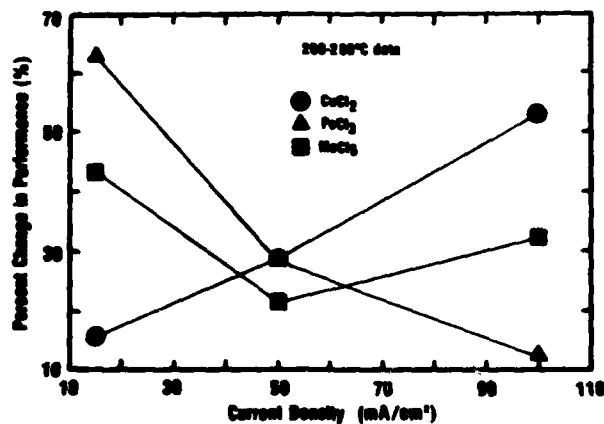


Figure 8. Temperature tolerance (measured as percent change in performance) of the three cell types.

