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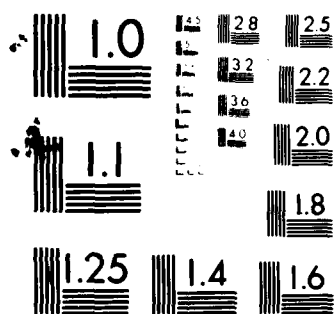
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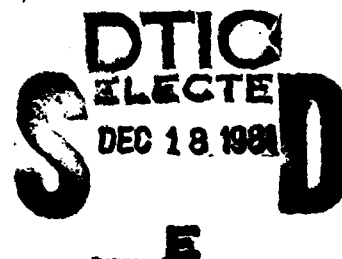


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FRANK J. SEILER RESEARCH LABORATORY

**FJSRL TECHNICAL REPORT 81-0012
NOVEMBER 1981**

**FINAL REPORT ON LOW TEMPERATURE,
CHLOROALUMINATE THERMAL CELLS**



CAPT ROBERT L. VAUGHN

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PROJECT 2303

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

81 18 023

FJSRL-TR-81-0012

This document was prepared by the Physical Chemistry and Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit number 2303-F2-07. Capt Robert L. Vaughn was the project scientist.

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FINAL REPORT ON LOW TEMPERATURE,
CHLOROALUMINATE THERMAL CELLS

by
Capt Robert L. Vaughn

TECHNICAL REPORT FJSRL-TR-81-0012
November 1981

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Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) —> This report summarizes the results of single cell studies on thermal cells containing sodium tetrachloroaluminate electrolyte. The best performing cells delivered 100 Wh/kg at a lifetime of 143 minutes to 75% of initial closed circuit voltage. Such cells operated at 200°C at a current density of 15mA/cm ² . A limited photomicroscopy study revealed a reaction between the lithium alloy anode and separating electrolyte when the cell is stored at 80°C. MoO ₃ Cl ₂ and [Et ₄ N(MoCl ₆)] were studied as possible alternate molybdenum cathodes, but these materials did not show promising performance.		

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PREFACE

This is the final report for Work Unit F2-07 and summarizes the work performed in this work unit through 30 September, 1981. A number of people contributed to this project throughout its existence. Contributors included G. D. Brabson, D. W. Seegmiller, L. A. King, A. A. Fannin, J. C. Nardi, J. K. Erbacher, and C. L. Hussey.

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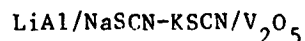
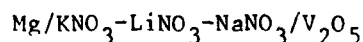
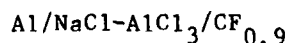
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INTRODUCTION

Production thermal batteries use LiCl-KCl electrolyte and operate only at very high temperatures (400-600°C). Use of this high temperature electrolyte maximizes current density, but imposes severe thermal stress on surrounding components and causes undesirable reactions within the battery that limit useful lifetimes.

A low temperature thermal battery would have a number of advantages over a high temperature battery. Reduced pyrotechnic and insulating materials, use of high-potential anodes and inexpensive sealing techniques have been cited (1,2). A low temperature thermal battery would give a longer lifetime because of the lower temperature differential between battery and environment and because undesirable corrosion reactions would less likely occur, or occur at a lower rate.

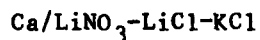
A number of electrochemical systems have been investigated for use in low temperature thermal batteries. Workers at the Harry Diamond Laboratory looked at three systems:



They found that the thiocyanate system gave the highest current output and studied that system in more detail. Two-cell batteries, with fusible alloy heat reservoirs for thermal balance, produced 2.5 V peak voltage at 5 mA/cm² (2).

Workers at the Naval Weapons Center are currently investigating molten nitrate mixtures as thermal battery electrolytes. The nitrate melt itself serves as the oxidizer, eliminating the depolarizer

component. They have operated the system



in single cells over the temperature range 250 to 450°C, and obtained an experimental energy density of 142 Wh/kg at 300°C and 10 mA/cm². Performance deteriorated above 20 mA/cm² due to polarization of the anode, probably due to formation of CaO. The best lifetime measured to 75% of peak voltage was 45 minutes at 250°C (1).

An electrolyte we have investigated for use in low temperature thermal batteries is equimolar NaCl-AlCl₃ (NaAlCl₄). This electrolyte melts at 152°C and has a conductivity of 0.378 (Ω cm)⁻¹ at 175°C (3). We used the electrolyte in pelletized single cells similar to those used in actual thermal batteries. These cells were tested at temperatures of 175 to 275°C and at current densities of 15 to 150 mA/cm².

This report summarizes the results of single cell tests of chloroaluminate thermal cells and reports on recent studies pertaining to alternate molybdenum cathodes and photomicroscopy of discharged CuCl₂ cells.

CELL COMPOSITION

The electrolyte used for single cell fabrication was a mixture of 90 w/o equimolar NaCl-AlCl₃ and 10 w/o SiO₂ as binder. This mixture will be referred to as the the electrolyte-binder mixture (EBM) throughout the remainder of this report. Ryan varied the binder content between 7 and 15 w/o and found that 10 w/o did give the best cell performance (4).

Single cells having a surface area of 6.42 cm² were fabricated as three-layer pellets. Details of cell fabrication have been given elsewhere (5).

Aluminum and lithium alloys of various composition were tested as anodes. The optimum anode contained 0.27g active material. The best LiAl alloy contained 28 w/o Li. A total of 40 halides, oxides, and sulfides were screened for the best cathode materials, and the halides of molybdenum(V), iron(III), and copper(II) were selected for detailed study. Cathodes were a mixture of active cathode material, EBM, and graphite. The optimum cathode compositions varied depending on active material and are given in Table I. The optimized configuration was used in cells discharged at constant current densities of 15 to 150 mA/cm² and temperatures of 165 to 275°C.

TABLE I. Cathode Compositions.

	ACTIVE	EBM	GRAPHITE
<u>CATHODE</u>	<u>MATERIAL(g)</u>	<u>(g)</u>	<u>(g)</u>
MoCl ₅	0.72	0.64	0.23
FeCl ₃	1.56	0.64	0.23
CuCl ₂	1.50	0.64	0.23

The separator in FeCl₃ and CuCl₂ cells consisted of 0.99g EBM and in MoCl₅ cells, 0.78g.

SUMMARY OF RESULTS OF SINGLE CELL DISCHARGE EXPERIMENTS

Initial anode studies showed that lithium-aluminum having 28 w/o lithium was the best material. The open circuit voltages for the

optimized cells were 2.4, 2.3, and 1.8 V, respectively for MoCl_5 , FeCl_3 , and CuCl_2 cathodes. The experimental energy densities for these cells were measured at 80% of initial closed circuit voltage, and were used to compare the relative cell performances. The energy densities of each cell type are summarized in Figures 1, 2, and 3 for the current densities and temperatures used in the experiments. The highest energy density, 72.6 Wh/kg, was obtained from a CuCl_2 cell at 15 mA/cm² and 200°C. The superiority of the CuCl_2 cells was due to their long operational lifetimes.

LiAl/MoCl₅ CELL PERFORMANCE

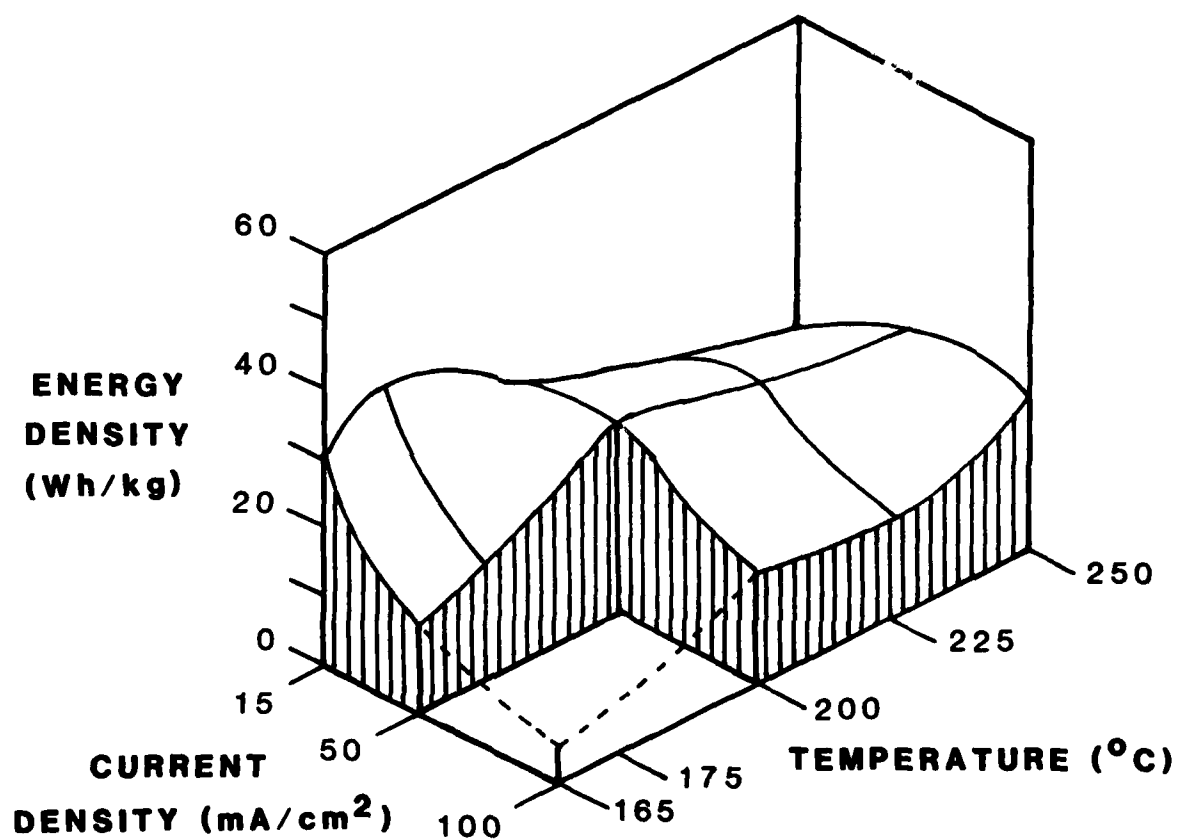


Figure 1. Performance Summary for LiAl/MoCl₅ Single Cells.

LiAl/FeCl₃ CELL PERFORMANCE

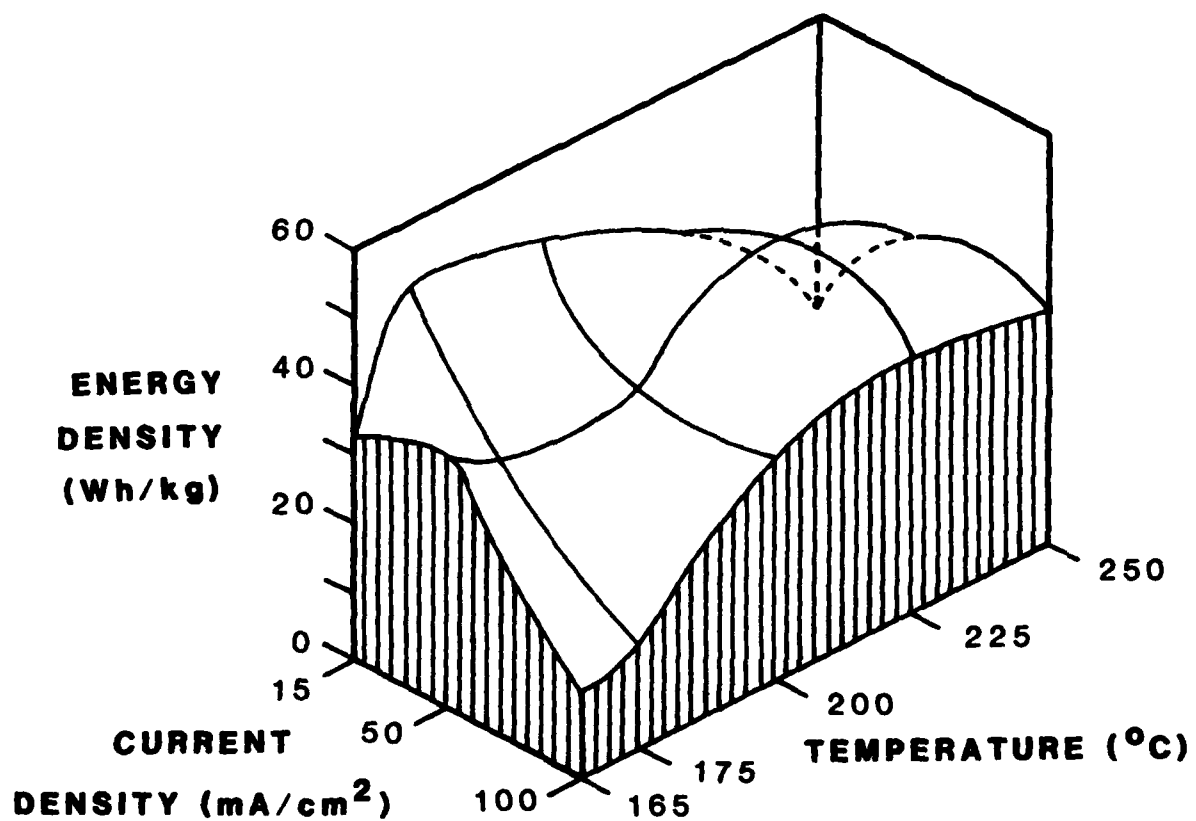


Figure 2. Performance Summary for LiAl/FeCl₃ Single Cells.

LiAl/CuCl₂ CELL PERFORMANCE

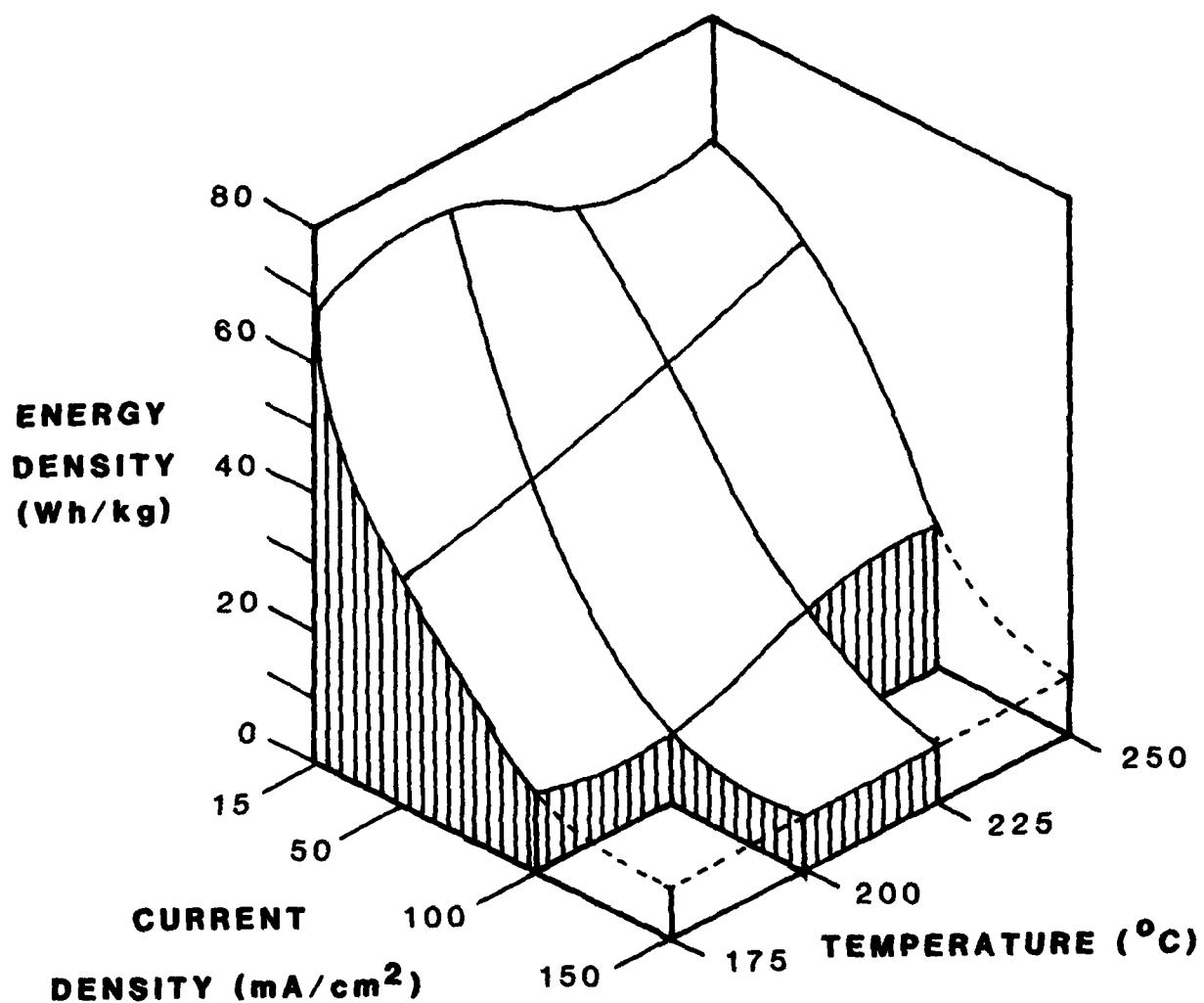


Figure 3. Performance Summary for LiAl/CuCl₂ Single Cells.

The best lifetimes of the three cell types were 30, 58, and 106 minutes respectively for MoCl_5 , FeCl_3 , and CuCl_2 cells. Figure 4, which compares the discharge curves for the best cell of each type, clearly shows the superior discharge curve of CuCl_2 cells.

Since the CuCl_2 cells showed the best energy densities, they were used in subsequent evaluation of lithium silicon anodes. Lithium-silicon alloys composed of 40, 45, and 55 w/o lithium were studied. The alloy 55 w/o in lithium gave the best performance and the results presented here will be for the 55 w/o material. Figure 5 summarizes the performance of LiSi/CuCl_2 cells. The highest energy density with LiSi/CuCl_2 was 96.4 Wh/kg at 15 mA/cm² and 200°C. This cell had a lifetime of 137.5 minutes to 80% of initial closed circuit voltage and 146.5 minutes to 70%.

ALTERNATE MOLYBDENUM CATHODES

For higher current capability, MoCl_5 appeared to be the best cathode material, however battery engineering efforts showed that MoCl_5 had severe storage limitations (4). Attempts were made to solve the storage problem by purifying commercial MoCl_5 and searching for new molybdenum cathodes.

Since MoOCl_4 is produced as an impurity in MoCl_5 (6), commercial MoCl_5 was heated at 80°C for about three weeks. Cells using this treated material were discharged at 200°C and 20Ω constant load and compared to cells made with commercial MoCl_5 . As seen in Figure 6, there was no difference in the discharge curves and voltages. A cell made with treated MoCl_5 was stored for 8 days between platens maintained at 80°C, and then was discharged at 200°C

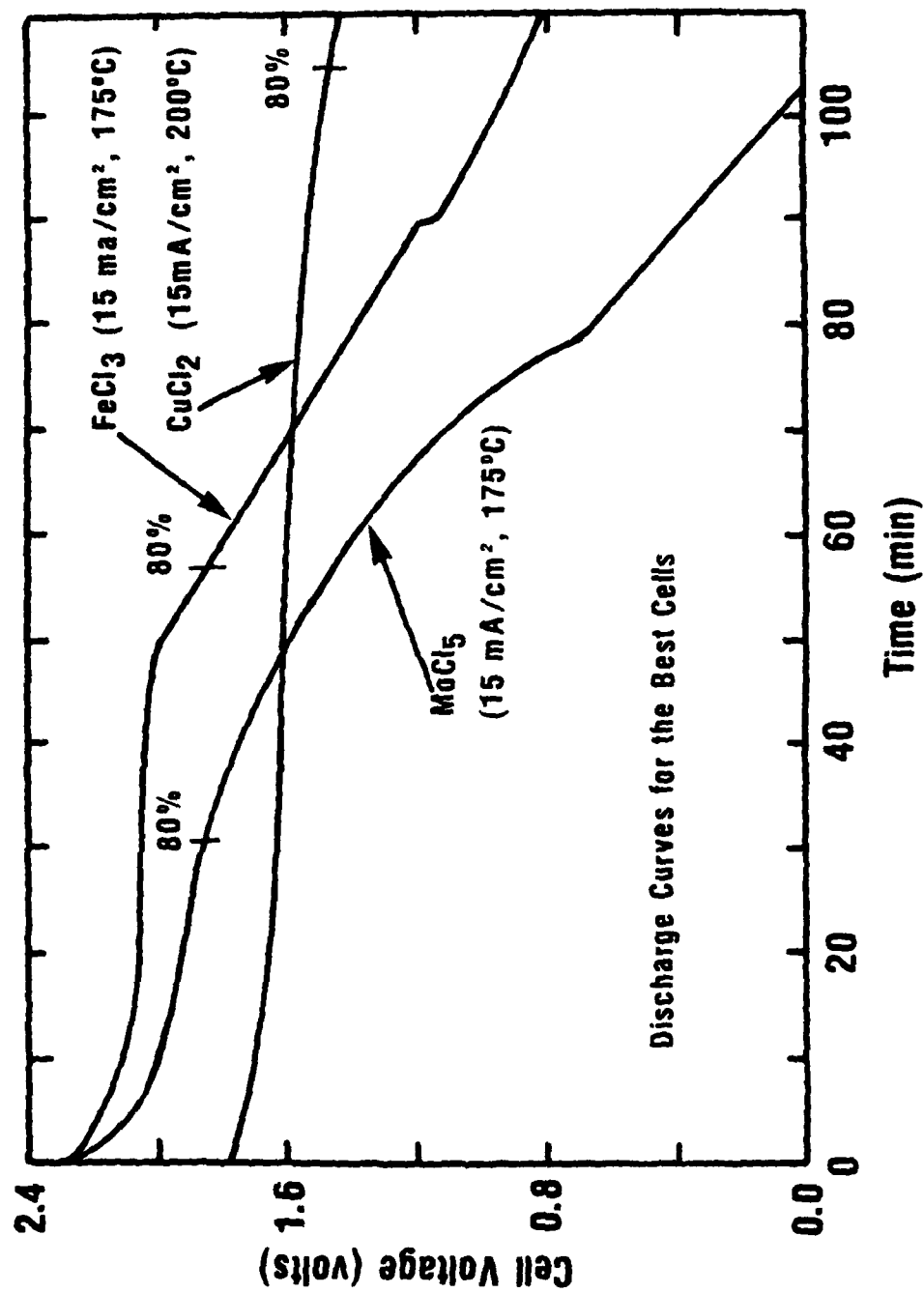


Figure 4. Discharge Curves for the Best Cell of Each Type.

LISI/CuCl₂ CELL PERFORMANCE

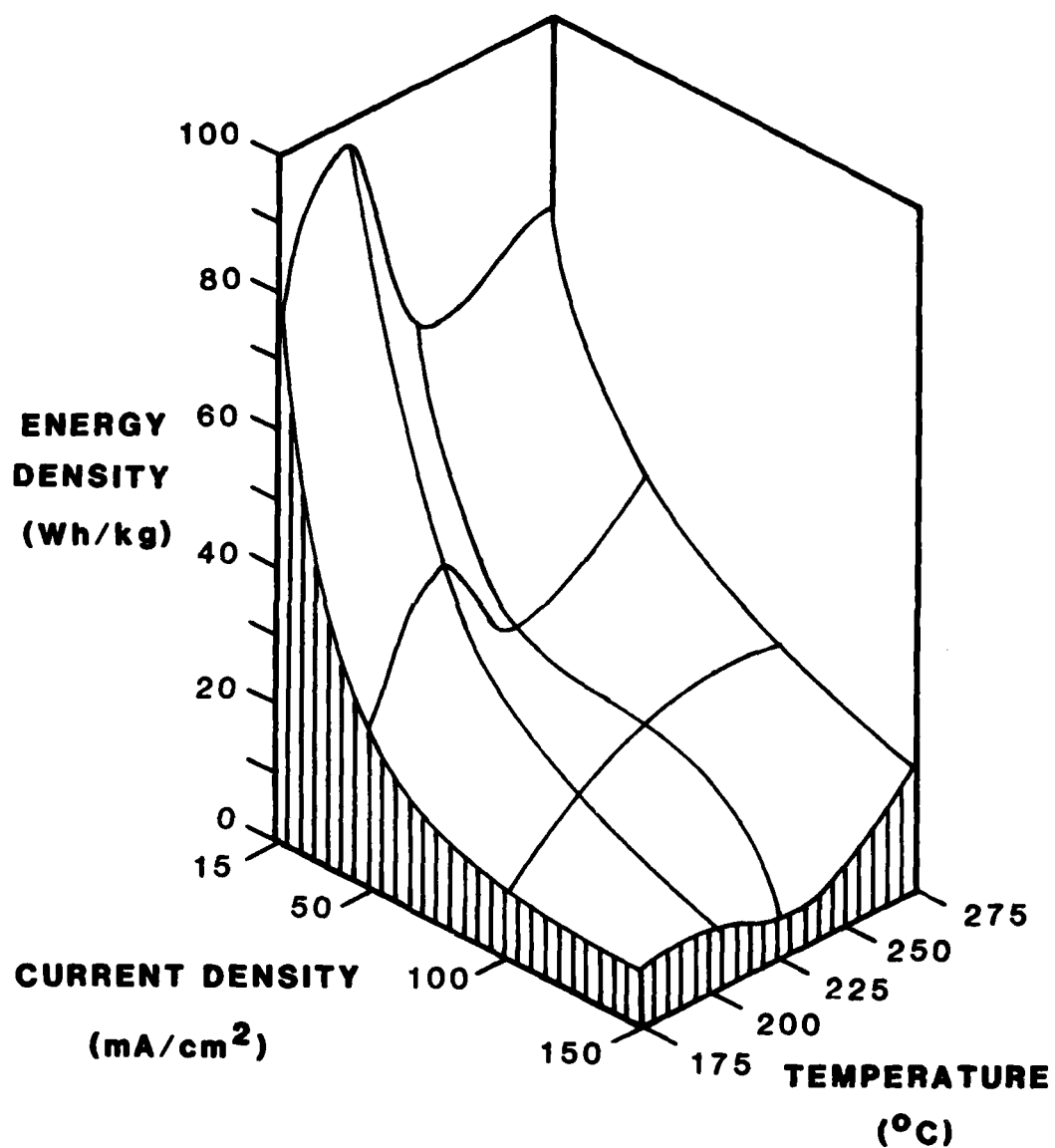


Figure 5. Performance Summary for LiSi/CuCl₂ Single Cells.

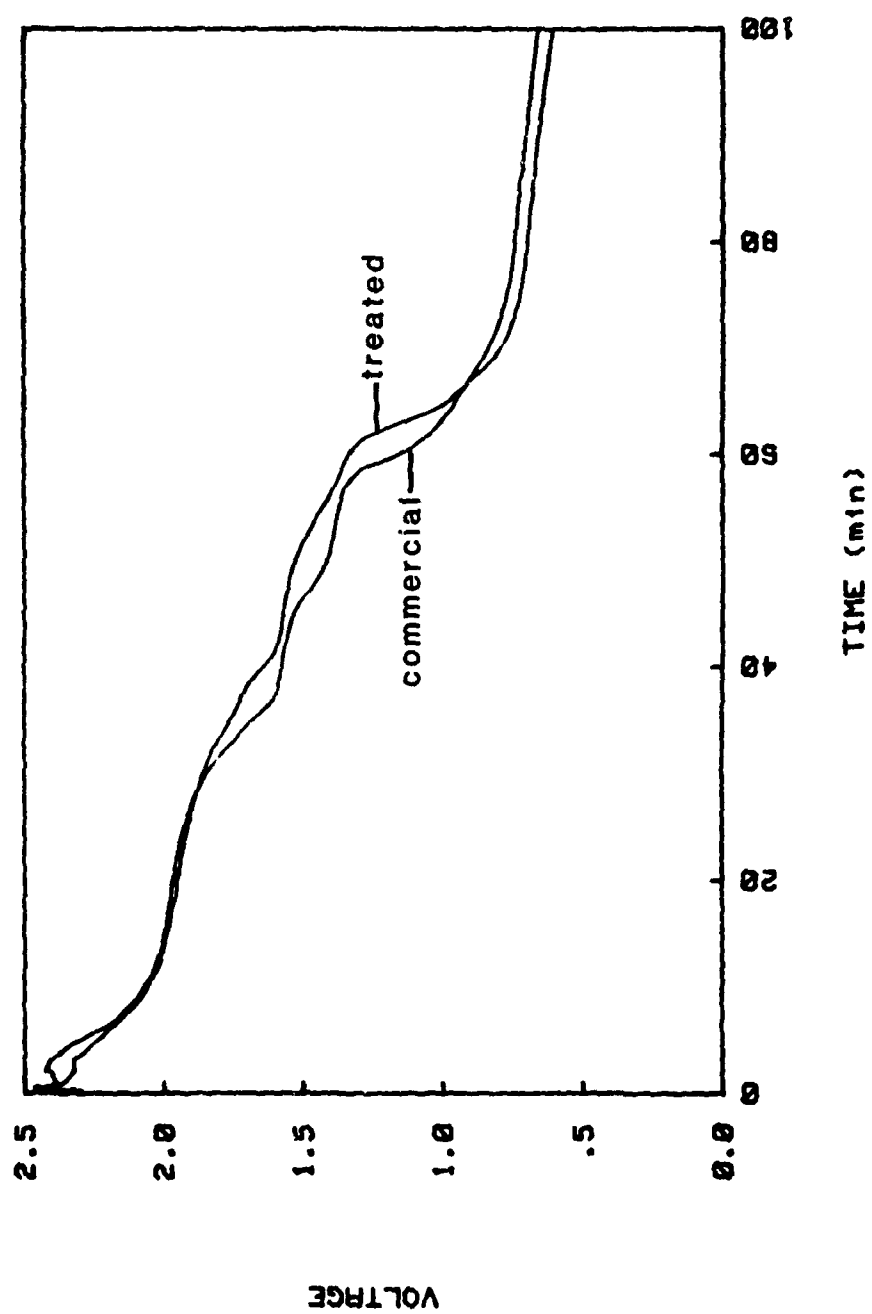


Figure 5. Discharge Curves Comparing Cathodes Made with
Commercial versus Treated MoCl_5 .

across a 20 Ω load. This discharge curve was compared to that for a cell made with commercial MoCl₅ and discharged when made. The stored cell showed a much broader and lower voltage spike than the fresh cell. The open circuit voltage of the stored cell did not stabilize and discharge was started at about 9.5 minutes for the fresh cell when its voltage did stabilize. The stored cell had a much larger voltage drop when the load was connected than did the fresh cell. From the point cell discharge was started, the stored cell showed lower voltages and shorter plateaus except for the later stage of discharge where the voltages were equal. These results indicate that purified MoCl₅ does not alleviate the performance degradation of stored cells.

Another approach was to try other Mo-containing compounds, including those containing MoCl₆⁻. The reasoning was that complexed Mo would be more stable. Dr. Kenneth Seddon, Oxford University, supplied MoO₂Cl₂ and Et₄N[MoCl₆] in quantities to make some single cells. Cells made with these materials were compared to MoCl₅ cells. The cathode compositions were the same as for MoCl₅ cathodes except for the amount of test material. Not enough test materials were available to attempt optimizing those cells. Discharge curves are shown in Figures 7 and 8. Both MoO₂Cl₂ and Et₄N[MoCl₆] were characterized by an initially very steep discharge curve. Neither material appeared to warrant further investigation.

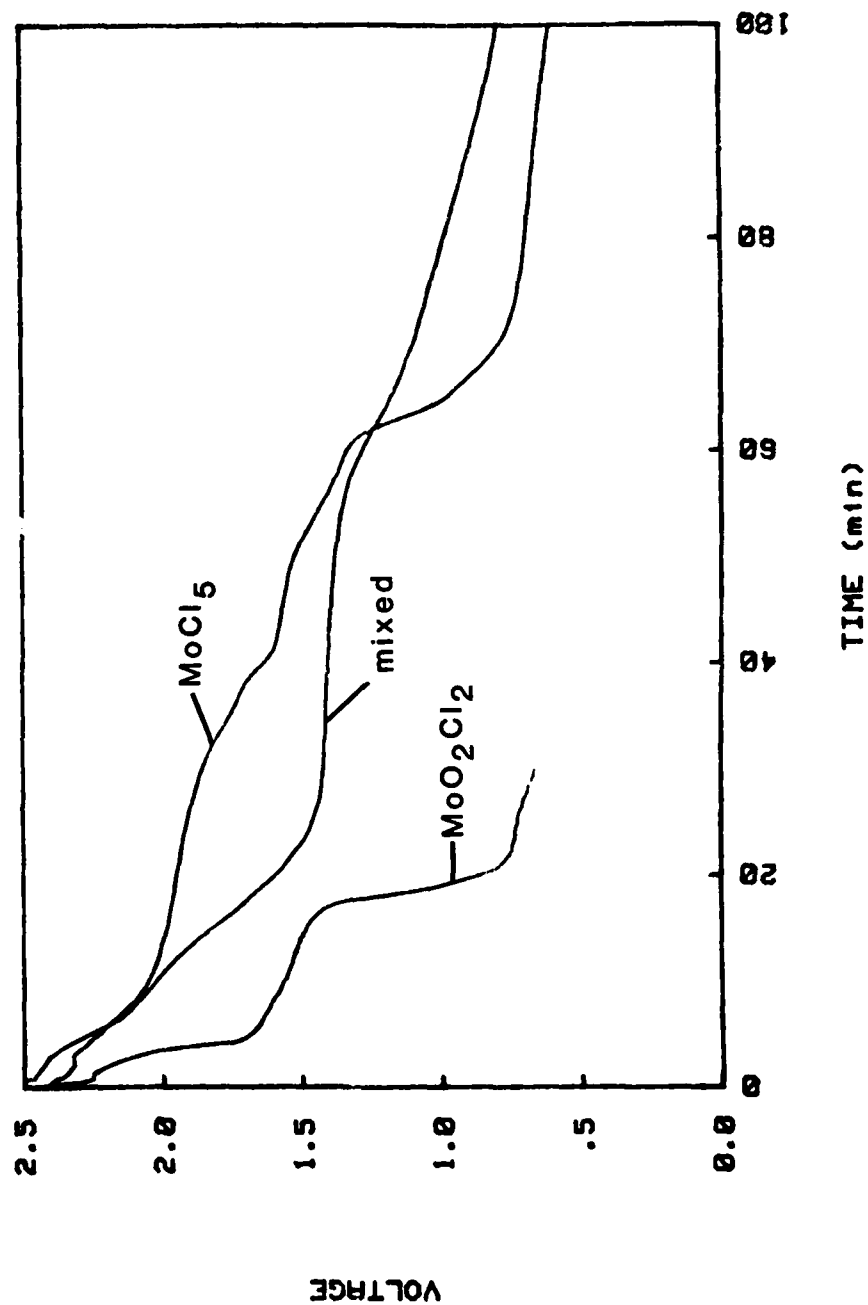


Figure 7. Discharge Curves for Cells with MoO_2Cl_2 , MoCl_5 , and Mixed $\text{MoO}_2\text{Cl}_2 + \text{MoCl}_5$ Cathodes.

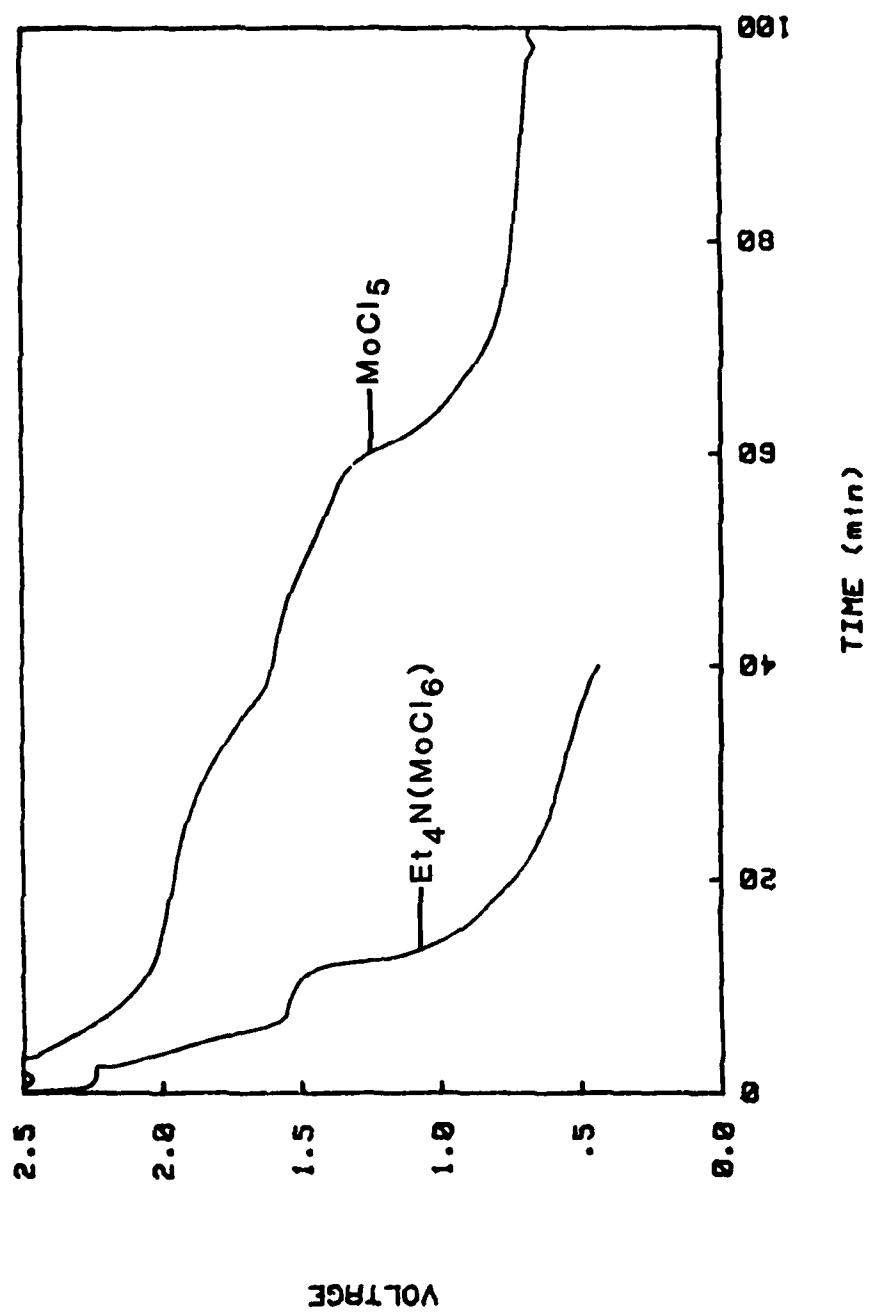


Figure 8. Discharge Curves Comparing Cells with MoCl_5 and $\text{Et}_4\text{N}[\text{MoCl}_6]$ Cathodes.

PHOTOMICROSCOPY STUDY

A short photomicroscopy study was undertaken to determine changes in cell components during storage and discharge. Optimized LiAl/CuCl_2 cells were used for the study. Besides having good performance, CuCl_2 cells contained materials that had readily observable color changes as a function of discharge. Cells were cut in half in the drybox before being transferred outside where the microscope was located. The cells were sufficiently stable to allow several photographs before the cell noticeably deteriorated. All photographs discussed here were taken at 20X magnification. The results are presented here as idealized drawings representing the distinct areas present in actual photographs.

Figure 9 is the representation of a fresh, undischarged cell. All interfaces are sharp and well defined. Area A, the anode is dark and homogeneous. Area B, the separating electrolyte shows as a white homogenous layer. Area C, the cathode, is inhomogeneous with yellow-orange CuCl_2 particles intermixed with black graphite and a few white particles of electrolyte.

Figure 10 represents an undischarged cell stored at 80°C for three days. The only change is the penetration of the separator by a black material. The original anode/separator interface is still discernable although the color of the anode at the interface is lighter in color than in the fresh cell. Another cell was stored under the same conditions except that a $10\text{ M}\Omega$ load was connected across the cell and the voltage was monitored. The results showed the same kind of

separator penetration as for the cell stored on open circuit. The voltage during storage was about 3.05V and did not drop during the test. The source of the penetrating material is probably a reaction between the Li alloy and the SiO_2 binder, a reaction known to occur in LiCl-KCl thermal cells (7).

Cells were discharged at 15 and 150 mA/cm² and at 200 and 275°C to cut-off voltages of 0.0, 0.70, and 1.0 volts. Changes within the cells could then be studied as a function of discharge rate, depth of discharge, and temperature. After discharge, the cells were immediately removed from the tester and allowed to cool.

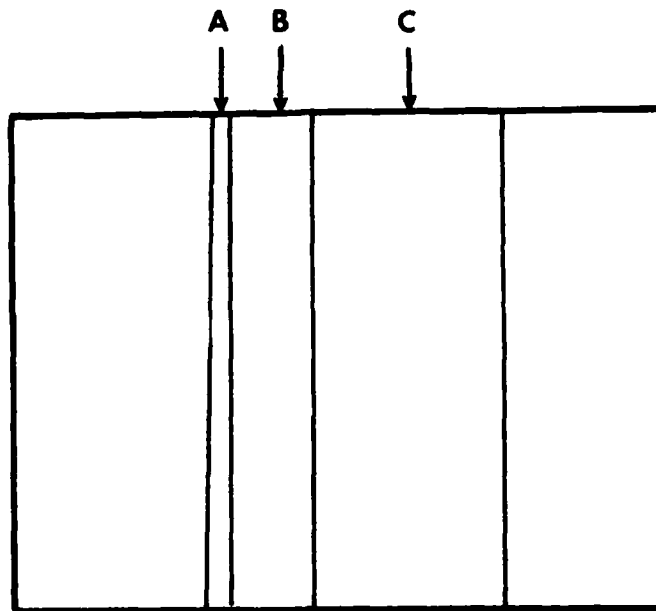


Figure 9. Depiction of Fresh Cell. A-anode; B-Separator; and C-Cathode.

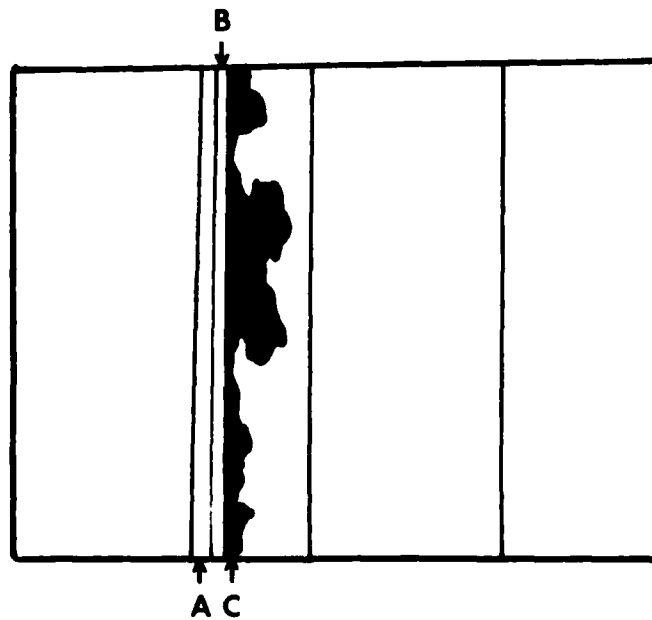
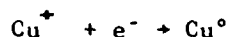
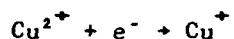


Figure 10. Depiction of Cell Stored at 80°C. A-Unchanged Anode; B-Changed Anode; C-Penetrating Material.

The results were evaluated by examining the changes within the cell and the number of coulombs discharged. The assumed cathodic reaction is (8)



resulting in a two-plateau discharge. Based on the mass of CuCl_2 contained in the cathode, each reaction should account for 1060 coulombs for a total of 2120 coulombs theoretical capacity.

Generally, two types of changes occurred within the cell during discharge. First was a penetration of the separator by a material from the anode. This material was lighter and usually more inhomogeneous than the material observed in the storage tests. The second type of change involved the cathode. A band of copper and/or a band of darkened cathode material were observed. The relative thickness of the these bands depended on the temperature, discharge rate, and depth of discharge as manifested by the number of coulombs drawn from the cells.

The results are presented for cells in the order of increasing delivered capacity.

Cells discharged at 150 mA/cm^2 had very short lifetimes to the cut-off voltages and delivered relatively few coulombs. Photomicrographs showed very few changes. With a 1.0 volt cut-off, cells discharged at 150 mA/cm^2 delivered only 21 coulombs at 200°C and 307 coulombs at 275°C . At these levels, changes were observed only at the anode-separator interface. At 21 coulombs there was no

penetration of the separator and only slight penetration at 307 coulombs. At 0.7 volt cut-off at 275°C, 400 coulombs were delivered. The photomicrograph showed a dark, thin, smooth line at the anode-separator interface, and in the cathode there was a darkened layer about one-third the thickness of the cathode adjacent to the separator (see Figure 11). The remainder of the cathode was not changed.

The cell discharged at 200°C to a 0 volt cut-off delivered 730 coulombs. This cell showed an irregular penetration into about one-half of the separator thickness. (Refer to Figure 12). The cathode showed a thin band of copper adjacent to the separator. Adjacent to the copper band was a darkened band. The combined thickness of these two bands was about one-third of the total cathode thickness. The other two-thirds of the cathode was unchanged.

The cell discharged at 15 mA/cm² and 200°C to a 1 volt cut-off delivered 824 coulombs. The photomicrograph showed the irregular penetration of the separator, at some points extending the entire separator thickness. (see Figure 13). A blackened layer in the cathode extended from the separator about half way across the cathode thickness. However, no copper was observed.

At 15 mA/cm², 275°C, and 1 volt cut-off, 927 coulombs were delivered. A dark almost homogeneous penetration of the separator was observed. On higher magnification, the penetrating layer seemed to be two separate layers with some connecting material. Figure 14 shows the two layers. The total penetration was about one-half the

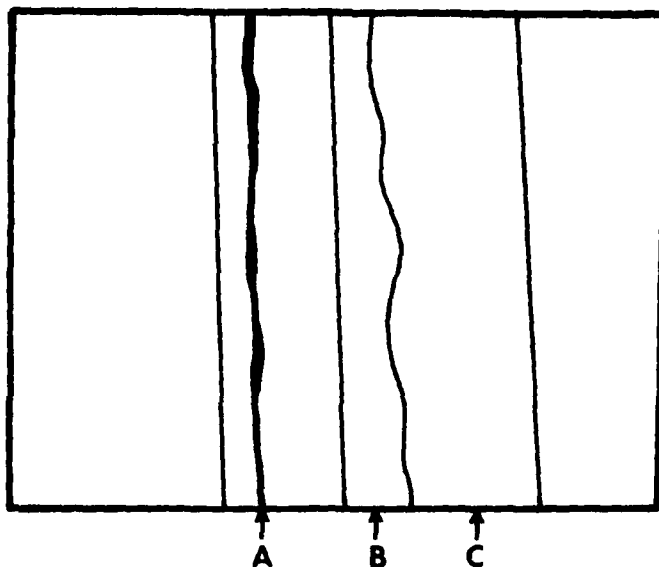


Figure 11. Depiction of Cell Discharged at 150 mA/cm^2 and 275°C to 0.7 Volt. Delivered 400 Coulombs.
 A-Change at Anode-Separator Interface;
 B-Darkened Layer in Cathode; C-Unchanged Cathode.

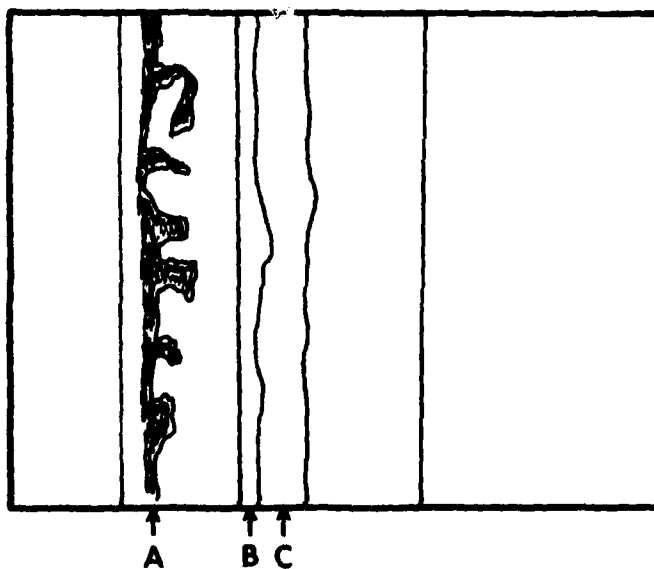


Figure 12. Depiction of Cell Discharged at 150 mA/cm^2 and 200°C to 0 Volt. Delivered 730 Coulombs.
 A-Penetration of Separator; B-Copper Formation;
 C-Darkened Band.

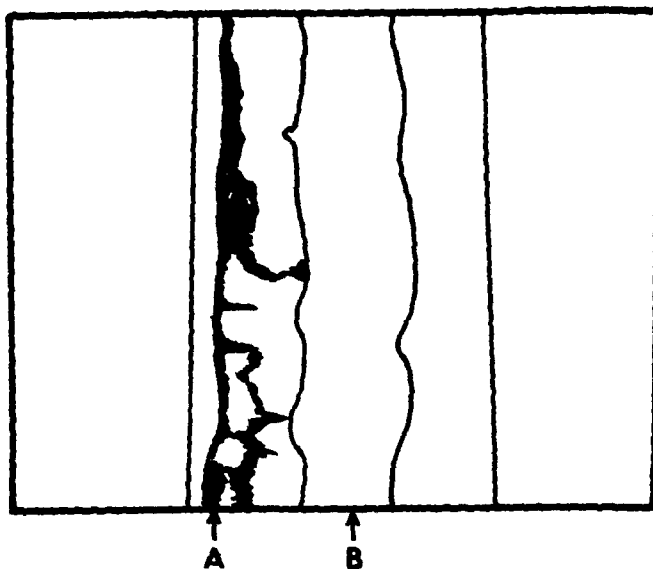


Figure 13. Depiction of Cell Discharged at 15 mA/cm^2 and 200°C to 1.0 Volt. Delivered 824 Coulombs. A-Penetration of Separator; B- Darkened Band.

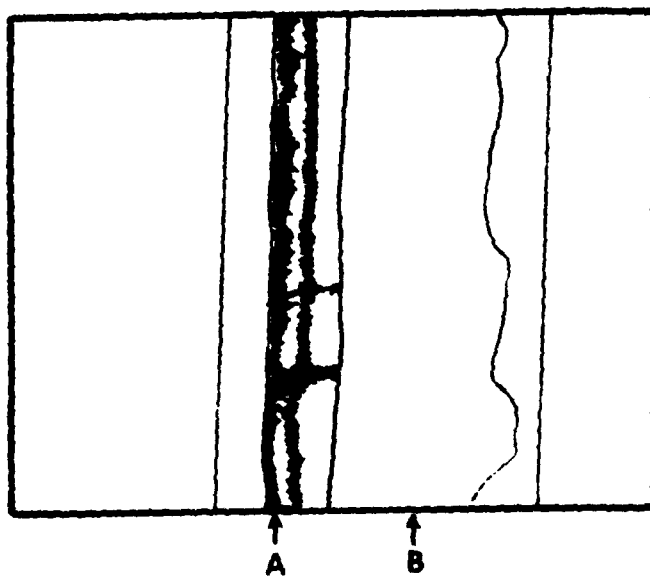


Figure 14. Depiction of Cell Discharged at 15 mA/cm^2 and 275°C to 1.0 Volt. 927 Coulombs Delivered. A-Penetration of Separator; B-Darkened Cathode.

separator thickness, but at places thin dendrite-like penetration was over the entire separator thickness. The cathode layer was darkened about three-fourths across the cathode thickness.

The cell discharged at 150 mA/cm² and 275°C to 0 volt cut-off delivered 1300 coulombs. The discharge curve did not show a distinct high voltage plateau but there was a definite low voltage plateau. About 700 coulombs of the delivered capacity was associated with the lower plateau. The separator did not show any penetration from the anode, although the separator interfaces had become irregular. A band of copper was present in the cathode along with a darkened band. The outside third of the cathode was greyish without the yellow color of unreacted CuCl₂ (see Figure 15).

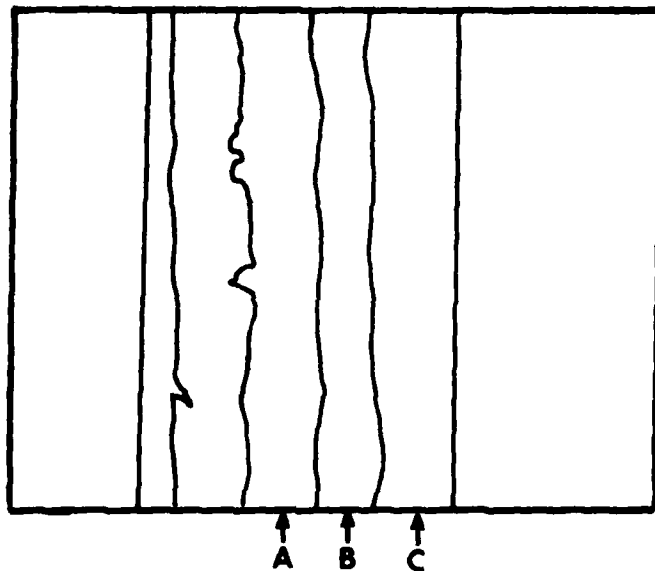


Figure 15. Depiction of Cell Discharged at 150 mA/cm^2 and 275°C to 0 Volt. A-Copper in Cathode; B-Darkened Cathode Material; C-Greyish Layer Having No Yellow CuCl_2 .

The cell discharged at 15 mA/cm^2 and 275°C showed very different behavior in its discharge curve. This cell had a voltage "hump" at about 700-800 coulombs followed by an abrupt voltage drop at about 900 coulombs. See Figure 16. The lower plateau then accounts for only about 550 coulombs, about half of the theoretical. The photomicrograph of this cell, Figure 17, also showed copper formation all the way through the cathode. This single copper layer had large particle sizes throughout. The material penetrating the separator was more diffuse and in places penetrated the entire thickness of the separator.

The greatest number of coulombs, 2048, was obtained from the cell discharged at 15 mA/cm^2 and 200°C to 0 volt. This value is reasonably close to the theoretical capacity and was taken as a complete discharge. The discharge curve, shown in Figure 18, shows three voltage plateaus. The high voltage plateau ends at about 800 coulombs and is followed by a very short plateau. These two plateaus account for about 1000 coulombs. The low voltage plateau accounts for the remaining cathode capacity. The photomicrograph for this cell, depicted in Figure 19, shows very irregular penetration of material from the anode into the separator to a maximum depth of about two-thirds of the separator thickness. The cathode shows formation of copper throughout its thickness, however the half of the cathode adjacent to the separator has much smaller particle size than the other half and is lighter in color. The half of the cathode away from the separator had particle sizes similar to those in the previous cell.

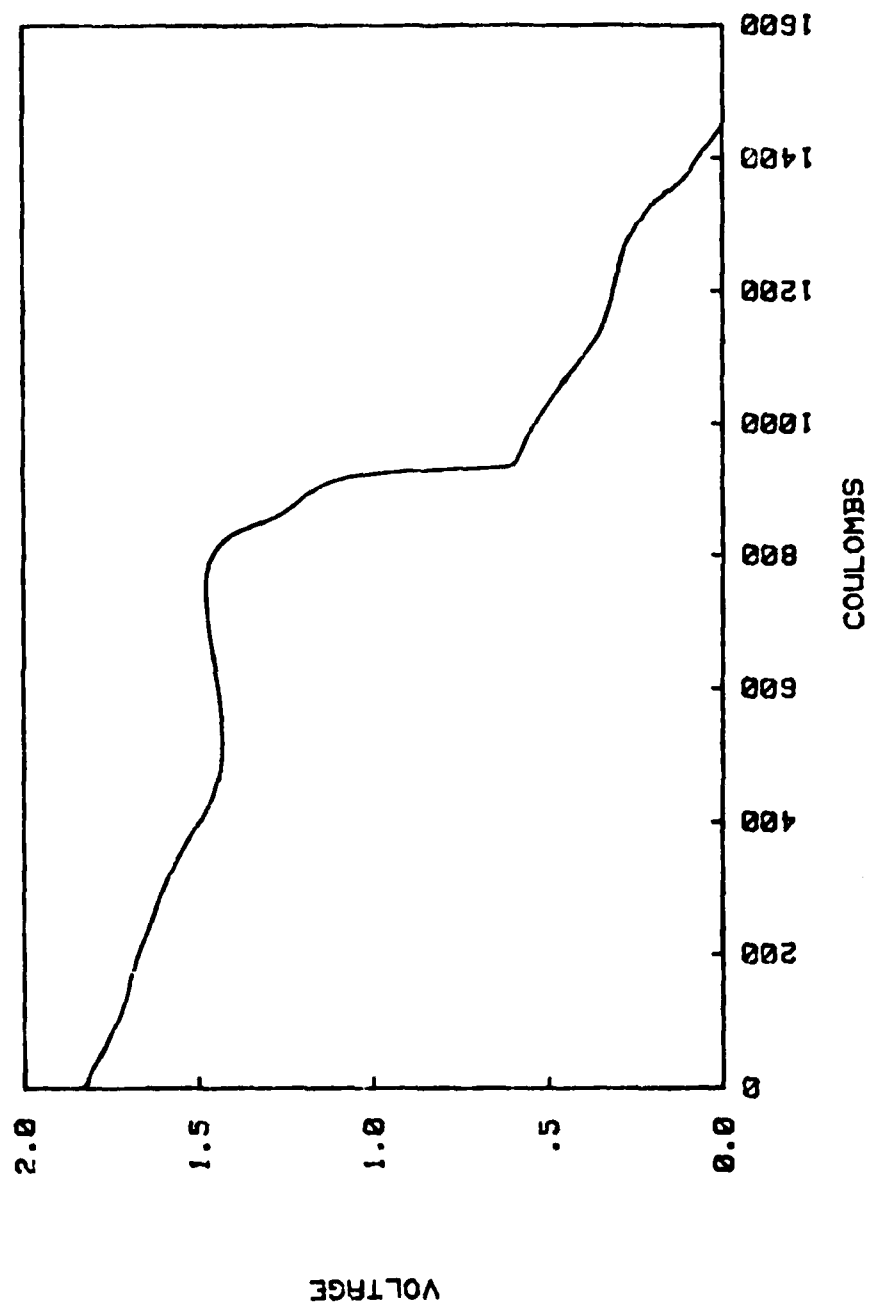


Figure 16. Discharge Curve for Cell Discharged at 15 mA/cm² and 275°C.

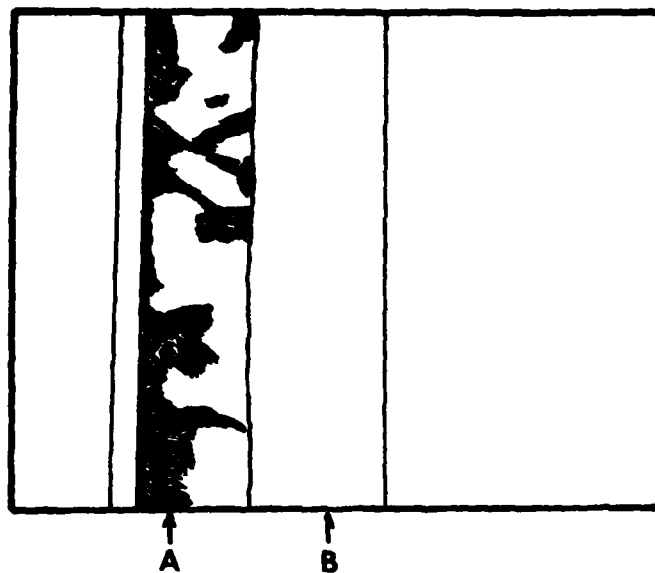


Figure 17. Depiction of Cell Discharged at 15 mA/cm^2 and 275°C to 0 Volt. A-Penetration of Separator; B-Coarse-grained Copper Deposit.

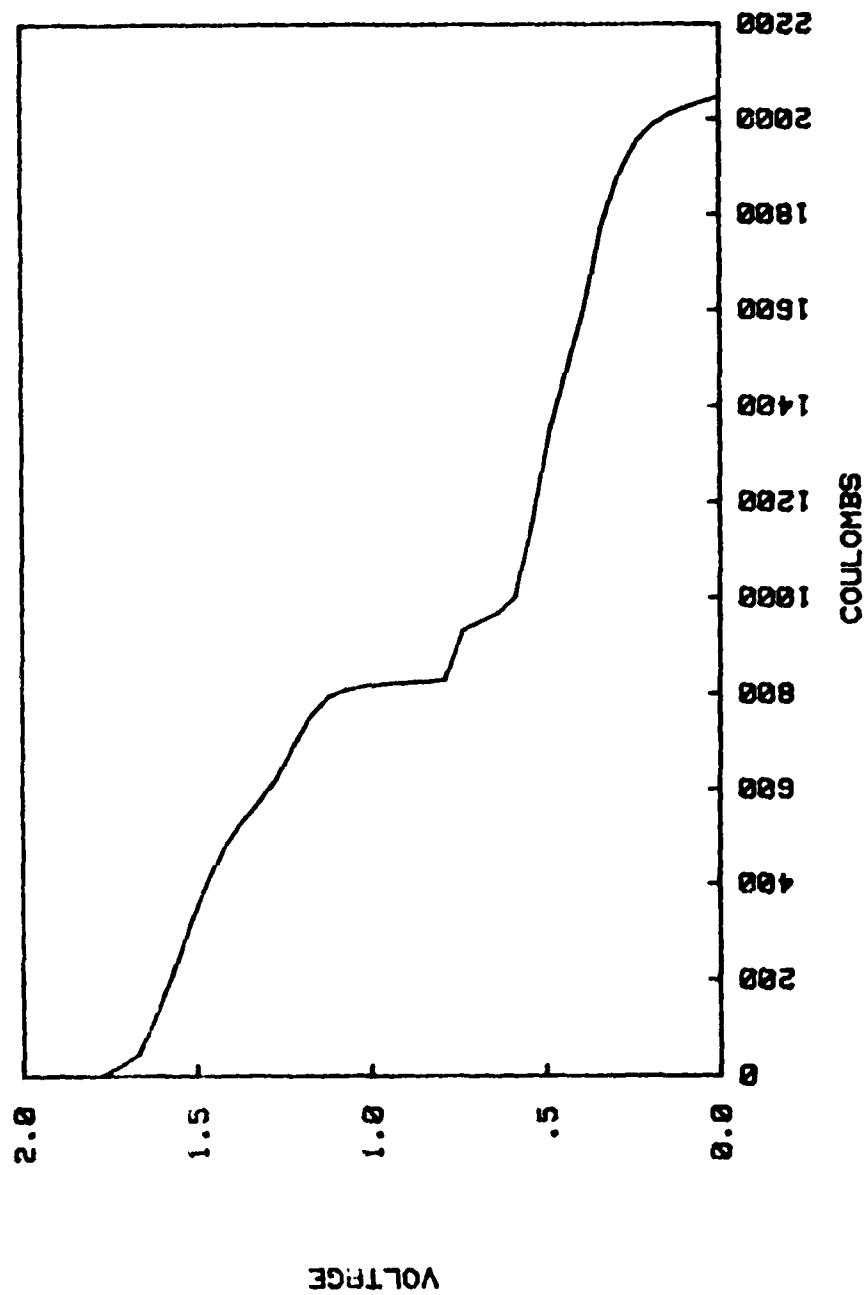


Figure 18. Discharge Curve for Cell Discharged at 15 mA/cm^2 and 200°C .

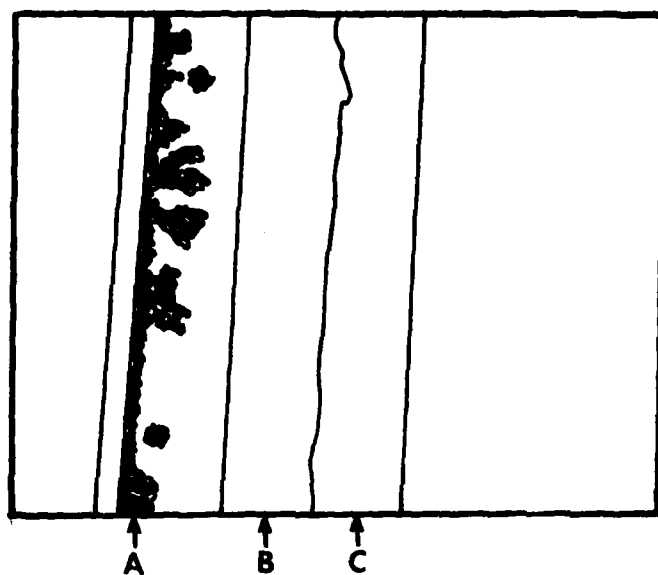


Figure 19. Depiction of Cell Discharged at 15 mA/cm^2 and 200°C to 0 Volt. A-Penetration of Separator; B-Fine-grained Copper Deposit; C-Coarse-grained Copper Deposit.

The photomicroscopy results confirm the assumed two-step cell reaction. There is a transport of material across the separator, the cell reaction occurs at the separator-cathode interface, and proceeds across the cathode.

CONCLUSIONS

Table II is an attempt to compare the chloroaluminate thermal cells with the low temperature systems studied by the laboratories cited at the beginning of this report.

TABLE II. Comparison of Low Temperature Thermal Battery Systems

SYSTEM	TEMP (°C)	VOLTAGE (V)	CURRENT		ENERGY ^a
			DENSITY	LIFETIME ^a	DENSITY
			(mA/cm ²)	(min)	(Wh/kg)
Thiocyanate	100-250	1.25 (PV)	5	-	-
Nitrate	300	2.8 (OCV)	10	45(75%)	131(75%)
Chloroaluminate	200	1.8 (OCV)	15	143(75%)	100(75%)
				138(80%)	96(80%)

a. values in parentheses refer to percentage of initial voltage

The thiocyanate system is hard to compare to the other two systems because the system was tested in two-cell batteries. The per cell voltage and current density would indicate the thiocyanate is inferior to the other two systems. The nitrate system operated at a higher voltage and lower current density than the chloroaluminate system, but the useful lifetime of the chloroaluminate cells was more than 3 times longer than the nitrate cells.

The chloroaluminate system is the most fully developed low temperature thermal battery system. While the system does have limitations with respect to storage and current capability, it has demonstrated very long operational lifetimes in single cells. The chloroaluminate system should be competitive for those applications in which moderate currents can be tolerated but long lifetimes are required.

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