

FINAL REPORT

DEVELOPMENT OF HIGH ENERGY DENSITY  
PRIMARY BATTERIES

by

S. G. Abens, W. C. Merz, and C. R. Walk

prepared for

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22 June 1965 to 21 March 1967

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## DEVELOPMENT OF HIGH ENERGY DENSITY PRIMARY BATTERIES

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### ABSTRACT

Studies of the  $\text{CuF}_2$ -Li system for the development of high energy density primary batteries were undertaken. The solubility of  $\text{CuF}_2$  in  $\text{LiClO}_4$  electrolytes increased with increasing water content. Solubility was reduced by replacing  $\text{Li}^+$  with  $\text{Na}^+$  or  $\text{K}^+$  in  $\text{PF}_6^-$  and  $\text{AsF}_6^-$  electrolytes.  $\text{CuF}_2$  reduction efficiency of over 70% at  $0.5 \text{ mA/cm}^2$  was obtained with  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{NaClO}_4$ ,  $\text{NaAsF}_6$ , and  $\text{KAsF}_6$  solutes in propylene carbonate.  $\text{CuF}_2$ -Li cells with methyl formate- $\text{LiClO}_4$  electrolyte were discharged with 60 - 70% cathodic efficiency at  $10 - 20 \text{ mA/cm}^2$ . With  $\text{LiClO}_4$ -propylene carbonate electrolyte, wet shelf life of four weeks was obtained at  $-15^\circ\text{C}$ .



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## SUMMARY

The purpose of this program was to develop high energy density primary batteries. Studies of electrode and electrolyte materials and evaluation of electrode and cell construction methods were undertaken.

### A. Low Rate Battery Study

Work was performed toward development of batteries capable of 200 wh/lb at the 100 - 1000 hour discharge rate. The system of main interest indicated by earlier work was the  $\text{CuF}_2$ -Li couple with  $\text{LiClO}_4$ -propylene carbonate (PC) electrolyte.

#### 1. Electrolyte Studies

Studies of solvent purification, and stability of electrolytes to lithium and  $\text{CuF}_2$  attack were performed. Most of the work was performed with the  $\text{LiClO}_4$ -PC electrolyte system.

(a) Solvent Purification. Solvents were purified by fractional distillation, and/or by lithium powder treatment followed by redistillation. Water content of solvents could be substantially reduced by fractional distillation, but no changes in physical properties between fractions were detected (PC and butyrolactone were studied). With lithium powder treatment, water content could be reduced to below 20 ppm (limit of Karl Fischer test sensitivity).

(b) Lithium Stability Tests. Reduction of water content in  $\text{LiClO}_4$ -PC and  $\text{LiClO}_4$ -BL (butyrolactone) electrolytes from 1000 - 2000 ppm to 200 - 400 ppm and increase of  $\text{LiClO}_4$  concentration from 2.3 to 4.7M improved lithium stability. Of other solutes in PC,  $\text{LiBF}_4$  gave best stability. Potassium and sodium compounds showed more discoloration than their lithium counterparts. Among solvents studied, purified PC and DMSO gave best results.

(c)  $\text{CuF}_2$  Stability Tests. Increasing  $\text{H}_2\text{O}$  content and  $\text{LiClO}_4$  concentration increased the rate of dissolution of  $\text{CuF}_2$  into PC and BL electrolytes. Copper fluoride was less soluble in solutions of K- and Na- salts in PC than in Li-salt electrolytes. With  $\text{KAsF}_6$  solute, DMSO gave the highest  $\text{CuF}_2$  solubility (>4400 ppm in 24 days), and PC and nitromethane (NM) the lowest ( $\sim$ 100 ppm in 24 days). Acetic anhydride (AA) reacted with  $\text{CuF}_2$ .

(d) Pulse Load Tests. Two-plate  $\text{CuF}_2$ -Li cells were discharged with pulse current in various electrolytes. Reference electrode readings showed capacity to be limited by  $\text{CuF}_2$  electrode polarization in all electrolytes tested. Reduction efficiencies of 64 and 54% were obtained in  $\text{LiClO}_4$ -PC and  $\text{LiAsF}_6$ -PC electrolytes, respectively. Other solvents (DMSO, AA, NDA [N-nitroso dimethylamine], NM, and MA) gave poorer results than PC.

## 2. Copper Fluoride Studies

Methods for removal of water from  $\text{CuF}_2$  were studied. Both vacuum oven drying and sweeping with dry argon produced  $\text{CuF}_2$  with water below 0.3% (sensitivity of X-ray analysis), but the latter method was faster. Heating of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  (major impurity) produced  $\text{CuOHF} \cdot \text{CuF}_2$  and  $\text{CuOHF}$  as well as a compound having a major peak intensity at 4.15 Å.

## 3. Experimental Cell Tests

Three-plate  $\text{CuF}_2$ -Li cells having a nominal cathode capacity of 4 - 5 AH were tested. The cells were considered positive limited, since Li capacity was ca. 8 AH. The working area of the cells was 29  $\text{cm}^2$ . Microporous rubber separations and heat sealed polyethylene envelopes were employed.

(a) Effect of  $\text{CuF}_2$  on Shelf Life. Wet shelf life of cells was improved by drying of the  $\text{CuF}_2$ . After four weeks stand at  $-15^\circ\text{C}$ , cathode utilization with dried  $\text{CuF}_2$  in two cells was 56 and 62% vs. 15 and 21% with the same material undried. Prolonged argon drying reduced capacity before and after wet stand. Use of thermally decomposed  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  instead of normal  $\text{CuF}_2$  improved wet stand considerably, but greatly increased cell polarization at 0.5  $\text{mA/cm}^2$ .

(b) Effect of Additives to  $\text{CuF}_2$ . Effect of  $\text{CoF}_3$ ,  $\text{MnF}_3$ , and  $\text{SbF}_3$  added to  $\text{CuF}_2$  (ca. 4 mol %) on shelf life was tested. Addition of  $\text{SbF}_3$  was detrimental while the other additives showed no effect.

(c) Copper Fluoride Electrode Construction. Most of the work was performed with filter-mat  $\text{CuF}_2$  electrodes. The optimum composition was in the range of 4 - 8g paper fiber and 8 - 20g graphite per 100g of  $\text{CuF}_2$ . Cathodic utilization with PC- $\text{LiClO}_4$  electrolyte was up to 80% at 0.5  $\text{mA/cm}^2$ . Vacuum impregnation of cells with electrolyte was not beneficial. Pasted electrodes

using polystyrene or cellulose acetate binder and carbon black conductor also gave  $\text{CuF}_2$  reduction efficiencies of 80% at 0.5 to 0.7 mA/cm<sup>2</sup>.

(d) Effect of Discharge Rate. The 3-plate  $\text{CuF}_2$ -Li cells were discharged thru various resistive loads. With 200 $\Omega$  load (ca. 250 hour rate), cathode efficiency was 73%. With 100 $\Omega$  (ca. 100 hour rate) the efficiency dropped to 58%, while with 500 and 1000 $\Omega$ , this figure was 47 and 24%, respectively (ca. 400 hour rate with both loads). The cells showed evidence of copper dissolution in the 500 and 1000 $\Omega$  discharge cells.

(e) Effect of  $\text{LiClO}_4$  Concentration. Capacity and shelf life of  $\text{CuF}_2$ -Li cells with 10 and 20g of  $\text{LiClO}_4$ /100 ml PC were tested. The lower electrolyte concentration gave improved wet shelf life at 0°C. (74 vs 59% efficiency after 10 days wet stand).

(f) Effect of Solute. Performance of  $\text{CuF}_2$ -Li cells using propylene carbonate solutions of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{KPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{KAsF}_6$ ,  $\text{NaAsF}_6$ , and  $\text{LiBF}_4$  was compared. Cathode efficiencies of over 70% were obtained with all solutes except  $\text{KPF}_6$  and  $\text{LiPF}_6$ .

(g) Effect of Solvent. Performance of  $\text{CuF}_2$ -Li cells with  $\text{LiClO}_4$  and  $\text{KAsF}_6$  solutions in PC, DMSO, AA, NDA, NM and MA (methyl acetate) was compared. In these discharges, only  $\text{LiClO}_4$ -PC electrolyte gave cathode efficiency of over 70%.

## B. High Rate Battery Study

Work was performed toward development of batteries capable of 50 wh/lb at the 1 hour rate and operable at the 1 - 10 hour rate. The system under study was the  $\text{CuF}_2$ -Li couple with  $\text{LiClO}_4$ -methyl formate (MF) electrolyte.

### 1. Electrolyte Studies

The solvents MF and MA were purified by lithium powder treatment and distillation. Lithium treatment improved stability of Li in the  $\text{LiClO}_4$ -MF electrolyte but showed no effect on  $\text{CuF}_2$  solubility in  $\text{LiClO}_4$ -MF and  $\text{LiClO}_4$ -MA electrolytes. Changes in  $\text{LiClO}_4$  concentration showed no effect on Li stability.

## 2. Positive Limited Cell Studies

Pasted  $\text{CuF}_2$  electrode composition was evaluated in 3-plate positive limited  $\text{CuF}_2$ -Li cells. One gram of cellulose acetate and 10 - 15 grams of graphite/100g of  $\text{CuF}_2$  was an optimum composition.  $\text{CuF}_2$  reduction efficiencies were 50 - 70% at 5 - 15  $\text{mA/cm}^2$  to a 2.0VF cut-off. Increasing electrode thickness from 0.025" to 0.050" decreased the efficiency. Electrodes having less than 0.5% water in the  $\text{CuF}_2$  could not be discharged at 10  $\text{mA/cm}^2$  in MF- $\text{LiClO}_4$  electrolyte.  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  gave equal performance to  $\text{CuF}_2$  having 2% water. Optimum electrolyte concentration was 50g  $\text{LiClO}_4$ /100 ml MF.

## 3. Seven-Plate Cell Tests

Three 7-plate  $\text{CuF}_2$ -Li cells with 4 - 5 AH nominal capacity were built and tested. Discharge performance was about equal to that obtained with 3-plate cells at the same current densities. To a cut-off of 2.0 volts, 67%  $\text{CuF}_2$  reduction was obtained at the 4 hour rate, and 69% at the 5 hour rate. One cell was tested after 4 weeks of dry storage under argon at room temperature and gave 58%  $\text{CuF}_2$  reduction at the 4 hour rate.

## 1. INTRODUCTION

The purpose of this program is development of high energy density primary batteries suitable for space flight applications.

High energy battery development was initiated at Livingston Electronic Laboratory in 1963 under Contract NAS 3-2775 and continued under Contract NAS 3-6004. The goal of these programs was to develop batteries capable of delivering 200 watt hours per pound, i. e.; to at least triple the energy density available with the existing state of the art.

On these earlier programs, the  $\text{CuF}_2\text{-Li}$  couple was identified as the most promising system. The high energy density potential of this system was demonstrated in laboratory cell discharge tests, where energy-to-weight ratios of over 500 wh/lb of active material weight and over 200 wh/lb of cell weight were obtained. The most difficult problem associated with the  $\text{CuF}_2\text{-Li}$  system was its almost total lack of wet stand capability at room temperature.

The present report describes work performed under Contract NAS 3-7632, which is a direct continuation of the two previous contracts. Development of two types of batteries was pursued, namely: (1) batteries operating at the 100 - 1000 hour discharge rate, and (2) batteries capable of being discharged at the 1 - 10 hour rate.

For the low rate system the major effort was expended toward identification of causes for lack of wet stand capability in  $\text{CuF}_2\text{-Li}$  cells, and on efforts to make improvements in this area. For the high rate battery, the major portion of the work was expended toward increasing the discharge rate capability of the  $\text{CuF}_2\text{-Li}$  system.

## 2. LOW RATE BATTERY STUDY

### 2. 1. Electrolyte Studies

The purpose of the electrolyte studies pursued under this phase of the contract was to identify solvents and solutes best suited for a long life  $\text{CuF}_2\text{-Li}$  cell. The candidate solvents of primary interest identified by previous work, were butyrolactone and propylene carbonate. With the latter solvent, good test cell performance had been obtained.

The solute of primary interest from results of previous work was  $\text{LiClO}_4$ . Other electrolyte systems were studied in later phases of the program to search for electrolytes which would enhance wet shelf life of the  $\text{CuF}_2\text{-Li}$  couple.

#### 2. 1. 1. Solvent Purification

The general approach to solvent purification under this contract was as follows:

1. The highest purity level materials obtainable were analyzed for water by Karl Fischer titration.
2. The solvents were agitated with lithium powder dispersion in hexane until no rise in pressure in the containers could be observed.
3. The liquids were filtered and batch distilled, usually at lowered pressure.

Some modifications to the above procedure were used for investigative purposes, or where required by presence of high water concentration. In this case, lithium treatment was preceded by distillation or by chemical drying, usually by calcium oxide, or dolomitic lime (50%  $\text{CaO}$ , 50%  $\text{MgO}$ ).

2. 1. 1. 1. Distillation of "As Received" Butyrolactone and Propylene Carbonate.

Butyrolactone was batch distilled under reduced pressure thru a Vigraux column. Four fractions of the distillate were taken off, and analyses were performed with results as shown below:

TABLE I

DISTILLATION OF BUTYROLACTONE

Source: Matheson, Coleman & Bell  
Pressure: 17 mm Hg

	<u>Initial</u>	<u>Fractions</u>			
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Volume, cc	250	99	103	43	5
Boiling Range, °C	---	89	89-90	90-92	92+
Color	White	White	White	White	Brown
Refractive Index	1.433	1.434	1.434	1.434	---
Water, ppm	510	180	140	390	---

Propylene carbonate from the same source was distilled similarly, and results of two runs were as shown in Table II, page 4.

The sensitivity of the analyses performed was too low to yield any indication that the distillate fractions differed in any way except water content. Variations in temperature during distillation were probably caused by malfunctioning of the pressure regulator.

The total water recovered was always less than in the original solvent indicating that all of the water was not condensed. The water content appears to be high in the initial portion of the distillate, although high water was also observed in the last 20% in distillation of butyrolactone. These results indicated that the rejection of the first and last 10% of the distillate should be adequate.



TABLE II

DISTILLATION OF PROPYLENE CARBONATE

Source: Matheson, Coleman & Bell  
 Pressure: 10 mm Hg

Run No. 1

	<u>Initial</u>	<u>FRACTIONS</u>			
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Volume, cc	250	100	110	35	5
Boiling Range, °C	---	108	107	106	---
Color	White	White	White	White	Brown
Refractive Index	1.420	1.420	1.422	1.422	---
Water, ppm	580	120	140	180	---

Run No. 2

Volume, cc	230	25	200	5	---
Boiling Range, °C	---	107	107	---	---
Color	White	White	White	Reddish Yellow	---
Refractive Index	1.420	1.420	1.422	---	---
Water, ppm	580	380	120	---	---

2. 1. 1. 2.          Distillation of Lithium Treated Butyrolactone and  
Propylene Carbonate.

The method of agitating a solvent in the presence of lithium metal as a means of reducing trace water concentration and decomposing other possible impurities which would otherwise tend to attack the lithium electrode of the cell was studied extensively on this program. In this test, the solvents were agitated at room temperature with 1.0g of Li powder/100 grams of solvent in sealed containers. The pressure generated in the containers was relieved periodically, and agitation was continued until no additional pressure build-up was observed. The water content of the solvents was monitored at various intervals by the Karl Fischer analysis, and the results are presented in Table III.

TABLE III

RATE OF WATER REMOVAL IN PROPYLENE CARBONATE AND BUTYROLACTONE

<u>Butyrolactone</u>		<u>Propylene Carbonate</u>	
<u>Agitation time, Hrs.</u>	<u>Water Content, ppm</u>	<u>Agitation time, Hrs.</u>	<u>Water Content, ppm</u>
0	470	0	270
6	280	5	140
15	140	17	50*
27	40*	30	23**
50	23**		

\*No further pressure build-up.

\*\*Limit of K. F. analysis sensitivity.

The excess powdered lithium and the solid reaction products were removed by vacuum filtration through a fine gas washing tube. The insoluble decomposition products had the appearance of a gray, gelatinous mass, and gravitated to the bottom of the liquid phase (the powdered lithium floats). After removal of the decomposition products and excess powdered lithium, the solvents were vacuum distilled, and the fractions were analyzed.

Results of typical distillation runs for butyrolactone and propylene carbonate are presented in Tables IV and V. The lithium treatment had caused no observable change in the system; i. e.; the physical behaviour of the treated solvents upon distillation was not significantly different from that of the untreated material. The only difference in behaviour which could be observed for the Li treated material was a brief period of effervescence at the beginning of the vacuum distillation (possibly caused by the release of dissolved hydrogen).

These tests showed that solvents having very low water contents (below 20 ppm) can be produced by the lithium treatment and vacuum distillation method.

TABLE IV

VACUUM DISTILLATION OF LITHIUM-TREATED BUTYROLACTONE

	<u>Boiling Range</u>		<u>Percent Volume</u>	<u>Water, ppm</u>	<u>Color</u>
	<u>°C</u>	<u>mm Hg</u>			
Undistilled	---	---	100	23*	Off White
Forerun	21-50	8	0	----	Gas
Fraction I	68-72	8-10	4.2	1400	White
Fraction II	79-80	10	89.9	23*	White
Fraction III	---	---	5.9	----	Brown liquid Gray solids

TABLE V

VACUUM DISTILLATION OF LITHIUM-TREATED PROPYLENE CARBONATE

	<u>Boiling Range</u>		<u>Percent Volume</u>	<u>Water, ppm</u>	<u>Color</u>
	<u>°C</u>	<u>mm Hg</u>			
Undistilled	---	----	100	23*	Off White
Forerun	23-50	10-15	0	----	Gas
Fraction I	96-108	6-10	7.4	230	White
Fraction II	106-108	10	89.3	23*	White
Fraction III	---	----	3.3	----	Brown liquid Gray solids

\* Limit of sensitivity.

## 2. 1. 2. Lithium Stability Tests

The rate of attack on a Li test strip immersed in a solvent or an electrolyte solution was employed as a qualitative measure for the suitability of a candidate electrolyte for use in  $\text{CuF}_2$ -Li cells. While this method yields no quantitative measure of the rate and nature of the lithium decomposition reactions, it is direct and simple, and does indicate which electrolytes have good stability (i. e.; show no visible changes).

### 2. 1. 2. 1. Effect of Water Content

The effect of water contamination level on the stability of lithium samples in BL and PC and in  $\text{LiClO}_4$  solutions in the same solvents was observed by performing a comparative test on several materials at room temperature. Each of the two solvents was used with two water contamination levels (2000 and 390 ppm for butyrolactone, 710 and 180 ppm for propylene carbonate). The lithium perchlorate water content after vacuum drying was about 0.04 percent (400 ppm). The lithium test piece was a ribbon,  $1/2 \times 1/16 \times 1''$ , which had the petrolatum used for protection during storage removed by rinsing with heptane. One side of each strip was abraded before immersion to expose fresh metal. Tests were assembled under argon.

The detrimental effect of water on the stability of lithium in these solvents was clearly demonstrated by the more rapid discoloration of lithium in the higher water content solutions, but the presence of  $\text{LiClO}_4$  appeared to be beneficial. It would appear, therefore, that presence of  $\text{Li}^+$  ions has a stabilizing effect on lithium in BL and PC electrolytes.

Visual observations made during the stability test are listed in the Appendix, Tables A-1 and A-11.

### 2. 1. 2. 2. Effect of Treatment With Lithium Dispersion

A stability test similar to that described above was assembled to study the effect of pretreatment of propylene carbonate with powdered lithium dispersion. The untreated solvent was distilled at 10 mm Hg, and the water content was ascertained to be below 25 ppm. A portion of this solvent was retained, and the remainder was agitated for 40 hours with powdered lithium, filtered, and redistilled. Lithium test strips were cut to size  $1 \times 1/2 \times 1/16$  inch, and one side of each strip was abraded to expose fresh metal. The strips were then placed in test tubes containing 5 ml of solvent or

1M LiClO<sub>4</sub> solution under argon. The tubes were sealed and stored at 35°C, and the appearance of the lithium samples was recorded periodically.

In both lithium treated and untreated solvents, presence of 1M LiClO<sub>4</sub> enhanced chemical stability. In the solvent containing no solute, lithium treatment appeared to improve stability, but this could also be a result of a lower water contamination level, since additional drying probably occurs during lithium treatment. In the 1M LiClO<sub>4</sub> solutions, the stability was not significantly different with the treated and untreated solvents, indicating that impurities which are not removed by distillation are not particularly reactive with metallic lithium. However, lithium treatment was later used in the preparation of PC electrolytes for cell tests, since this procedure reduces water contamination levels effectively for solvents having high initial water content.

Observations made during these lithium compatibility tests are listed in the Appendix, Table A-3, page 123.

#### 2. 1. 2. 3. Effect of Other Solutes in Propylene Carbonate

The effect of a number of solutes on the stability of lithium in propylene carbonate solutions was evaluated. Some of the solutions in this test series were prepared by reaction between a perchlorate and a potassium salt, resulting in precipitation of potassium perchlorate. These solutions, therefore, were saturated with KClO<sub>4</sub> and are identified with the suffix (m).

Lithium stability tests were assembled as described above. The concentration of the electrolyte solutions was 1 mol of solute/liter of solvent, except where indicated otherwise. Propylene carbonate was lithium treated and distilled, and all salts were vacuum dried before preparation of solutions.

The electrolytes included in this test series, and their water contents (ppm) as determined by Karl Fischer analyses were as follows: LiClO<sub>4</sub>, 90; NaClO<sub>4</sub>, 72; KPF<sub>6</sub>, 97; KAsF<sub>6</sub>, 61; KBF<sub>4</sub>,<sup>1</sup> 97; LiBF<sub>4</sub>(m),<sup>2</sup> 169; LiPF<sub>6</sub>(m), 104; LiAsF<sub>6</sub>(m), 258; NaAsF<sub>6</sub>(m), 161; and LiBF<sub>4</sub>, 129.

After an exposure time of four weeks at 35°C, the lithium tetrafluoroborate solution was adjudged the most stable electrolyte. No change in appearance of test strip or solution could be observed. Lithium perchlorate caused dulling of lithium surfaces after 21 days of exposure.

All of the anions used in this test series (ClO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>) have good stability to lithium and differences in apparent rate of attack are probably due to varying levels of impurities and water content. However,

<sup>1</sup> Saturated.

<sup>2</sup> Metathetically prepared.

of the three cations ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ), lithium definitely shows the least amount of activity. Potassium electrolytes always gave a characteristic blackening of the lithium, particularly near and slightly above the liquid surface. No other evidence of chemical activity accompanied this phenomenon - the solutions remained clear. The darkening may thus be just a physical change (amorphization) of the lithium surface, although the difference in potential between potassium and lithium in some electrolytes may be sufficient to cause the displacement reaction to take place.

The sodium electrolyte gave a yellowish (organic) growth on the lithium, and some precipitate was formed in the tubes. Thus it would appear that sodium catalyzes some PC decomposition reaction on the metal surface.

Photographs taken of the best stability tests after 28 days of exposure are shown in Figure 1, page 10, while a complete description of visual observations is given in the Appendix, Table A-4, page 124.

#### 2. 1. 2. 4. Effect of Solvent

In this lithium stability test series, propylene carbonate (PC), dimethylsulfoxide (DMSO), acetic anhydride (AA), N-nitroso dimethylamine (NDA), and nitromethane (NM) were evaluated. The solutes selected for these tests were  $\text{LiClO}_4$  and  $\text{KAsF}_6$ .

About equal stability was indicated with both solutes, except for the characteristic darkening of the lithium surface observed in the  $\text{KAsF}_6$  electrolyte. Propylene carbonate and DMSO gave the least amount of evidence of reaction, while nitromethane was decomposing rapidly, especially in the presence of  $\text{LiClO}_4$ .

Photographs of the above tests taken after 21 days of exposure at  $35^\circ\text{C}$  are presented in Figure 2, page 11, while a verbal description of the appearance of the samples after 7, 14, and 21 days of stand are given in the Appendix, Table A-5, page 125.

#### 2. 1. 3. $\text{CuF}_2$ Stability Tests

A necessary requirement for electrolytes used in  $\text{CuF}_2$ -Li cells is their chemical compatibility with the positive and negative active materials. To evaluate the stability of  $\text{CuF}_2$  in the electrolyte, it was decided to use a test for dissolved copper as the stability criterion.

Effect of Solute on Lithium Stability

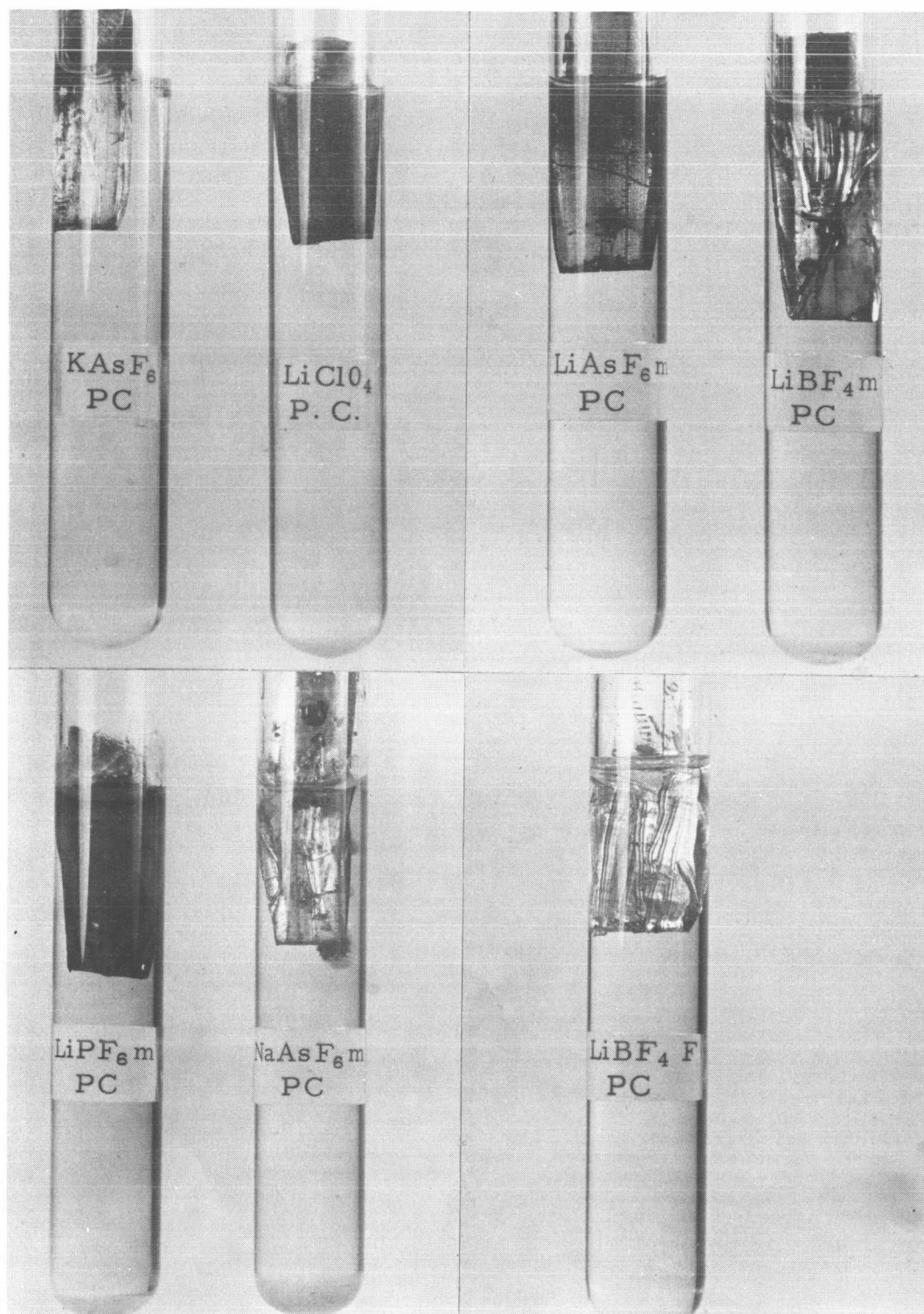


Fig. 1

Effect of Solvent on Lithium Stability

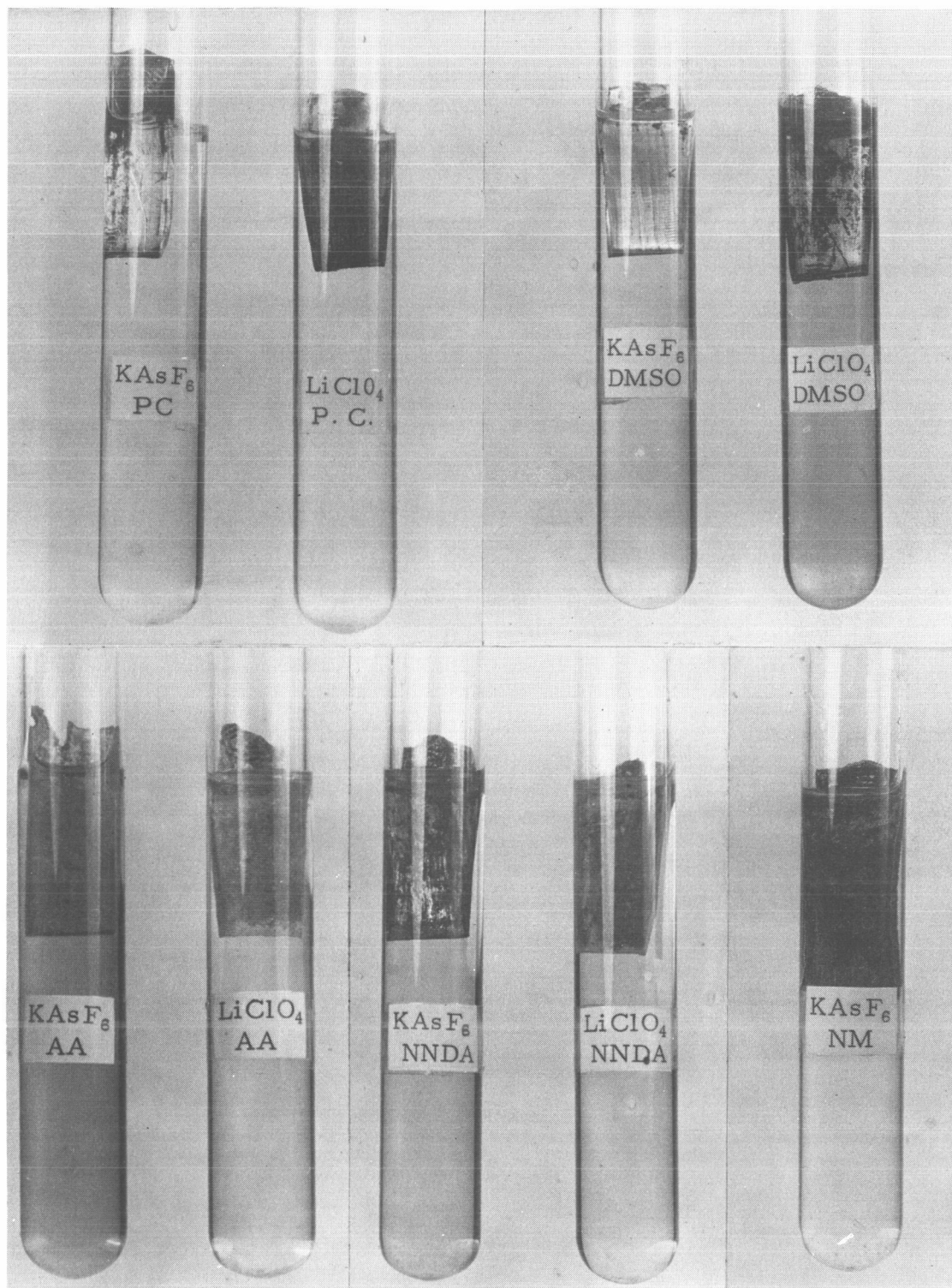


Fig. 2



### 2. 1. 3. 1. Effect of Water and Solute Concentration

A series of  $\text{CuF}_2$  solubility tests were performed in PC and BL with  $\text{LiClO}_4$  as the solute. The solvents were prepared by agitating with excess amounts of lithium powder until no further hydrogen pressure was produced; at this point, the residual water in both solvents was below the sensitivity of the Karl Fischer test (20 ppm). The lithium treatment was followed by distillation, rejecting the first and last 10 volume percent of the distillate.

The lithium perchlorate used in these tests was vacuum-dried at  $110^\circ\text{C}$  for 24 hours, and water content (Karl Fischer analysis) was approximately 600 ppm. Anhydrous  $\text{CuF}_2$  was used as received from Ozark-Mahoning Company. X-ray analysis showed the water level in this material to be about 0.33 percent (3300 ppm).

Serum bottles (60 ml volume) equipped with hermetic stoppers were filled with 40 ml of solvent, 1.0g of  $\text{CuF}_2$ , and 4.0, 8.0, or 12.0 grams of  $\text{LiClO}_4$ . Distilled water was added to the bottles in quantities calculated to produce total water contents in the range of 150 to 5000 ppm. The samples were agitated on a laboratory shaker with interruptions timed to allow the solid phase to settle. The samples were then compared for color, and the concentration of  $\text{Cu}^{++}$  in solution was determined by the thiosulphate titration. To minimize the effect of changes in laboratory temperature, all compatibility tests were performed concurrently.

Results of the copper ion determinations and the observed solution colors are listed in Tables VI and VII, pages 13 and 16. At equal  $\text{LiClO}_4$  concentration, increasing water content increased the copper concentration in the solution. For example, increasing water content from 180 ppm to 5000 ppm increased the copper concentration after 1000 hours of agitation from 710 ppm to 7300 ppm. The effect of  $\text{LiClO}_4$  on the solubility of  $\text{CuF}_2$  was much less pronounced than that of water contamination level. The solubility of  $\text{CuF}_2$  was found to be larger in butyrolactone than in propylene carbonate electrolytes.

The above results further demonstrate the need for very low water concentration in the  $\text{CuF}_2$ -Li system in order to minimize loss of capacity during wet shelf life of the cells. The solubility tests may prove of value for evaluation of  $\text{CuF}_2$  drying methods, since the X-ray examination is of limited utility where low water contents are encountered. To make this approach practical, a method for decreasing the time required for the analysis would have to be developed.

TABLE VI

SOLUBILITY OF  $\text{CuF}_2$  IN PROPYLENE CARBONATE ELECTROLYTE

Materials: Propylene Carbonate, MC & B, Li dried and distilled;  
 $\text{H}_2\text{O}$  <20 ppm.  
Lithium Perchlorate, Foote Mineral Co., vacuum dried  
at  $110^\circ\text{C}$  for 24 hours;  $\text{H}_2\text{O}$  = 600 ppm.  
Cupric Fluoride, Ozark Mahoning Co., as received;  
 $\text{H}_2\text{O}$  = 3300 ppm.

Series A - 10 gm.  $\text{LiClO}_4$ /100 ml PC; Solution Density = 1.25 gm/ml.

<u>Water Content, ppm</u>	<u>Agitation Time, Hours</u>	<u>Copper (II) Concentration</u>		<u>Solution Color</u>
		<u><math>\mu</math> moles/ml</u>	<u>ppm</u>	
120	25	2.5	125	Off White
	125	6.6	335	Off White
	290	7.0	335	Off White
	650	12.5	635	Light Tan
	1000	12.5	635	Tan
400	25	5.5	280	Off White
	125	7.0	355	Off White
	290	11.5	585	Off White
	650	14.2	720	Light Tan
	1000	15.0	765	Tan
810	25	6.0	305	Off White
	125	11.0	560	Off White
	290	15.7	800	Off White
	650	20.0	1015	Light Yellow Green
	1000	25.0	1270	Yellow Green
2200	25	18.0	915	Light Green
	125	32.5	1650	Light Green
	290	40.0	2030	Olive Green
	650	40.0	2030	Olive Green
	1000	52.0	2640	Olive Green
6050	25	101	5100	Blue Green
	125	113	5750	Green
	290	118	6000	Green
	650	145	7400	Green
	1000	175	8900	Green

TABLE VI (Continued)

SOLUBILITY OF CuF<sub>2</sub> IN PROPYLENE CARBONATE ELECTROLYTE

Materials: Propylene Carbonate, MC & B, Li dried and distilled;  
 H<sub>2</sub>O < 20 ppm.  
 Lithium Perchlorate, Foote Mineral Co., vacuum dried  
 at 110°C for 24 hours; H<sub>2</sub>O = 600 ppm.  
 Cupric Fluoride, Ozark Mahoning Co., as received;  
 H<sub>2</sub>O = 3300 ppm.

Series B - 20 gm. LiClO<sub>4</sub>/100 ml PC; Solution Density = 1.30 gm/ml.

<u>Water Content, ppm</u>	<u>Agitation Time, Hours</u>	<u>Copper (II) Concentration</u>		<u>Solution Color</u>
		<u>μ moles/ml</u>	<u>ppm</u>	
150	25	4.6	224	Off White
	125	6.2	303	Off White
	290	6.5	317	Off White
	650	12.5	610	Light Tan
	1000	13.0	635	Light Tan
430	25	5.0	245	Off White
	125	6.8	333	Off White
	290	99.5	465	Off White
	650	17.5	855	Tan
	1000	17.0	830	Tan
960	25	4.7	230	Off White
	125	8.5	416	Off White
	290	15.6	765	Off White
	650	25.0	1220	Olive Yellow
	1000	24.5	1200	Olive Yellow
1760	25	4.8	235	Off White
	125	24.6	1210	Very Light Green
	290	36	1770	Light Green
	650	39.0	1900	Olive Green
	1000	38.8	1890	Olive Green
4960	25	32	1570	Light Blue Green
	125	90	4400	Green
	290	100	4890	Green
	650	135	6600	Green
	1000	135	6600	Green

TABLE VI (Continued)

SOLUBILITY OF CuF<sub>2</sub> IN PROPYLENE CARBONATE ELECTROLYTE

Materials: Propylene Carbonate, MC & B, Li dried and distilled;  
 H<sub>2</sub>O < 20 ppm.  
 Lithium Perchlorate, Foote Mineral Co., vacuum dried  
 at 110°C for 24 hours; H<sub>2</sub>O = 600 ppm.  
 Cupric Fluoride, Ozark Mahoning Co., as received;  
 H<sub>2</sub>O = 3300 ppm.

Series C - 30 gm. LiClO<sub>4</sub>/100 ml PC; Solution density = 1.30 gm/ml.

Water Content ppm	Agitation Time, Hours	Copper (II) Concentration		Solution Color
		$\mu$ moles/ml	ppm	
180	25	4.9	232	Off White
	125	7.8	370	Off White
	290	9.4	446	Off White
	650	15.5	735	Light Tan
	1000	15.0	710	Light Tan
430	25	4.5	214	Off White
	125	7.8	370	Off White
	290	11.0	525	Off White
	650	17.5	830	Tan
	1000	17.5	830	Tan
980	25	4.5	214	Off White
	125	9.4	446	Off White
	290	15.5	740	Very Light Green
	650	25.0	1185	Olive Yellow
	1000	24.5	1160	Olive Yellow
2000	25	5.2	247	Off White
	125	32.0	1530	Very Light Green
	290	29.0	1860	Light Green
	650	50.0	2370	Olive Green
	1000	49.0	2320	Olive Green
5000	25	70	3330	Light Green
	125	104	5000	Green
	290	121	5800	Green
	650	155	7300	Green
	1000	155	7300	Green

TABLE VII

SOLUBILITY OF CuF<sub>2</sub> IN BUTYROLACTONE ELECTROLYTE

Materials: Butyrolactone, MC & B, Li dried and distilled;  
H<sub>2</sub>O < 20 ppm.  
Lithium Perchlorate, Foote Mineral Co., vacuum dried  
at 110°C for 24 hours; H<sub>2</sub>O = 600 ppm.  
Cupric Fluoride, Ozark Mahoning Co., as received;  
H<sub>2</sub>O = 3300 ppm.

Series A - 10 gm. LiClO<sub>4</sub>/100 ml BL; Solution Density = 1.18 gm/ml.

<u>Water Content, ppm</u>	<u>Agitation Time, Hours</u>	<u>Copper (II) Concentration</u>		<u>Solution Color</u>
		<u>μ moles/ml</u>	<u>ppm</u>	
120	25	5.9	305	Off White
	125	8.4	435	Off White
	290	12.6	655	Pale Yellow
	650	14.7	790	Yellow Green
	1000	14.5	780	Yellow Green
430	25	4.0	215	Off White
	125	4.5	240	Off White
	290	10.0	540	Pale Yellow
	650	14.0	755	Yellow Green
	1000	18.5	995	Light Olive
850	25	5.0	270	Off White
	125	8.8	475	Very Light Green
	290	17.9	965	Light Yellow Green
	650	22.7	1220	Yellow Green
	1000	29.0	1560	Olive
2340	25	18.0	970	Light Green
	125	31.0	1670	Green
	290	53.0	2850	Green
	650	90	4850	Green
	1000	115	6180	Green
6440	25	113	6100	Blue Green
	125	125	6730	Blue Green
	290	162	8700	Dark Green
	650	226	12200	Emerald Green
	1000	285	15300	Emerald Green

TABLE VII (Continued)

SOLUBILITY OF CuF<sub>2</sub> IN BUTYROLACTONE ELECTROLYTE

Materials: Butyrolactone, MC & B, Li Dried and Distilled;  
 H<sub>2</sub>O < 20 ppm.  
 Lithium Perchlorate, Foote Mineral Co., vacuum dried  
 at 110°C for 24 hours; H<sub>2</sub>O - 600 ppm.  
 Cupric Fluoride, Ozark Mahoning Co., as received;  
 H<sub>2</sub>O = 3300 ppm.

Series B - 20gm. LiClO<sub>4</sub>/100 ml BL; Solution Density = 1.22 gm/ml.

<u>Water Content, ppm</u>	<u>Agitation Time, Hours</u>	<u>Copper (II) Concentration</u>		<u>Solution Color</u>
		<u>μ moles/ml</u>	<u>ppm</u>	
160	25	4.8	250	Off White
	125	8.0	415	Pale Yellow
	290	15.0	785	Yellow Green
	650	21.4	1115	Olive Yellow
	1000	24.0	1250	Olive Yellow
460	25	5.6	290	Pale Yellow
	125	10.8	565	Pale Yellow Green
	290	21.2	1105	Yellow Green
	650	34.5	1800	Olive
	1000	40.5	2110	Olive
1020	25	8.0	415	Pale Yellow
	125	16.8	875	Yellow Green
	290	38.0	1980	Green
	650	60.0	3120	Olive Green
	1000	68.0	3540	Olive Green
1870	25	12.8	665	Pale Green
	125	54	2810	Green
	290	75.0	3910	Dark Green
	650	76.0	3960	Dark Green
	1000	120	6250	Dark Green
5260	25	73	3800	Green
	125	165	8600	Emerald Green
	290	230	12000	Emerald Green
	650	235	12200	Emerald Green
	1000	240	12500	Dark Emerald Green

TABLE VII (Continued)

SOLUBILITY OF  $\text{CuF}_2$  IN BUTYROLACTONE ELECTROLYTE

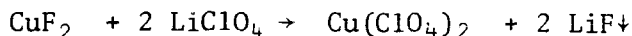
Materials: Butyrolactone, MC & B, Li dried and distilled;  
 $\text{H}_2\text{O} < 20$  ppm.  
 Lithium Perchlorate, Foote Mineral Co., vacuum dried  
 at  $110^\circ\text{C}$  for 24 hours;  $\text{H}_2\text{O} = 600$  ppm.  
 Cupric Fluoride, Ozark Mahoning Co., as received;  
 $\text{H}_2\text{O} = 3300$  ppm.

Series C - 30gm.  $\text{LiClO}_4/100$  ml BL; Solution Density = 1.27 gm/ml.

<u>Water Content, ppm</u>	<u>Agitation Time, Hours</u>	<u>Copper (II) Concentration</u>		<u>Solution Color</u>
		<u><math>\mu</math> moles/ml</u>	<u>ppm</u>	
190	25	6.5	325	Pale Yellow
	125	10.9	545	Pale Yellow Green
	290	16.0	800	Yellow Green
	650	24.0	1200	Olive
	1000	27.5	1375	Olive
460	25	7.2	360	Light Yellow Green
	125	12.8	640	Light Yellow Green
	290	21.6	1080	Yellow Green
	650	27.0	1350	Olive Green
	1000	43.0	2150	Olive Green
1040	25	9.3	465	Light Yellow Green
	125	23.6	1180	Light Green
	290	39.0	1960	Green
	650	50.0	2500	Olive Green
	1000	84.0	4200	Dark Olive Green
2100	25	16.9	845	Yellow Green
	125	70	3500	Green
	290	79.0	3960	Dark Green
	650	89.5	4480	Dark Green
	1000	135	6750	Dark Green
5250	25	64	3200	Green
	125	177	8860	Emerald Green
	290	215	10750	Emerald Green
	650	250	12500	Dark Emerald Green
	1000	250	12500	Dark Emerald Green

### 2. 1. 3. 2. Effect of Electrolyte Salts

It was believed that decomposition of  $\text{CuF}_2$  in the  $\text{LiClO}_4$  electrolytes probably proceeds according to the reaction



and that the low solubility of  $\text{LiF}$  acts as the driving force for this reaction to proceed nearly to completion. To test this assumption, a number of other candidate electrolyte salts were compared to  $\text{LiClO}_4$  in  $\text{CuF}_2$  stability tests. (With some exceptions, the same salts were evaluated in the lithium stability tests described in Section 2.1.2.3).

Electrolyte solutions with the concentration of 1 mol of salt per liter of solution were prepared using lithium-treated and distilled PC and vacuum dried salts. Forty milliliters of solution and 1.0 gram of  $\text{CuF}_2$  were placed on the laboratory shaker, agitated, and analyzed iodometrically at one week intervals for copper II content. Results of these analyses as well as water concentrations (Karl Fischer) and specific conductance of the solutions are shown in Table VIII, page 20.

The most significant trend displayed by these tests was the high solubility of  $\text{CuF}_2$  with lithium as compared to potassium and sodium electrolytes. This would suggest that, for improved wet shelf life, a salt of the latter two alkali metals rather than one of lithium should be selected. Apparently,  $\text{NaF}$  and  $\text{KF}$  have a higher solubility in propylene carbonate than does  $\text{LiF}$ , thereby reducing the rate of the double decomposition reaction.

### 2. 1. 3. 3. Effect of Solvent

This test series was designed to evaluate the effect of various solvents on the stability of  $\text{CuF}_2$  in the presence of  $\text{LiClO}_4$  and  $\text{KAsF}_6$ . Stability tests were performed as described in the previous section. All solvents were lithium treated and distilled, except for nitromethane which was not distilled because of the potential explosion hazard involved.

The two solutes were selected for the tests to further study the effect of the lithium and potassium ion on the stability of  $\text{CuF}_2$ . Also,  $\text{KAsF}_6$  appeared to be more uniformly soluble than  $\text{KPF}_6$  in the solvents studied. Concentrations (except where indicated) were 1 mol solute/liter of solvent.

Specific conductance, Karl Fischer water content, and results of the iodometric analyses for Cu II are presented in TABLE IX, page 21.

In the acetic anhydride electrolytes, a chemical reaction between the solvent and  $\text{CuF}_2$  took place as indicated by a blue voluminous precipi-



TABLE VIII

CuF<sub>2</sub> STABILITY IN PC ELECTROLYTES

1.0 Molar Solutions  
Room Temperature

Salt	$\mu\text{g H}_2\text{O/ml}$ of Electrolyte	$L_s,$ $\Omega^{-1}\text{cm}^{-1}$	Cu <sup>++</sup> Concentration			
			7 days	14 days	21 days	28 days
LiClO <sub>4</sub>	90	$5.4 \times 10^{-3}$	364	492	536	660
NaClO <sub>4</sub>	72	5.6	32	64	96	160
KPF <sub>6</sub>	97	7.8	71	70	90	77
KAsF <sub>6</sub>	61	8.1	83	64	192	96
LiBF <sub>4</sub> (m) *	170	6.4	800	896	1110	1056
LiPF <sub>6</sub> (m)	105	6.4	500	691	1343	1600
LiAsF <sub>6</sub> (m)	260	6.2	960	905	1322	1152
NaAsF <sub>6</sub> (m)	160	8.2	51	192	77	64
LiBF <sub>4</sub>	129	2.9	320	320	557	544

\* The solutions designated with the suffix (m) were prepared by mixing 2 M solutions of LiClO<sub>4</sub> and of the required potassium salt and filtering off the precipitated KClO<sub>4</sub>.

TABLE IX

STABILITY OF CuF<sub>2</sub> IN LiClO<sub>4</sub> AND KAsF<sub>6</sub> SOLUTIONSA. LiClO<sub>4</sub> Solutions

<u>Solvent</u>	<u>KFA</u> <u>μg H<sub>2</sub>O/ml</u>	<u>L<sub>s</sub></u> <u>Ω<sup>-1</sup>cm<sup>-1</sup></u>	<u>Cu II CONCENTRATIONS</u>			
			<u>3 days</u>	<u>10 days</u>	<u>17 days</u>	<u>24 days</u>
PC	180	5.2 x 10 <sup>-3</sup>	806	384	384	557
DMSO	175	11.6	>6400	---**	---	---
AA*	125	10.6	64	<32	160	96
NDA	185	15.7	>6400	---**	---	---
NM	1000	7.4	>6400	---**	---	---
			<u>7 days</u>	<u>14 days</u>	<u>21 days</u>	<u>28 days</u>
MA	76	1.4	331	384	511	692

\* Saturated (≈ 0.5M)

\*\* Solutions having Cu II concentrations in excess of 6400 μg/ml after 3 days were dropped from the program.

<u>B. KAsF<sub>6</sub> Solutions</u>			<u>Cu II CONCENTRATION</u>			
			<u>3 days</u>	<u>10 days</u>	<u>17 days</u>	<u>24 days</u>
PC	155	8.1	38	96	<30	96
DMSO	75	11.6	1830	3600	3610	4430
AA	45	13.6	145	160	154	192
NDA	75	22.3	215	138	960	384
NM	1365	10.8	64	<30	96	102
			<u>7 days</u>	<u>14 days</u>	<u>21 days</u>	<u>28 days</u>
MA	90	10.9	64	96	160	83

tate formed in the serum bottles. The copper content in these solutions was low.

With all solvents,  $\text{LiClO}_4$  produced considerably higher  $\text{CuF}_2$  solubilities than did  $\text{KAsF}_6$ . This was particularly evident with nitromethane solutions, where  $\text{LiClO}_4$  produced over 6400 ppm Cu II after 3 days of contact, while  $\text{KAsF}_6$  produced only 100 ppm after 24 days of agitation. Both solutes gave low copper concentration in AA, but as stated before, this is due to a chemical reaction yielding an insoluble product.

If solubility of  $\text{CuF}_2$  is the main impediment to wet shelf life for the  $\text{CuF}_2$ -Li system, improved stand properties should result with  $\text{KAsF}_6$  or other solutes giving low Cu II concentrations. This needs to be verified in cell tests.

#### 2. 1. 4. Pulse Load Tests

To correlate results of electrode stability tests with cell performance with the various electrolytes, two-plate  $\text{CuF}_2$ -Li cells were constructed and discharged. The lithium electrodes were constructed by pressing 1/16 inch thick lithium ribbon onto expanded silver. Copper fluoride electrodes were prepared by a filter press technique using cellulose fibers as binders, or by hot press molding with powdered polyethylene binder. The construction techniques are described in detail in the Appendix, Table A-6, page 134.

Cells were constructed with electrodes measuring 1.5 x 0.5 in. and separated by 0.03 inch thick microporous rubber. Glass slides were used for external cell support with rubber bands supplying compression. Activation was accomplished by lowering the cells into 1.0 inch I. D. test tubes containing sufficient electrolyte (5 ml) to cover about 1/4 of the electrode height. A silver wire or lithium reference electrode was dipped in the electrolyte solution. The cell components and the assembled cell is pictured in Figure 3, page 23, and Figure 4, page 24.

In order to determine the individual electrode potential and the IR drop in the electrolyte, a discharge circuit similar to that described by Kordesch and Marko<sup>3</sup> was employed. A particularly attractive feature of this test method is that reference electrode positioning is not critical, since the potential reading is taken only during the current-off half cycle of the load profile. A circuit diagram of the equipment constructed and employed is shown in Figure 5, page 25.

<sup>3</sup> K. Kordesch and A. Marko: J. Electrochemical Society, 107, 480 (1960).

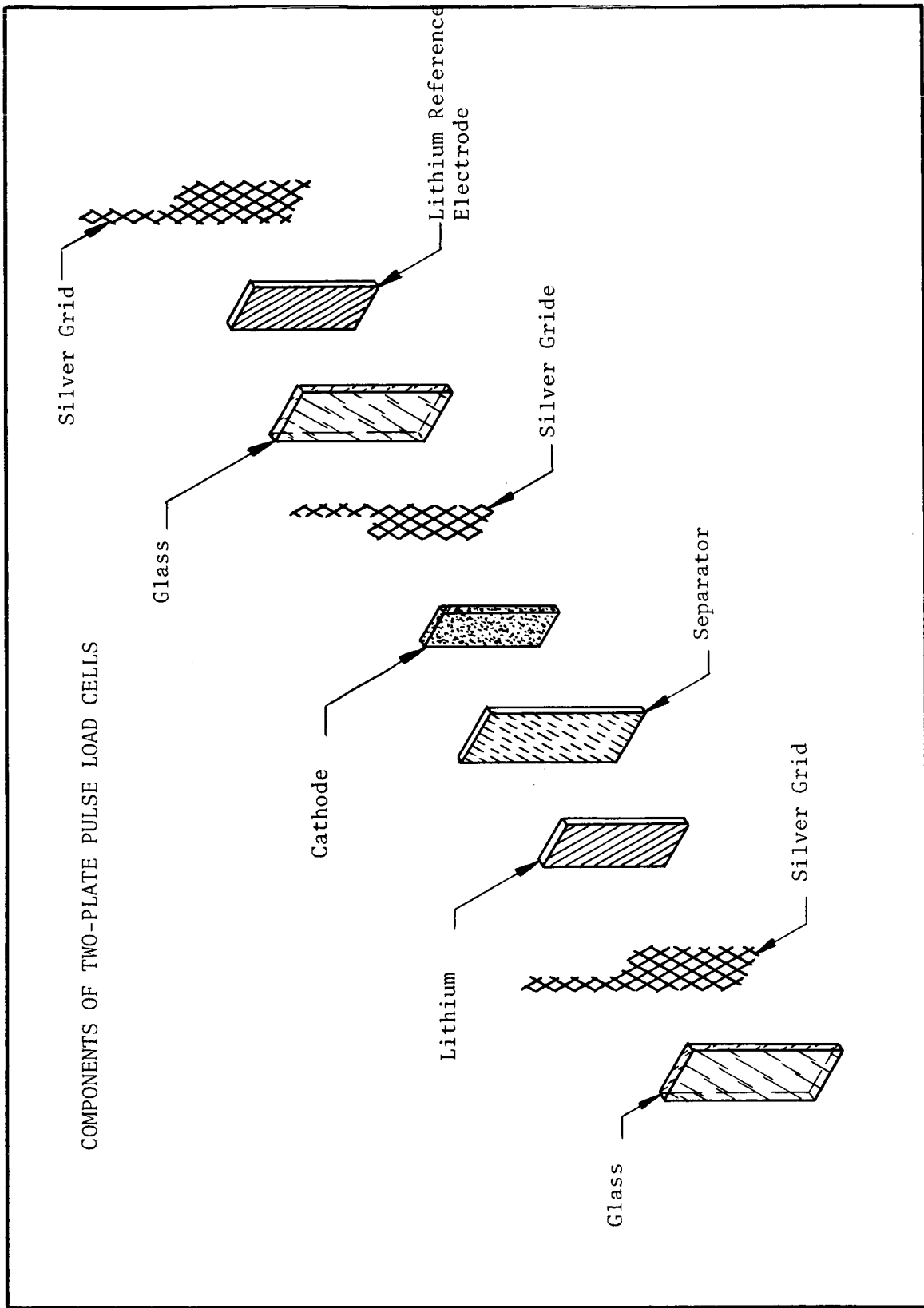


FIGURE 3

TWO-PLATE CELL ASSEMBLY FOR PULSE LOAD TESTS

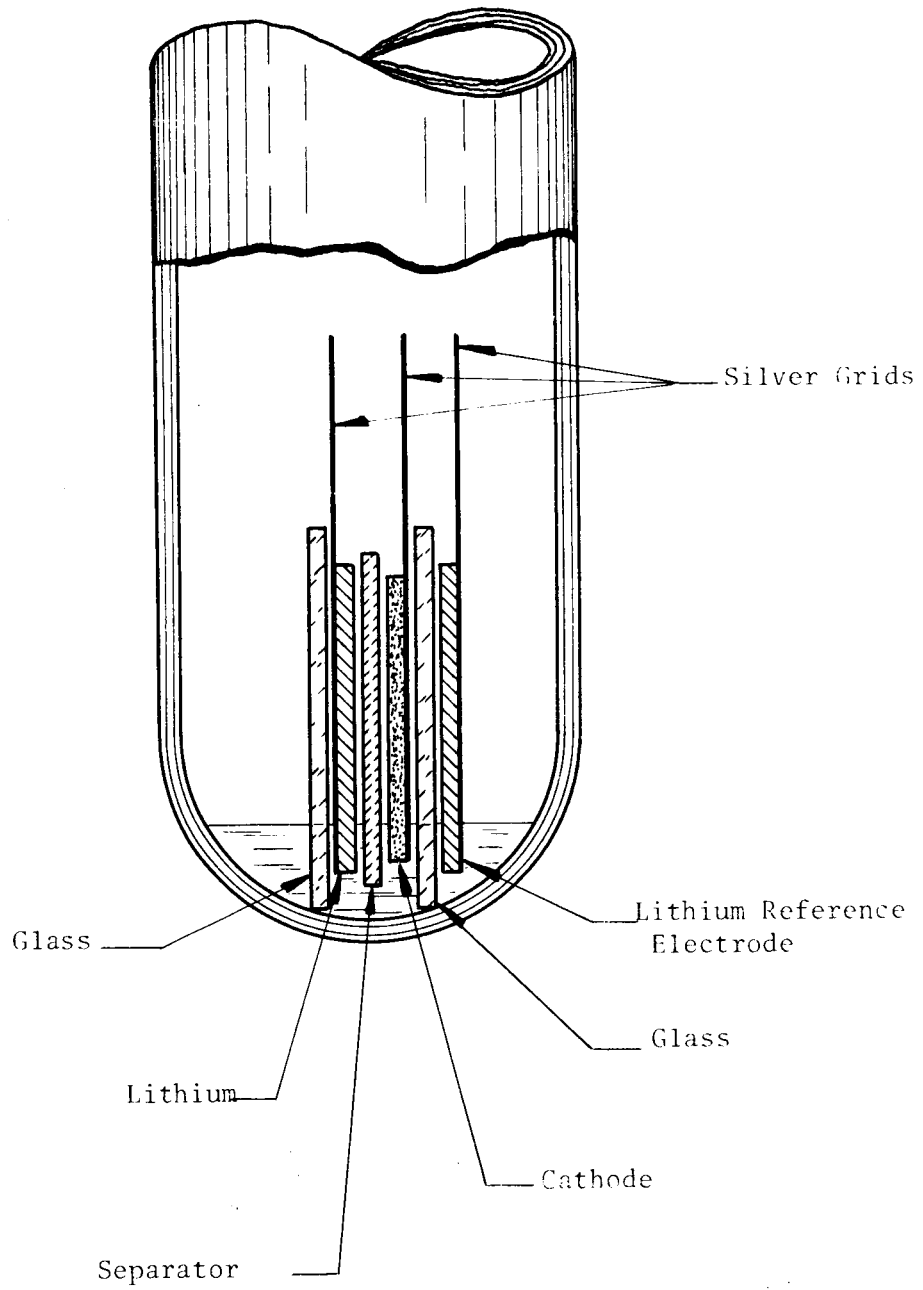


FIGURE 4

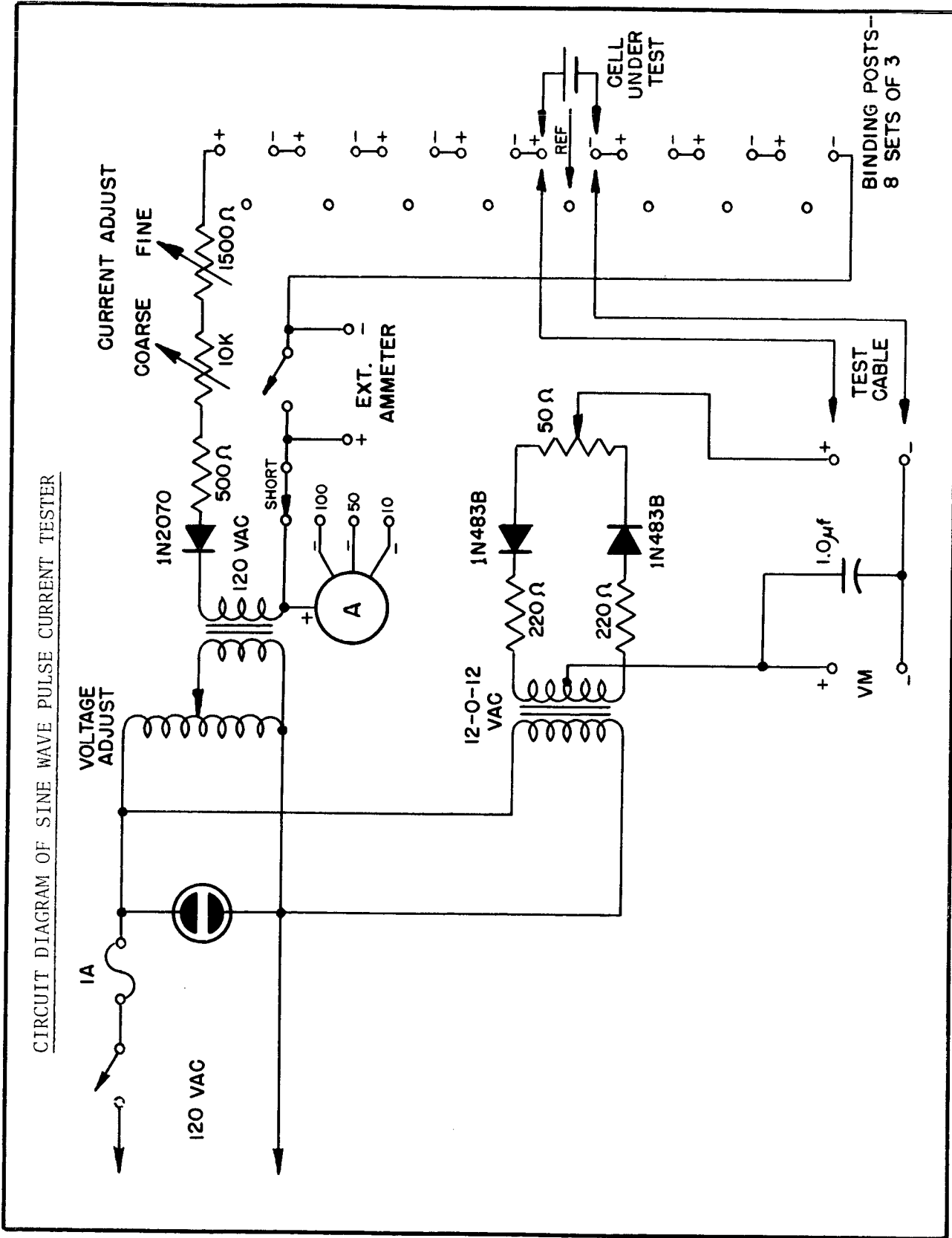


FIGURE 5

#### 2. 1. 4. 1. Effect of Electrolyte Salts

Cells were constructed as described on page 22, and activated with electrolytes having 1 mol of salt/liter of PC. The solutes in this series were  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KPF}_6$ ,  $\text{KAsF}_6$ ,  $\text{LiPF}_6(\text{m})$ ,<sup>4</sup>  $\text{LiBF}_4$ ,  $\text{LiAsF}_6(\text{m})$ , and  $\text{NaAsF}_6(\text{m})$ . Discharge of the cells was commenced at  $0.6 \text{ mA/cm}^2$  two hours after addition of the electrolyte. All tests were performed at  $35^\circ\text{C}$ .

Construction and discharge data for the cells are summarized in TABLE X, page 27. Voltage-time data for the best cell in each replicate set are shown in Figures 6 to 10, pages 28 to 32, (except for  $\text{LiPF}_6$  and  $\text{KPF}_6$  cells which gave less than 10 hours discharge to 2.0 VF).

The potential of the silver wire reference electrode was not entirely stable in the electrolytes used, becoming more positive during the course of the discharge. However, the measurements obtained do show cell capacity to be limited by polarization of the  $\text{CuF}_2$  electrode. The highest  $\text{CuF}_2$  reduction efficiencies were obtained in  $\text{LiClO}_4$  (64%) and  $\text{LiAsF}_6$  (54%). Practically no capacity could be obtained with  $\text{LiPF}_6$  or  $\text{KPF}_6$  solutes.

#### 2. 1. 4. 2. Effect of Solvent

Other two-electrode cells were constructed as described before and tested for discharge performance in  $\text{LiClO}_4$  and  $\text{KAsF}_6$  solutions in PC, DMSO, AA, NDA, NM and MA. In this series, the reference electrodes were lithium pressed onto expanded silver, but other test parameters, including electrolyte concentration, were as described in the previous section. Results of these tests are shown in Table XI, page 33.

The best discharge performance was obtained with the  $\text{LiClO}_4$ -PC electrolyte (67.5%  $\text{CuF}_2$  reduction efficiency). Both DMSO and NDA cells gave  $\text{CuF}_2$  reduction efficiencies around 30% with  $\text{LiClO}_4$  solute. Results with  $\text{KAsF}_6$  electrolytes were generally poorer. Reference electrode measurements taken at various times during the discharge again showed capacity to be limited by cathode polarization.

#### 2. 1. 5. Specific Conductance Measurements

Specific conductance of electrolyte solutions was determined during various phases of this investigation. The results of most of these measurements are presented together with other data in the appropriate sections of the report.

<sup>4</sup> The suffix (m) indicates solution prepared by double decomposition.

TABLE X  
EFFECT OF ELECTROLYTE SALT ON  $\text{CuF}_2$ -Li PERFORMANCE IN PC

Cell No.	Solute	Theo. $\text{CuF}_2$ Cap., AH	Initial OCV	Discharge to 2.0 VF Hours	Discharge to 2.0 VF AH	$\text{CuF}_2$ Reduction Eff., %	Av. Discharge Potential to 2.0 VF, Volts
1	$\text{LiClO}_4$	0.434	3.43	96.4	0.289	64.4	2.93
2	"	0.387	3.52	87.0	0.261	62.8	2.89
3	$\text{NaClO}_4$	0.413	3.39	20.2	0.061	10.4	2.79
4	"	0.452	3.56	70.0	0.210	13.3	2.46
5	$\text{KPF}_6$	0.526	3.38	5.3	0.016	2.04	2.63
6	"	0.509	3.50	4.2	0.013	1.97	2.59
7*	$\text{KAsF}_6$	0.387	3.39	0.48	0.144	0.18	2.81
8	"	0.386	3.40	52.0	0.156	38.1	2.64
9	$\text{LiBF}_4$	0.434	3.42	47.5	0.143	30.8	2.98
10	"	0.431	3.55	60.0	0.180	39.6	2.86
11	$\text{LiPF}_6$ (m)	0.542	3.44	9.5	0.029	3.9	2.74
12	"	0.319	3.50	5.9	0.018	4.7	2.65
13	$\text{LiAsF}_6$ (m)	0.348	3.44	55.6	0.167	43.7	2.95
14	"	0.418	3.42	81.0	0.243	53.7	2.99
15*	$\text{NaAsF}_6$ (m)	0.392	3.41	7.1	0.021	0.4	2.79
16	"	0.640	3.49	85.0	0.255	31.0	2.75

\* Cell failed due to external short circuit.



PERFORMANCE OF  $\text{CuF}_2\text{-Li "R"$  CELL IN  $\text{LiClO}_4/\text{PC}$  ELECTROLYTE

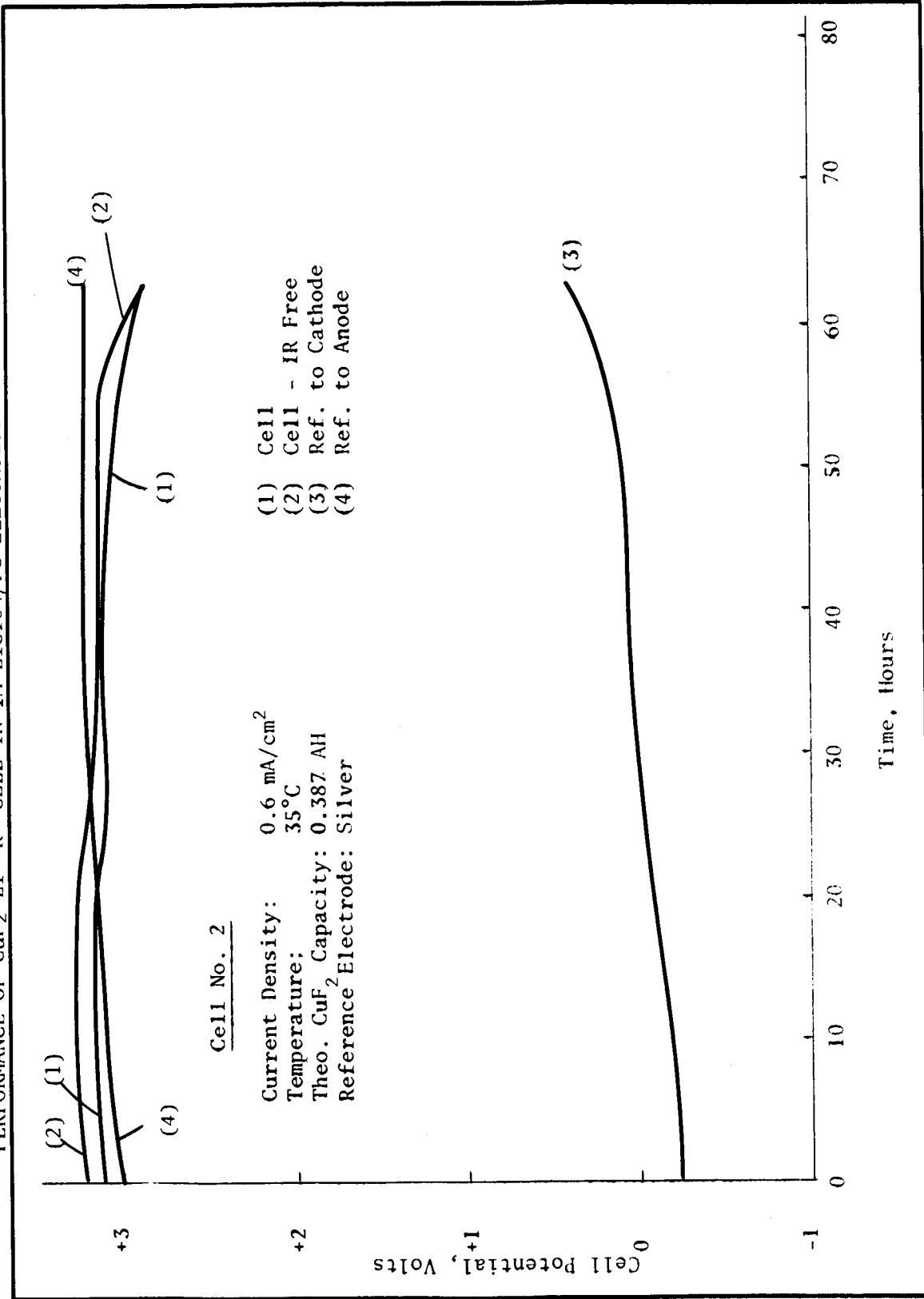


FIGURE 6

PERFORMANCE OF  $\text{CuF}_2\text{-Li "R" CELLS IN 1 M NaClO}_4\text{/PC ELECTROLYTE}$

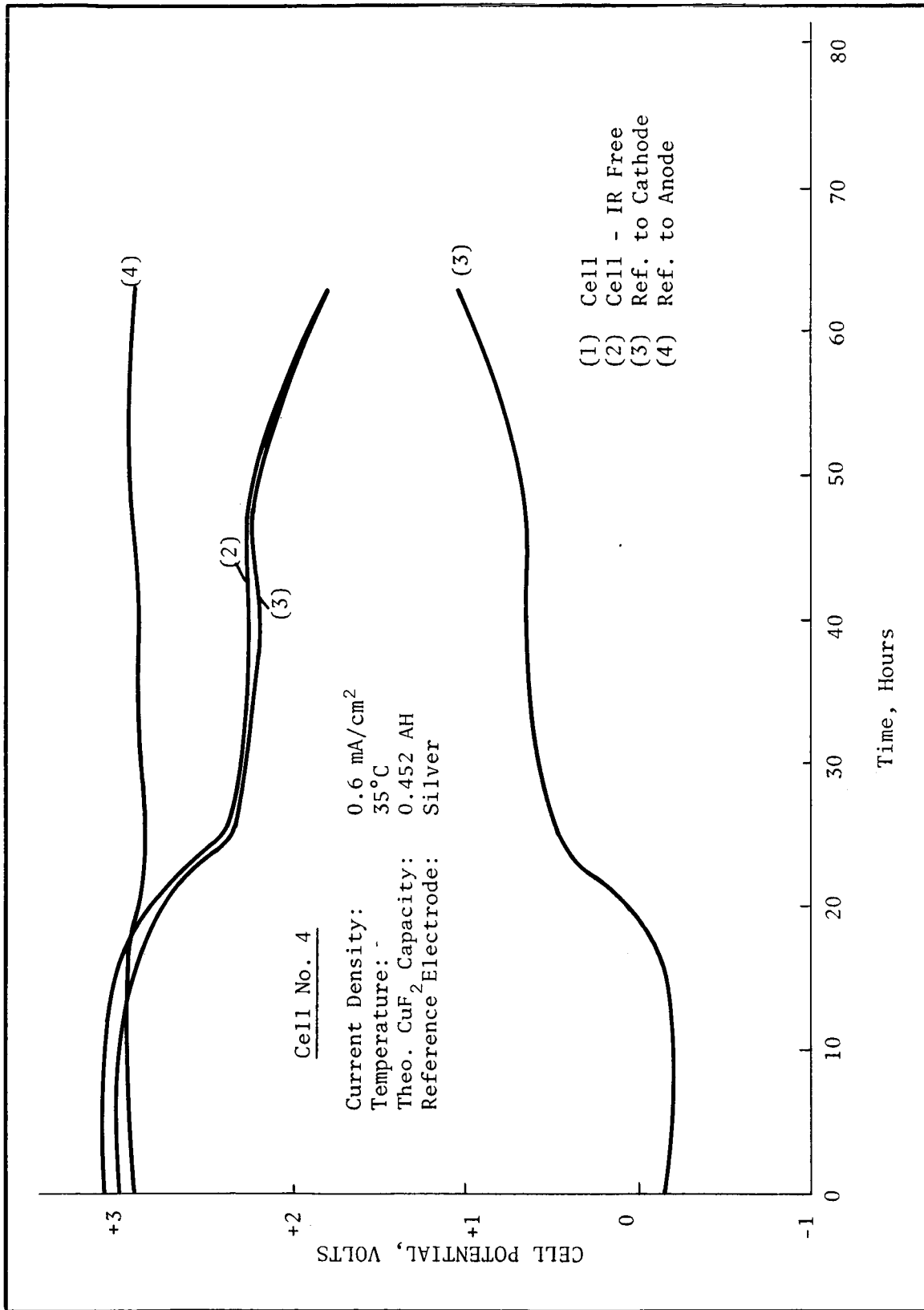


FIGURE 7

PERFORMANCE OF  $\text{CuF}_2\text{-Li "R"$  CELLS IN  $1\text{M LiBF}_4/\text{PC}$  ELECTROLYTE

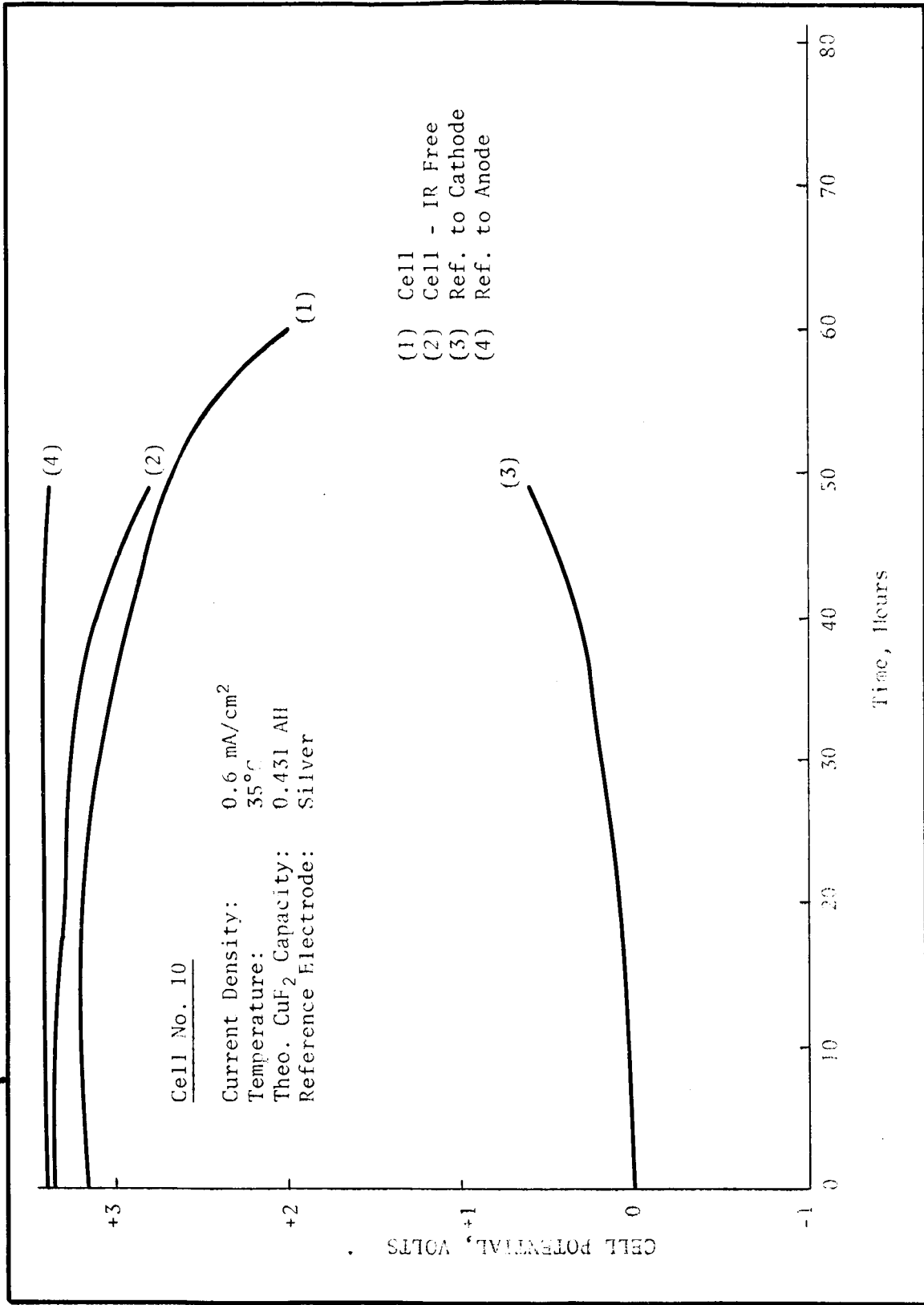


FIGURE 8

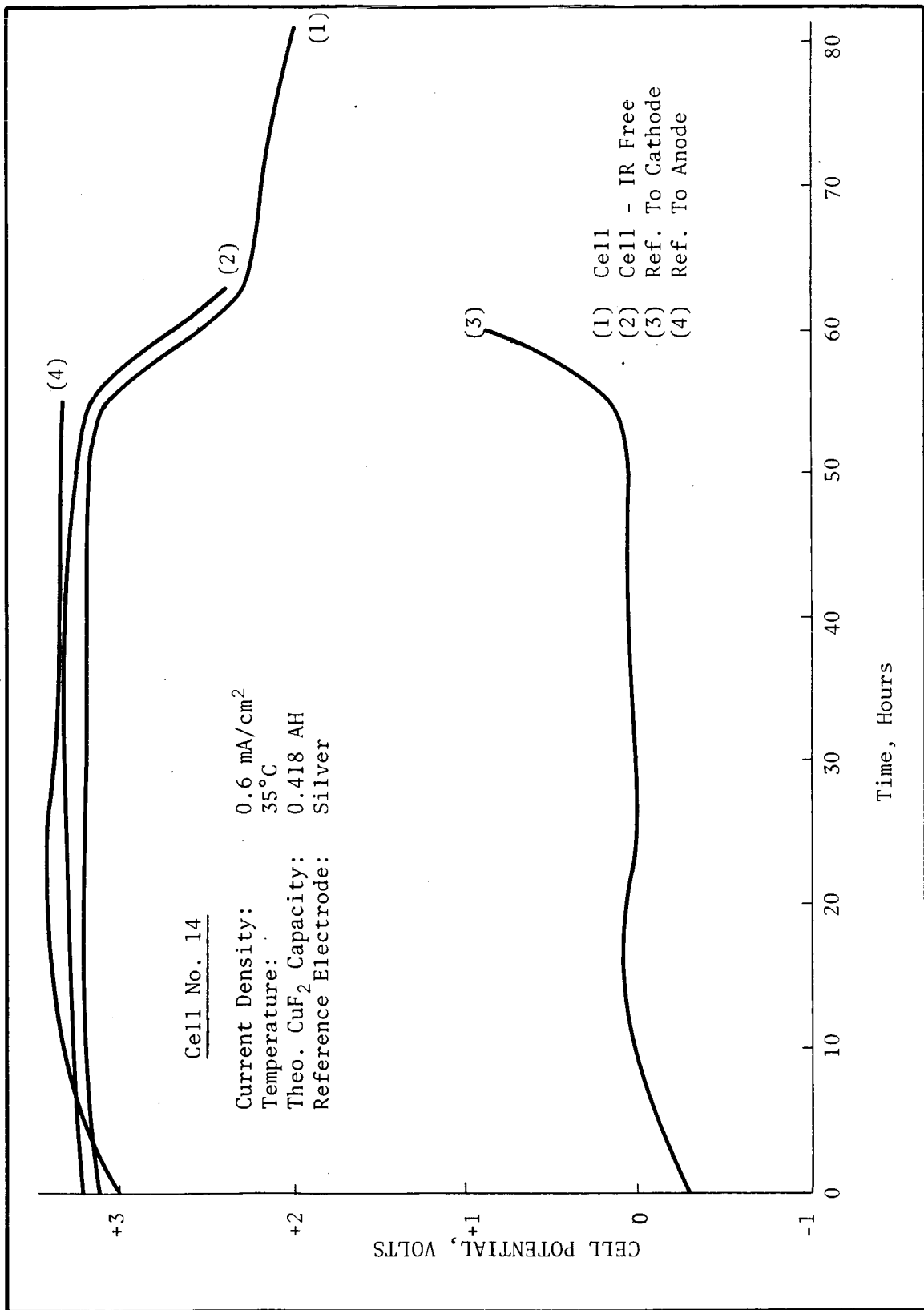
PERFORMANCE OF  $\text{CuF}_2\text{-Li "R" CELLS IN IM LiAsF}_6\text{ (m) ELECTROLYTE}$ 

FIGURE 9

PERFORMANCE OF  $\text{CuF}_2\text{-Li}$  "R" CELLS IN 1M NaAsF<sub>6</sub>(m) ELECTROLYTE

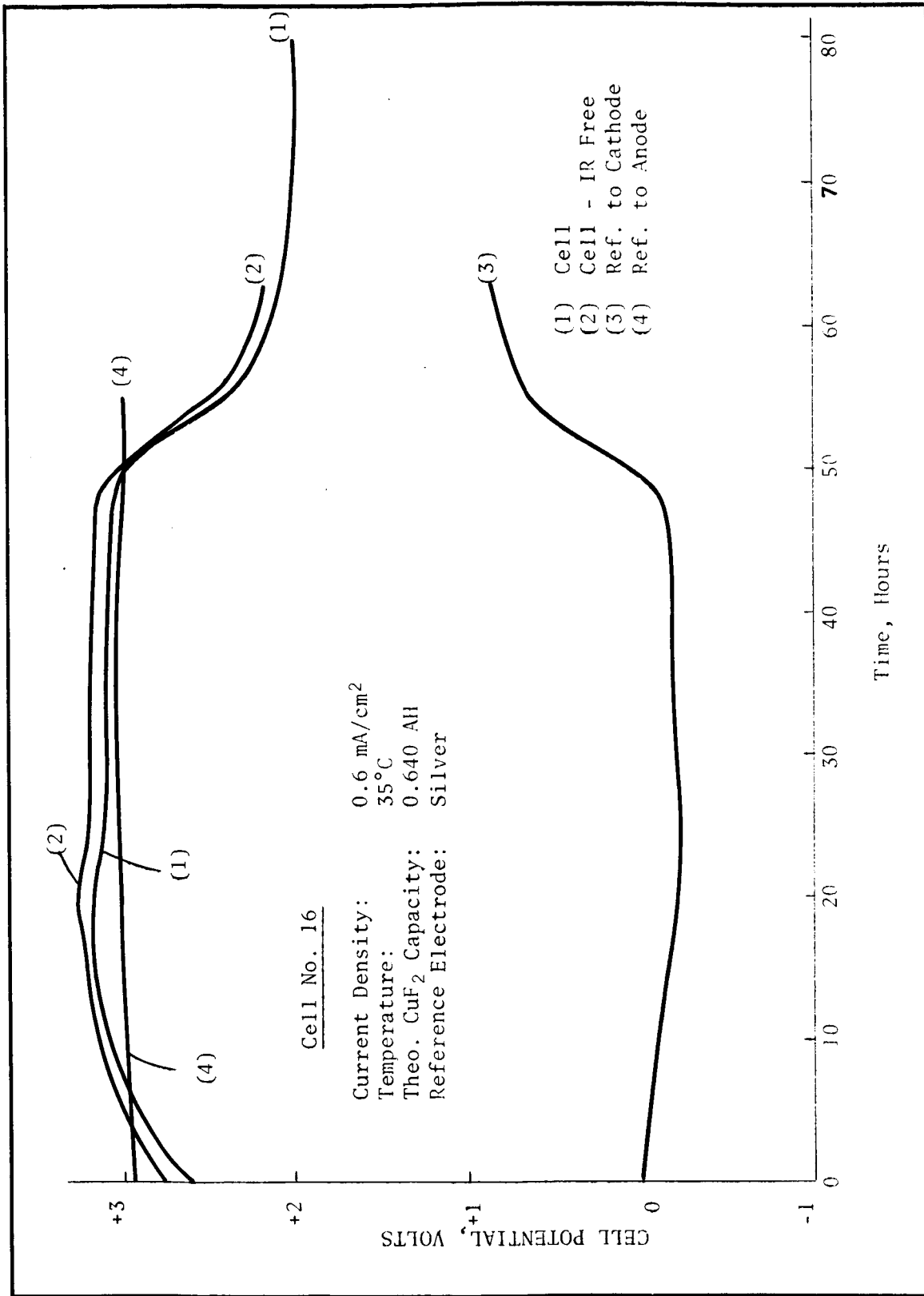


FIGURE 10

TABLE XI

EFFECT OF SOLVENT ON CuF<sub>2</sub>-Li CELL PERFORMANCE

Electrolyte Concentration: 1 mol Solute/Liter of Solvent

Current Density: 0.6 mA/cm<sup>2</sup>

Temperature: 35°C

Cell No.	Solvent	Solute	$\mu\text{g H}_2\text{O/ml}$	Theo. CuF <sub>2</sub> Cap. AH	Time to 2.5 VF, Hours	Cap. to 2.5 VF, AH	Efficiency Percent
1	PC	LiClO <sub>4</sub>	69	.396	89.0	0.267	67.5
2	PC	"	69	.383	65.5	0.196	51.3
3	DMSO	"	109	.270	29.5	0.088	32.5
4	DMSO	"	109	.309	32.0	0.096	31.1
5	NDA	LiClO <sub>4</sub>	99	.296	24.0	0.072	29.3
6	NDA	"	99	.504	28.5	0.085	29.8
7	NM	"	241	.296	1.5	0.005	1.7
8	NM	"	241	.313	1.5	0.005	1.6
9	AA	LiClO <sub>4</sub>	150	.566	42.8	0.128	22.6
10	PC	KAsF <sub>6</sub>	245	.374	20.5	0.056	17.6
11	DMSO	"	110	.583	41.0	0.123	21.1
12	DMSO	"	110	.305	30.5	0.092	30.1
13	NDA	KAsF <sub>6</sub>	146	.266	25.5	0.076	28.5
14	NDA	"	146	.422	34.5	0.104	24.7
15	NM	"	121	.305	14.0	0.060	14.6
16	AA	"	114	.305	20.0	0.092	19.7

To facilitate reference to the conductivity values, all measurements contained in the various sections of the report have been summarized in Table A-7, page 135, of the appendix. This table also contains conductivity measurements which were obtained in the course of contract work but have not been included in the body of the report.

#### 2. 1. 6. Purification of Salts

Some studies of solute purification methods were undertaken in this program. The following two methods were used for the purification of electrolyte salts by reprecipitation:

Method 1: (Table XII)

The salts were dissolved in a polar solvent and any insoluble impurities were removed by filtration. The desired salt was reprecipitated from the filtrate by the addition of a non-polar solvent. The crystals were filtered off, washed with the non-polar solvent and dried.

Method 2: (Table XIII, page 35)

The salts were dissolved in the minimum amount of hot solvent from which the desired salt would recrystallize on cooling. The most desirable solvents are ones which give large increases in salt solubility with increasing temperature. After cooling to room temperature, the crystals were filtered off, washed with a small amount of the crystallizing solvent and dried.

The methods for crystallization of  $\text{KAsF}_6$  shown in Table XII gave a solvent-free product consisting of colorless regular crystals. Recrystallization of  $\text{LiClO}_4$  from acetic anhydride yielded a disolvate which could not be converted to the unsolvated salt by heating under hard vacuum. (Decomposition was indicated by discoloration of the material). Recrystallization of  $(\text{C}_2\text{H}_5)_4\text{NF}$  from acetonitrile did not reduce the water content of the salt. Although the appearance of this material was improved ("as received" material was yellowish-brown, while the reprecipitated salt was white), it was still decomposed by heating in a vacuum oven ( $50^\circ\text{C}$ ), as evidenced by a strong odor of triethylamine.

TABLE XII

RECRYSTALLIZATION FROM MIXED SOLVENTS

(Method 1)

<u>Solute</u>	<u>Weight Solute g</u>	<u>Recrystallization System</u>	<u>Insoluble Impurities</u>	<u>Yield g</u>	<u>Remarks</u>
$\text{KAsF}_6^*$	5	Acetone (5 ml) - Dioxane or Toluene (5 ml).	25 mg	3.9	Dried at $110^\circ\text{C}$ and hard vacuum.
$\text{KAsF}_6$	5	Acetone (5 ml) - Dioxane (1 ml).	25 mg	2.2	Crystals formed over a period of 3 days by the slow evapora- tion of acetone.

\* $\text{H}_2\text{O}$  content before and after purification less than  $100 \mu\text{g/g}$ .

TABLE XIII  
RECRYSTALLIZATION FROM A SINGLE SOLVENT

(Method 2)

<u>Solute</u>	<u>Weight Solute g</u>	<u>Recrystallization Solvent</u>	<u>Yield g</u>	<u>Remarks</u>
KAsF <sub>6</sub> *	1	Ether (25 ml)		Insufficiently soluble.
KAsF <sub>6</sub>	1	Ethyl Acetate (25 ml)		Insufficiently soluble.
LiClO <sub>4</sub> **	1	Ether (2 ml)		No precipitation by cooling or by the addition of non-polar solvents.
LiClO <sub>4</sub>	1	Ethyl Acetate (2 ml)		No precipitation by cooling or by the addition of non-polar solvents.
LiClO <sub>4</sub>	1	Acetone (2 ml)		No precipitation by cooling or by the addition of non-polar solvents.
LiClO <sub>4</sub>	5	Acetic Anhydride (25 ml)	12.5	Material is a disolvate of Ac <sub>2</sub> O. Decomposes on heating.
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NF	25	Acetonitrile (50 ml)	11.5	Decomposes on heating.

\* Water content less than 100 µg/g before purification.

\*\* Water content less than 3000 µg/g before purification.

\*\*\* Water content 6500 µg/ml before and after purification.



## 2. 2. Copper Fluoride Studies

Since copper fluoride was the cathode material of major interest in this program, some investigations of its purity and methods for improvement of same were undertaken.

As received from the manufacturer<sup>5</sup>,  $\text{CuF}_2$  typically contained between 0.5 and 5.0% water in the form of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ . Solubility data obtained for  $\text{CuF}_2$  in electrolyte solutions, indicated that much lower water contents may be required.

### 2. 2. 1. $\text{CuF}_2$ Drying Studies

It has been reported in the literature<sup>6</sup> that  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  decomposes with formation of  $\text{CuOHF}$  when heated at  $132^\circ\text{C}$ . Assuming that this reaction proceeds to completion, a simple analysis for water appears possible by heating the material and determining weight loss. Such analyses were performed with materials received from the suppliers and the results were compared to those of X-ray analyses. Results of these tests are listed in Table XIV.

TABLE XIV  
WATER CONTENT OF  $\text{CuF}_2$

<u>Lot No.</u>	<u>Water Content, %</u>	
	<u>X-Ray</u>	<u>Weight Loss</u>
2	3.9	3.3
3	1.0	0.8
4	5.8	3.6
6	2.8	2.6

As can be seen from these figures, the weight loss method gives low results compared to X-ray analysis.<sup>7</sup> The agreement becomes even poorer when samples of more than a few grams are heated, indicating difficulty of water removal.

Removal of water from  $\text{CuF}_2$  to be used for cathode construction was of

<sup>5</sup> Material from A. D. McKay and Ozark-Mahoning Co., was used on this program.

<sup>6</sup> C. M. Wheeler and H. M. Haendler; J. Amer. Chem. Soc., 76, 263, (1954).

<sup>7</sup> Details of X-ray analysis for  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  are given in the Appendix, Table A-8.

major importance in this program, since the detrimental effect of water on the solubility of  $\text{CuF}_2$  had been demonstrated. Two basic procedures were employed for drying of  $\text{CuF}_2$ . The first method involved heating of the material under vacuum, while the second consisted of placing the material in a vertical tube heated by a constant temperature bath and continuously purging the tube with dry argon.

To study the effect of the various drying conditions, seven batches of anhydrous  $\text{CuF}_2$  (Lot 7) were treated. The method of treatment and the X-ray patterns obtained before and after drying are presented in Table XV, page 38. The relative concentration of each material in the samples is proportional to the peak intensity (counts/second), but the actual percentage figures can only be calculated for the materials which are available in pure form for calibration ( $\text{CuF}_2$  and  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ ).

It can be seen from examination of Table XV, that the main decomposition products which result from heating the salt are  $\text{CuOHF} \cdot \text{CuF}_2$  and  $\text{CuOHF}$ . An unknown compound having a major peak intensity at  $4.15 \text{ \AA}$  is also produced. Its concentration increases with drying time and with temperature.

#### 2. 2. 2. Decomposition of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$

Since decomposition of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  is of importance in removing water from  $\text{CuF}_2$ , this reaction was studied further in a series of decomposition tests performed on the dihydrate. In the first series of experiments, 50 grams of dihydrate were heated in a sealed vacuum oven having a volume of 6.5 L from which air was evacuated prior to application of heat. Results of the X-ray analyses of the initial and resulting material are given in Table XVI, page 39.

A second series of tests was performed by heating the dihydrate in a tube while purging with argon as described in the previous section; results of these runs are presented in Table XVII, page 40.

It can be seen from the X-ray data that the main decomposition products obtained by both methods are  $\text{CuOHF}$  and a compound having a major peak intensity at  $4.15 \text{ \AA}$ , the latter becoming more predominant with longer decomposition time and higher temperature. Thus it seems possible to control the composition of the product.

Some solubility tests with the resultant materials in  $\text{LiClO}_4$ -PC electrolyte were attempted and no Cu II could be detected in the solutions. Cathodes with these materials were constructed and evaluated in cell discharge tests described in the following section.

TABLE XV  
MAJOR PEAK INTENSITIES OF VARIOUS COMPOUNDS IN  
COPPER FLUORIDE SAMPLES

<u>Compound</u>	<u>As Rec'd</u>	<u>16 Hrs 70°C Oven</u>	<u>16 Hrs 130°C Argon Sweep</u>	<u>16 Hrs 130°C Argon Sweep</u>	<u>16 Hrs 130°C Argon Sweep</u>	<u>113 Hrs 130°C Argon Sweep</u>	<u>16 Hrs 180°C Argon Sweep</u>	<u>16 Hrs 152°C Argon Sweep</u>
CuF <sub>2</sub>	1840	1760	1248	1264	1440	1184	1408	1376
CuF <sub>2</sub> ·2H <sub>2</sub> O	178	108	13	11	12	N.D.	N. D.	24
CuOHF	N.D*	N.D.	16	12	28	24	12	N.D.
CuOHF·CuF <sub>2</sub>	N.D.	N.D.	72	72	12	16	104	100
CuO	N.D.	N.D.	12	12	N.D.	N.D.	N.D.	N.D.
Cu <sub>2</sub> O	N.D.	N.D.	N.D.	12	N.D.	N.D.	N.D.	N.D.
Cu	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
4.15 Å	N.D.	N.D.	40	40	52	120	60	52
% water from CuF <sub>2</sub> ·2H <sub>2</sub> O    2.2    1.3								

\*None detected.

TABLE XVI

DECOMPOSITION OF  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , LOT A, SEALED CHAMBER

Compound	Value A	Relative Intensity	Counts/Second	Relative Intensity	CuF <sub>2</sub> ·2H <sub>2</sub> O, Lot A		Relative Intensity	Counts/Second	Relative Intensity	Counts/Second	Relative Intensity
					44-1	B54-1					
					CuF <sub>2</sub> ·2H <sub>2</sub> O, Lot A	55-7					
					Untreated						
	Sample No.										
	Time				32 Hrs.	20 Hrs.	20 Hrs.				
	Temperature				150°C	150°C	135°C				
	Chamber Pressure				Vacuum*	0.1 Atm.Abs.	1 Atm.Abs.				
	"D"										
	Value A	Relative Intensity	Counts/Second	Relative Intensity	Relative Intensity	Counts/Second	Relative Intensity	Counts/Second	Relative Intensity	Counts/Second	Relative Intensity
CuF <sub>2</sub> ·2H <sub>2</sub> O	4.78	100	2400	100	---	24	---	256	100		
	3.71	25	600	25	---	---	---	---	---		
	2.71	45	1080	45	---	---	---	**	---		
CuOHF·CuF <sub>2</sub>	4.22	100	---	---	---	---	---	320	---		
	3.54	85	---	---	---	---	---	---	---		
	3.45	70	---	---	---	68	---	392	---		
CuOHF	4.68	100	---	---	---	2496	100	1584	100		
	2.55	40	---	---	---	1044	42	768	48		
	1.97	35	---	---	---	576	23	352	22		
Unknown	4.15	---	---	---	100	---	---	---	---		
	2.77	---	---	---	49	---	---	---	---		
	2.75	---	---	---	28	---	---	---	---		

\* Vacuum pump was connected to chamber for 16 hours at which time chamber was sealed.

\*\* Line is obscured by CuOHF line.

TABLE XVII

DECOMPOSITION OF  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , LOT B, ARGON SWEEP

Sample No.	$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , Lot B Untreated	55-9	57-1	57-1	59-5			
Time		50 Hrs.	15 Hrs.	10 Hrs.	20 Hrs.			
Temperature		135°C	150°C	165°C	185°C			
"D"								
Compound	Value Å	Relative Intensity	Counts/ Second	Relative Intensity	Counts/ Second	Relative Intensity	Counts/ Second	Relative Intensity
$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	4.78	100	1696	100	---	---	---	---
	3.71	25	464	27	---	---	---	---
	2.71	45	800	47	---	---	---	---
$\text{CuOHF} \cdot \text{CuF}_2$	4.22	100	124	100	---	---	328	100
	3.54	85	124	100	---	---	264	80
	3.45	70	100	81	---	---	164	50
$\text{CuOHF}$	4.68	100	100	100	100	100	344	100
	2.55	40	64	64	44	672	224	65
	1.97	35	76	76	19	232	80	23
Unknown	4.15	---	---	---	100	448	370	100
	2.77	---	---	---	44	308	180	49
	2.75	---	---	---	36	172	---	---

### 2. 3. Experimental Cell Tests

At various points in the program, three-plate experimental cells were constructed and tested to study the many variables affecting the performance of the  $\text{CuF}_2$ -Li system. Construction of these cells was essentially as described in reports on earlier work performed at this laboratory.<sup>8</sup>

The two lithium electrodes were prepared by pressing 1/16 inch thick ribbon (Foote Mineral Co.) onto expanded silver. The petrolatum used to protect the lithium during shipment and storage, was dissolved with heptane before construction of the cells. The electrodes measure 1.5 x 1.5 inches and had about 7.8 AH of theoretical anode capacity.

The  $\text{CuF}_2$  electrodes were usually prepared by a filter press technique using paper fibers as the binder and graphite as the conductive component. A heptane slurry having the desired composition was prepared and filtered on a laboratory paper sheet mold. The filter mat was then cut to size, pressed onto expanded silver, and the heptane was removed by drying in vacuum.<sup>9</sup> Some tests were also performed with pasted electrodes made with polystyrene binder, and with hot pressed electrodes containing powdered polyethylene.

The theoretical reduction capacity of the  $\text{CuF}_2$  electrodes (0.526 AH/g  $\text{CuF}_2$ ) was generally in the range of 3 - 5 AH. Since this is only about 50% of the theoretical Li capacity (7.8 AH), the cell capacity was taken as a measure of positive electrode performance. The working area of the cells was 2 x 1.5 x 1.5 inches, or about 29cm<sup>2</sup>.

The experimental cell components before assembly are shown in Figure 11, page 42. The separation used for these cells was 0.03 inches thick microporous rubber, and a heat sealed polyethylene envelope served as the external case. The cells were generally supported between blocks held together with bolts as shown in Figure 12, page 42.

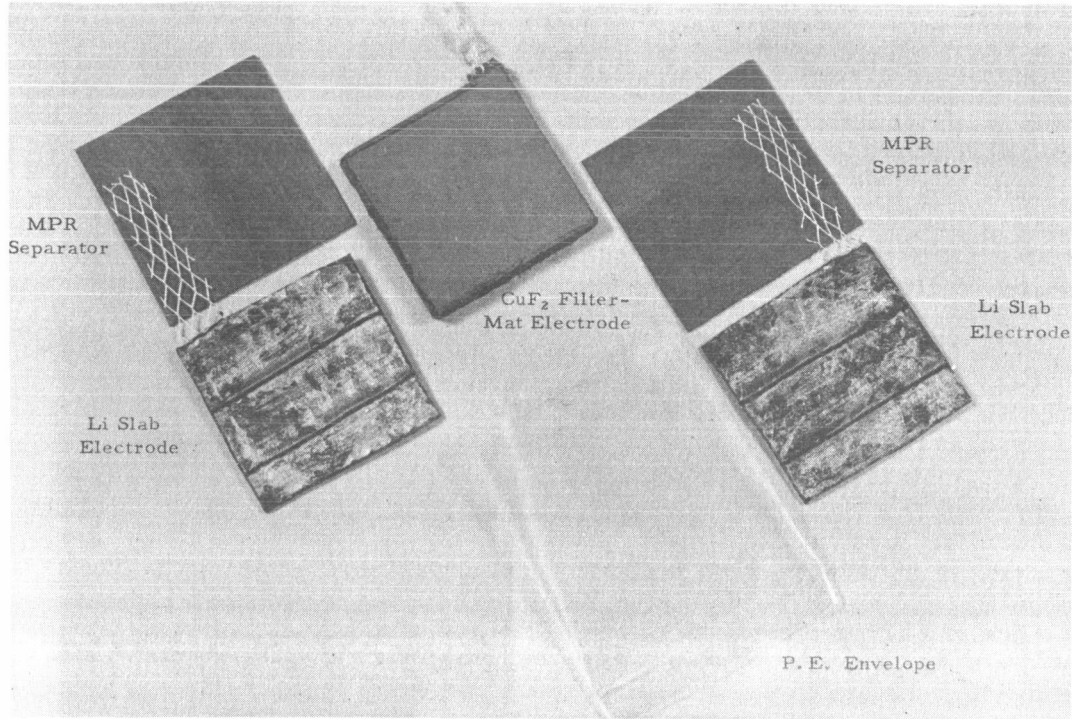
During both discharge and stand tests, the assembly was placed in a hermetically sealed container to avoid contamination with moisture from the air.

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<sup>8</sup> See, for example, NASA CR-54803, pp. 67-72.

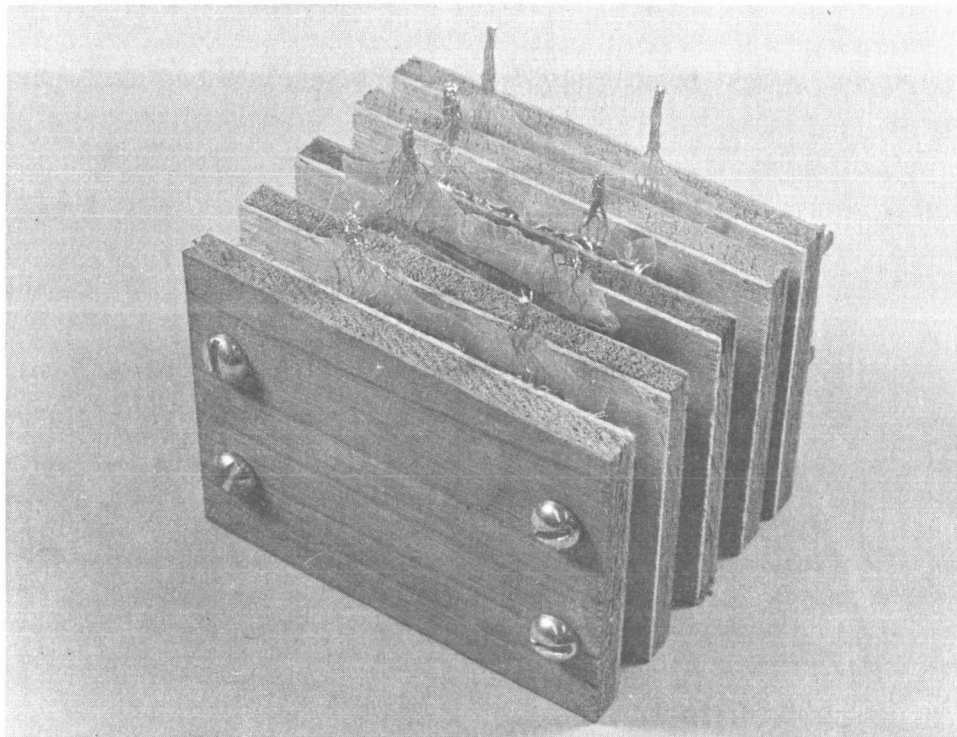
<sup>9</sup> Further details on this method are given in the Appendix, Table A-8.

Figure 11



CuF<sub>2</sub> - Li Test Cell Components

Figure 12



Cell Discharge Test Rack

### 2. 3. 1. Effect of Dried CuF<sub>2</sub> On Shelf Life

Evaluation of wet stand capabilities of CuF<sub>2</sub>-Li cells with LiClO<sub>4</sub>-PC electrolyte was conducted. The main variable in this study was the water content of the CuF<sub>2</sub> used for making the positive electrodes. The three-plate cells were built with filter mat positive electrodes having the composition:

CuF <sub>2</sub>	82%
Graphite	12%
Paper Fiber	6%

The separation was commercial microporous rubber 0.03 inches thick, and the electrolyte solution had the concentration 15g solute/100 ml solvent. The water content of the electrolyte was in the order of 500 ppm.

#### 2. 3. 1. 1. Effect of Vacuum Drying

In this test, two groups of 22 cells, identical except for treatment of CuF<sub>2</sub> before construction of electrodes, were built and tested. For one group of cells, CuF<sub>2</sub> having a water content of 2.8 percent (X-ray analysis) was used, while for the second group the same material was dried at 70°C for 16 hours under vacuum (100 - 200 microns). The water content of the dried material was not determined, but other drying tests on the same material indicated that the water content was in the range of 1 - 2 percent after drying.

After the test cells had been filled with the electrolyte, four cells from each group were put in discharge through 200Ω resistors at 35°C, while the remaining cells were stored at 35°C, -15°C, and -55°C. It was originally intended to discharge groups of two cells from each of the test environments after a stand of 1 month, 3 months, and 6 months; however, these intervals were changed to 2 weeks, 4 weeks, and 6 weeks after a rapid open circuit potential decay was observed in many cells after a stand of only 2 weeks.

Construction and discharge data for the test cells are summarized in Tables XVIII and XIX, pages 44 and 45. As expected, poor capacity retention was exhibited by the cells which had been on stand at 35°C at -15°C and -55°C, capacity retention was in the order of 80 percent after 4 weeks of stand for the cells built with the vacuum-dried CuF<sub>2</sub>. After 6 weeks of stand, less capacity was retained by cells at -15°C than at -55°C.

Inspection of the cells after discharge showed the lithium slab electrodes to be in good condition except for the reduction in thickness which results from discharge. The inside surfaces of the lithium electrodes (those facing the CuF<sub>2</sub> electrode) showed green deposits which were more pronounced in cells which had the poorest shelf life.



TABLE XVIII

SELF-DISCHARGE IN  $\text{CuF}_2$ -Li CELLS

Undried  $\text{CuF}_2$ : 2.8%  $\text{H}_2\text{O}$   
 Electrolyte: 15g  $\text{LiClO}_4/100$  ml PC  
 Electrode Area:  $29 \text{ cm}^2$   
 Load:  $200\Omega$

Cell No.	Stand Conditions		Theo. $\text{CuF}_2$ Cap., AH <sup>2</sup>	Hrs. to 2.0VF	Capacity to 2.0 VF, AH	Average Discharge Potential Volts	Cathode Eff., %
	Temp. °C	Time, wks.					
3-1			3.74	135	1.88	2.77	50
3-2			3.46	127	1.79	2.82	52
3-3			3.78	131	1.83	2.79	49
3-4			3.52	132	1.89	2.86	54
3-5 <sup>1</sup>	+35	2	----	---	----	----	--
3-6 <sup>1</sup>	+35	2	----	---	----	----	--
3-7 <sup>1</sup>	+35	2	----	---	----	----	--
3-8 <sup>1</sup>	+35	2	----	---	----	----	--
3-9 <sup>1,2</sup>	+35	2	----	---	----	----	--
3-10 <sup>2</sup>	+35	2	----	<6	----	----	--
3-11	-15	2	3.64	42	0.55	2.61	15
3-12	-15	2	4.04	64	0.85	2.65	21
3-13	-15	4	4.66	49	0.49	2.76	11
3-14	-15	4	4.03	43	0.56	2.62	14
3-15 <sup>1</sup>	-15	6	4.18	---	----	----	--
3-16	-15	6	3.69	<12	----	----	--
3-17	-55	2	4.05	101	1.42	2.81	35
3-18	-55	2	4.04	65	0.92	2.81	23
3-19	-55	4	3.65	88	1.20	2.72	33
3-20	-55	4	4.12	99	1.32	2.65	32
3-21	-55	6	4.23	56	0.74	2.64	17
3-22 <sup>1</sup>	-55	6	3.32	---	----	----	--

<sup>1</sup> Cell potential below 2 volts after stand.

<sup>2</sup> Cell had 5000 ohm load across terminals during stand.

TABLE XIX

SELF-DISCHARGE IN CuF<sub>2</sub>-Li CELLSCuF<sub>2</sub> Dried at 70°C for 16 HoursElectrolyte: 15g LiClO<sub>4</sub>/100 ml PCElectrode Area: 29 cm<sup>2</sup>

Load: 200Ω

Cell No.	Stand Conditions		Theo. CuF <sub>2</sub> Cap., AH	Hrs. to 2.0VF	Capacity to 2.0 VF, AH	Average Discharge Potential Volts	Cathode Eff., %
	Temp. °C	Time, wks.					
3-1			3.88	166	2.44	2.94	63
3-2			4.23	198	2.89	2.91	68
3-3			3.88	161	2.32	2.88	60
3-4			4.17	175	2.59	2.96	62
3-5 <sup>1</sup>	+35	2	----	---	----	----	--
3-6 <sup>1</sup>	+35	2	----	---	----	----	--
3-7	+35	2	3.82	33	0.41	2.45	11
3-8 <sup>1</sup>	+35	2	----	---	----	----	--
3-9 <sup>1,2</sup>	+35	2	----	---	----	----	--
3-10 <sup>2</sup>	+35	2	3.98	24	0.28	2.34	7
3-11	-15	2	3.98	155	2.19	2.83	55
3-12	-15	2	3.74	147	2.07	2.82	55
3-13	-15	4	3.74	147	2.09	2.85	56
3-14	-15	4	3.84	164	2.38	2.90	62
3-15	-15	6	3.64	72	1.01	2.80	28
3-16 <sup>3</sup>	-15	6	3.64	48	0.64	2.67	17
3-17	-55	2	3.53	101	1.41	2.79	40
3-18	-55	2	4.15	87	1.30	2.99	31
3-19	-55	4	3.87	148	2.09	2.81	54
3-20	-55	4	4.10	148	2.10	2.84	51
3-21	-55	6	4.33	168	2.37	2.82	55
3-22	-55	6	4.00	185	2.65	2.86	61

<sup>1</sup> Cell potential below 2 volts after stand.<sup>2</sup> Cell had 5000 ohm load across terminals during stand.<sup>3</sup> 2.52 VF.

### 2. 3. 1. 2. Effect of Argon Drying

A second test series was conducted using  $\text{CuF}_2$  dried in a stream of argon. One lot of the material was dried at  $130^\circ\text{C}$  for 16 hours, while the second lot was dried under the same conditions for 113 hours. Subsequent X-ray analyses showed the water content of the treated materials to be below 0.3%. The stand temperatures for this series of cells were  $35^\circ\text{C}$  and  $-15^\circ\text{C}$ , while the discharges again were conducted at  $35^\circ\text{C}$  thru  $200\Omega$  loads.

Without open circuit stand, capacity was somewhat higher for the cells which had  $\text{CuF}_2$  dried for the shorter period (16 hours), indicating that some decomposition of  $\text{CuF}_2$  may have resulted from the argon drying. After a two week stand at  $35^\circ\text{C}$ , only two of the six cells with each type of  $\text{CuF}_2$  had any significant capacity above 2.5 volts. After stand periods of 2, 4, and 6 weeks at  $-15^\circ\text{C}$ , cell performance was not significantly different than had been obtained from cells which had received no open circuit stand. Results of the discharge tests are summarized in Tables XX and XXI, pages 47 and 48. The voltage-time data for the cells are presented in Figures 13 to 17, pages 49 to 53, and the extent of shelf discharge under the various test conditions for the highest performance cell in each group is displayed graphically in Figure 18, page 54.

Inspection of the cells at the end of the test did not reveal clearly why the cells failed to discharge after the open circuit stand period at  $35^\circ\text{C}$ . All cell components appeared to be in good condition, and no evidence of short-circuiting could be found. However, the unabsorbed portion of the electrolyte had disappeared during the stand period, and an ester-like odor was always evident in the constant temperature chamber. This suggests loss of solvent by decomposition and evaporation, which contributes to the loss of capacity after stand. Also, the loss of electrolyte is more pronounced in the cells which show more extensive capacity loss during stand. This factor requires further study with hermetically sealed cell assemblies.

### 2. 3. 2. Evaluation of Thermally Decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$

For this test, the positive active material was prepared by heating  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  in a tube swept by argon for 57 hours at  $180 - 188^\circ\text{C}$ . The resulting material showed a 23 percent weight loss from the dihydrate and the composition was shown by X-ray analysis to be:

TABLE XX

SELF DISCHARGE IN CuF<sub>2</sub>-Li CELLSCuF<sub>2</sub> Dried 16 Hours at 130°C Under Argon

Electrolyte: 15g LiClO<sub>4</sub>/100 ml PC  
 Electrode Area: 29 cm<sup>2</sup>  
 Load: 200Ω

Cell No.	Stand Conditions		Theo. CuF <sub>2</sub> Cap., AH	Hours to 2.5 VF	Capacity to 2.5 VF, AH	Average Discharge Potential Volts	Cathode Eff., %
	Temp. °C	Time, wks.					
3B-1	---	-	3.72	170	2.64	3.10	71
3B-2	---	-	3.98	201	3.16	3.14	79
3B-3	---	-	3.93	108	1.65	3.06	42
3B-4	---	-	4.18	184	2.85	3.09	68
3B-5	+35	2	3.83	7	----	----	--
3B-6	+35	2	3.39	0	----	----	--
3B-7	+35	2	3.97	12	----	----	--
3B-8	+35	2	3.80	18	0.25	2.76	7
3B-9	+35	2	4.20	12	----	----	--
3B-10	+35	2	4.04	42	0.59	2.81	15
3B-11	-15	2	3.90	82	1.25	3.05	32
3B-12 <sup>1</sup>	-15	2	4.32	46	0.75	3.25	17
3B-13	-15	4	3.52	141	2.16	3.06	61
3B-14	-15	4	3.50	107	1.64	3.05	47
3B-15	-15	6	4.00	138	2.06	3.03	52
3B-16	-15	6	3.44	138	2.08	3.07	61

<sup>1</sup> Cell had internal short circuit.

TABLE XXI

SELF-DISCHARGE IN CuF<sub>2</sub>-Li CELLSCuF<sub>2</sub> Dried 113 Hours at 130°C Under Argon

Electrolyte: 15g LiClO<sub>4</sub>/100 ml PC  
 Electrode Area: 29 cm<sup>2</sup>  
 Load: 200Ω

Cell No.	Stand Conditions		Theo. CuF <sub>2</sub> Cap., AH	Hours to 2.5 VF	Capacity to 2.5 VF, AH	Average Discharge Potential Volts	Cathode Eff., %
	Temp. °C	Time, wks.					
3B-17	---	--	4.67	170	2.64	3.10	57
3B-18	---	--	4.58	170	2.50	2.94	55
3B-19	---	--	4.77	202	3.15	3.11	66
3B-20	---	--	4.24	122	1.80	2.94	42
3B-21	+35	2	4.79	41	0.58	2.81	12
3B-22	+35	2	4.42	2	----	----	--
3B-23	+35	2	4.83	12	0.17	2.77	3
3B-24	+35	2	4.84	0	----	----	--
3B-25	+35	2	4.36	12	----	----	--
3B-26	+35	2	4.58	12	----	----	--
3B-27	-15	2	4.20	168	1.62	3.11	39
3B-28	-15	2	4.04	156	2.40	3.07	59
3B-29	-15	4	4.11	155	2.40	3.09	58
3B-30	-15	4	4.27	173	2.65	3.05	62
3B-31	-15	6	4.81	180	2.72	3.06	57
3B-32	-15	6	4.62	159	2.35	2.99	51

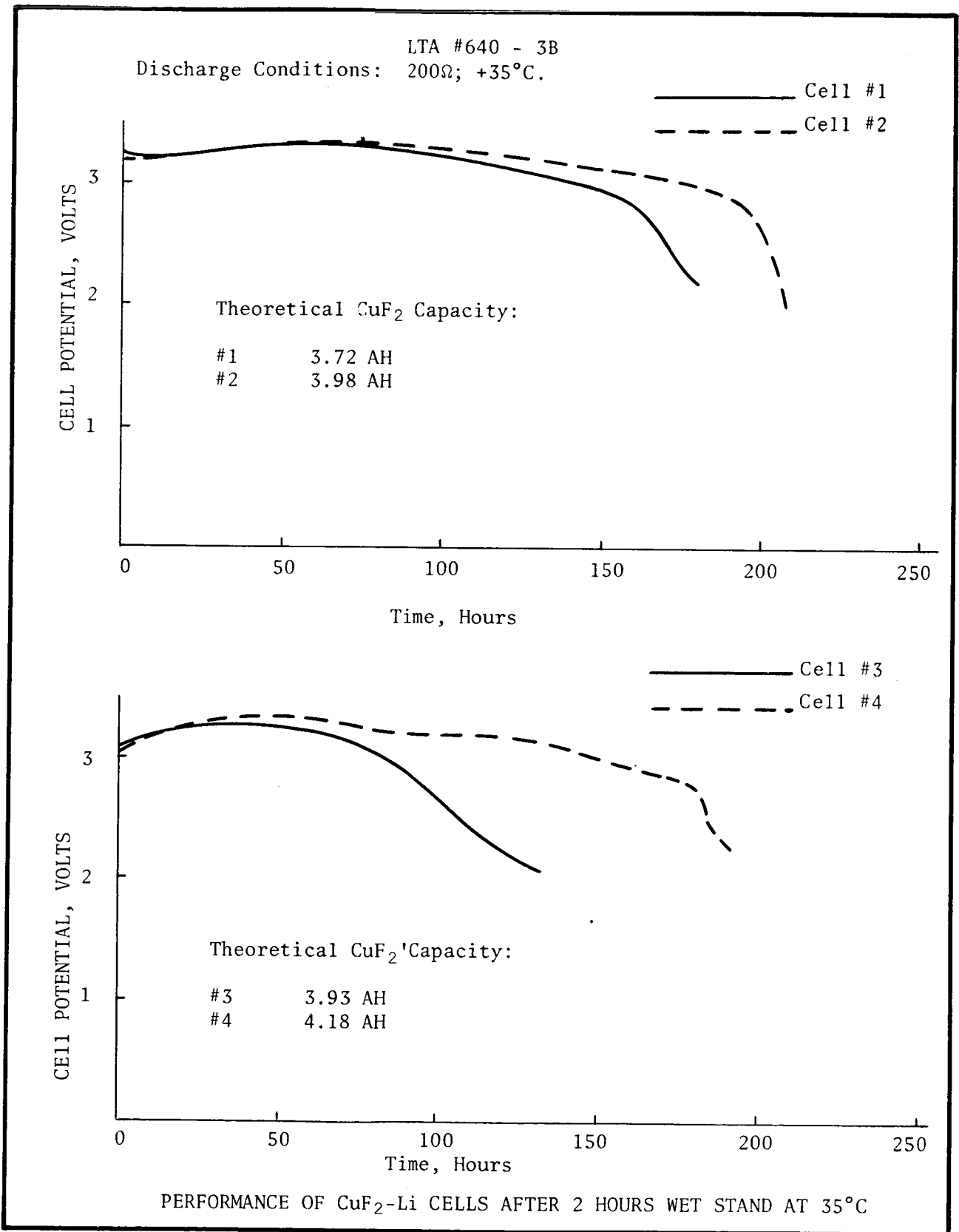


FIGURE 13

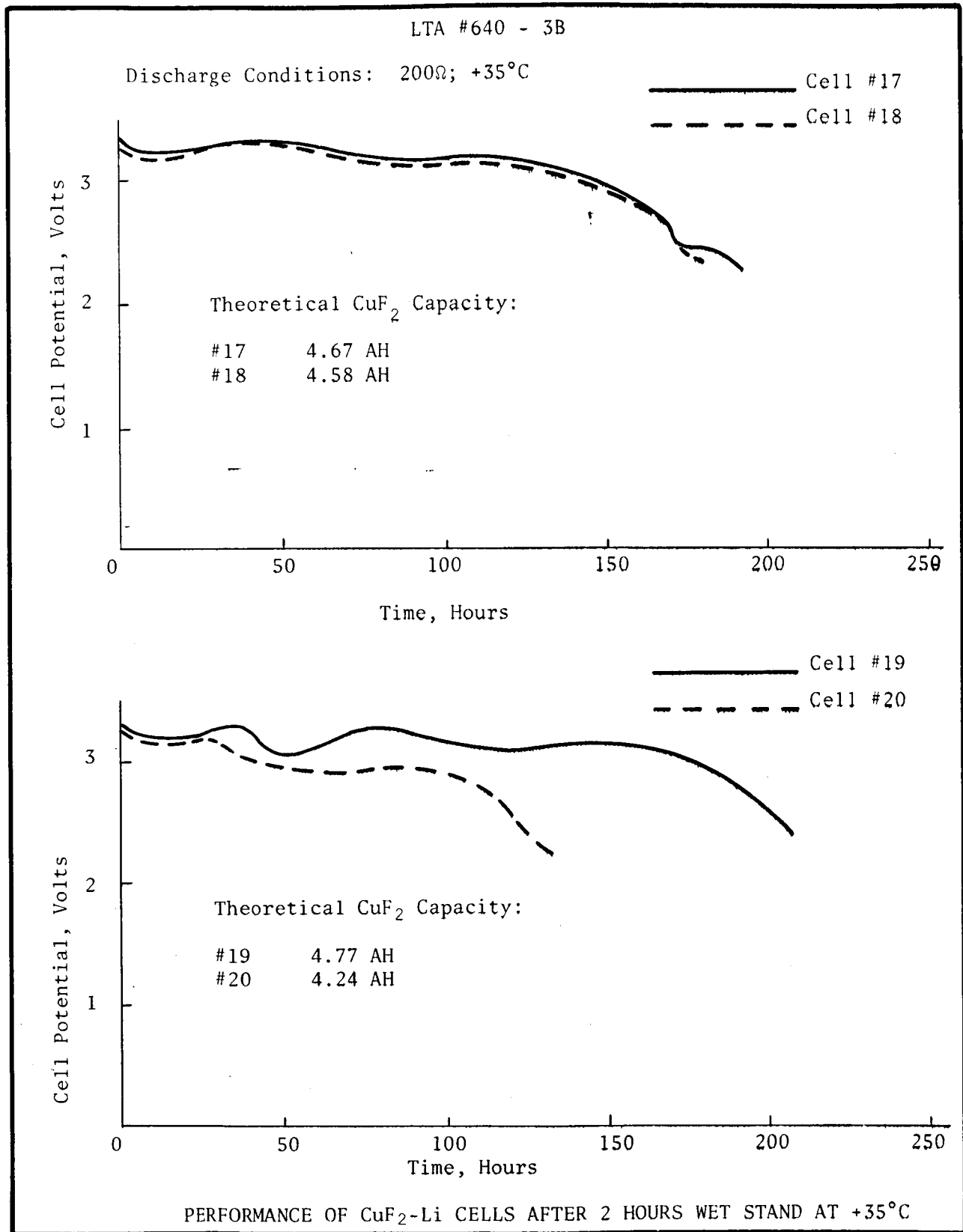


FIGURE 14

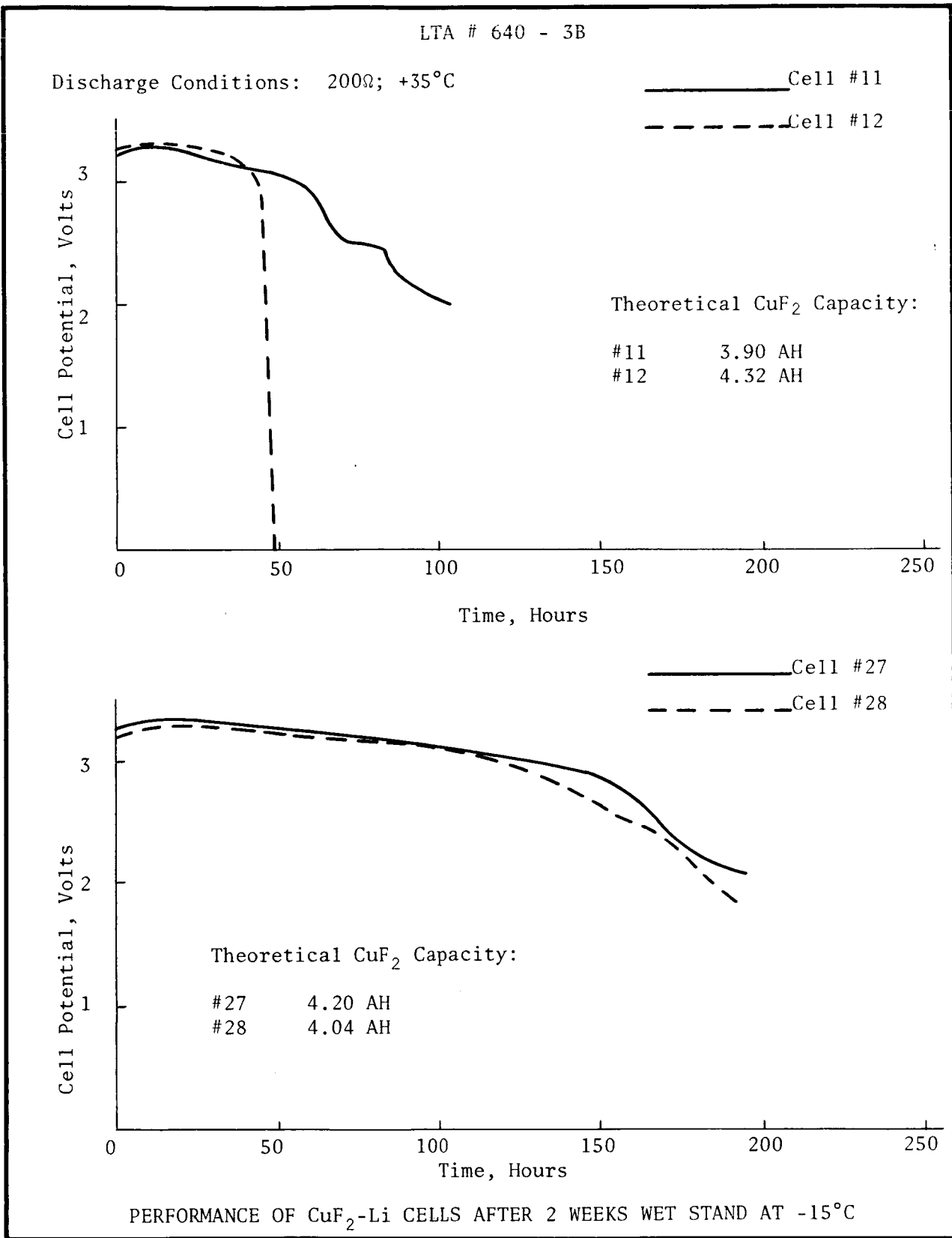


FIGURE 15



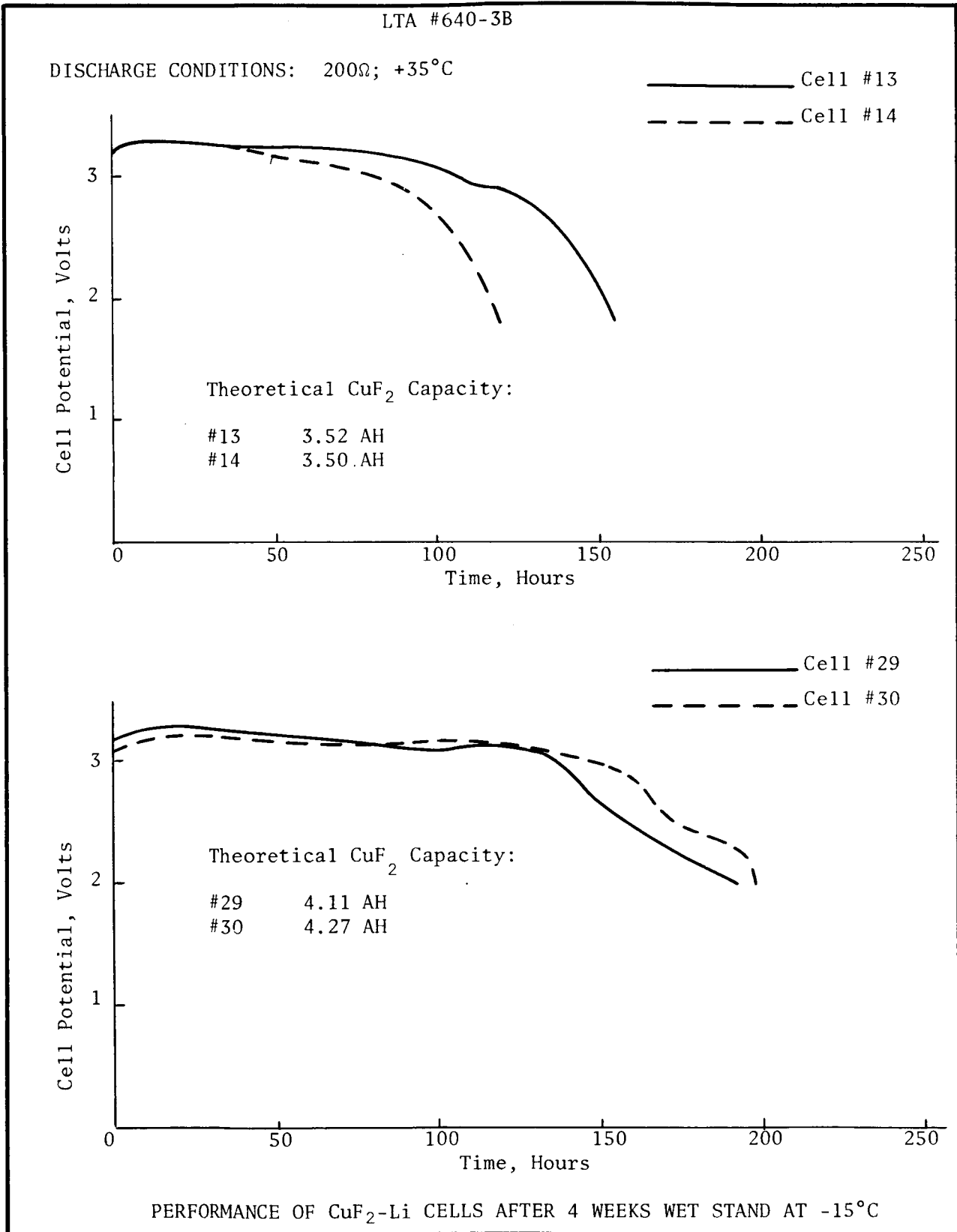


FIGURE 16

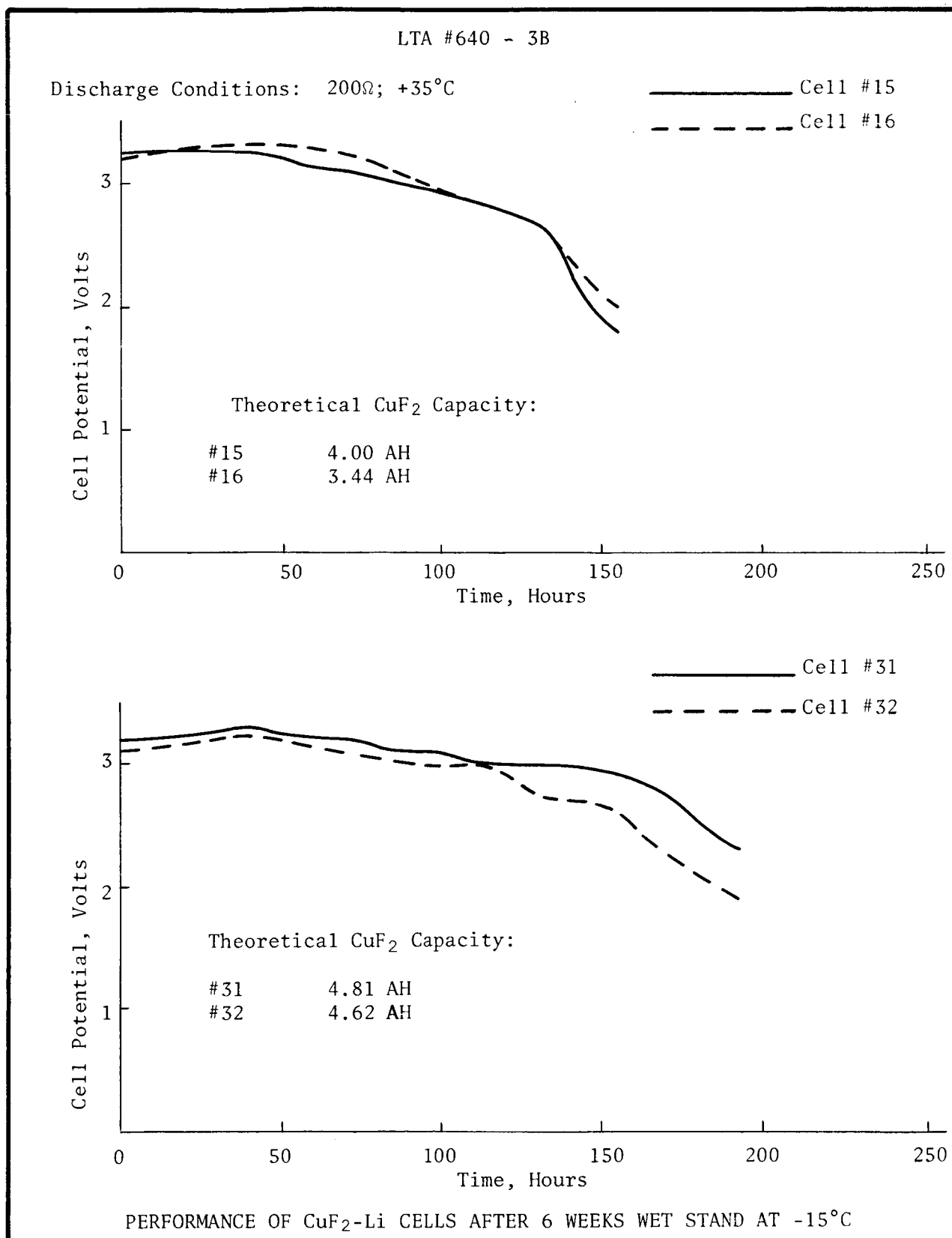
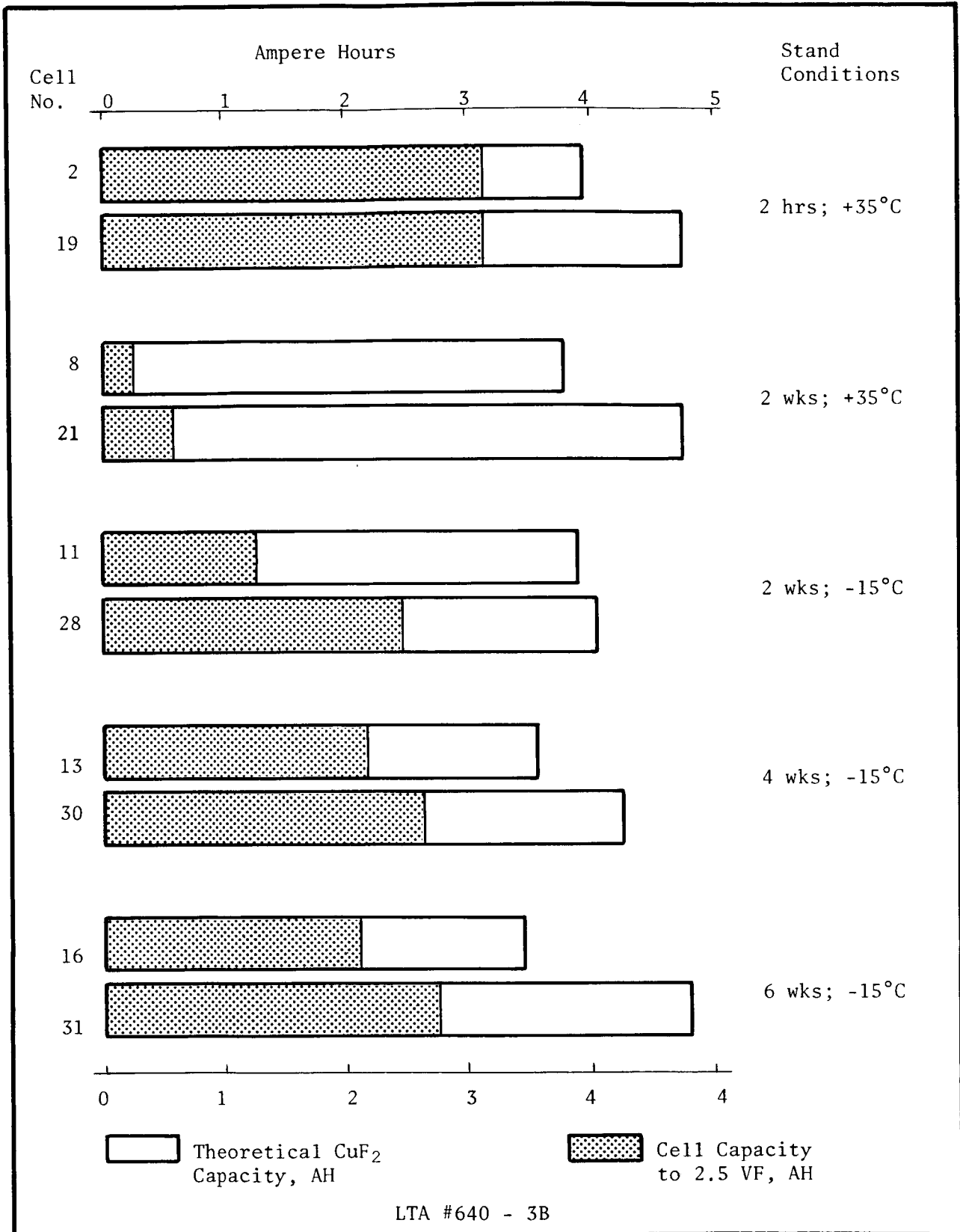


FIGURE 17



LTA #640 - 3B

CAPACITY LOSS IN  $\text{CuF}_2$ -Li CELLS AFTER WET STAND

FIGURE 18

Unknown Material*	63%
CuOHF	28%
CuOHF·CuF <sub>2</sub>	<u>12%</u>
Total	103%

\*Major peak intensity at 4.15 Å.

Filter mat electrodes were prepared by the method described previously.<sup>10</sup>  
The mix composition was

Active Material	104
Graphite	14
Paper Fiber	7

Twelve 3-plate CuF<sub>2</sub>-Li test cells were constructed and activated with 15g LiClO<sub>4</sub>/100 ml propylene carbonate electrolyte (water 50 ppm by Karl Fischer analysis). Groups of four cells were assembled and sealed (with cell terminals protruding) in polyethylene containers measuring 4 x 4 x 3 inches. Four cells were put on discharge thru 200Ω loads at 35°C, while the remaining cells were discharged under the same conditions after open circuit stand periods of 9 and 30 days at 35°C.

Discharge data for the cells are summarized in Table XXII, page 56, and cell open circuit potentials during stand are given in Table XXIII, page 57. Voltage-time data during discharge and open circuit stand have been plotted for the best cell in each group in Figures 19 and 20, pages 58 and 59.

In comparison to the normal CuF<sub>2</sub>, the decomposed CuF<sub>2</sub>·2H<sub>2</sub>O produced higher cell polarization with the 200Ω loads. All cells, except Cell #1, fell to below 2.5V after 4 hours of discharge (because of the distinctly green electrolyte color in Cell #1, it was suspected that this cell had been contaminated with water, possibly thru the use of an improperly dried hypodermic syringe). The positive active material utilization efficiency was likewise reduced, being about one-half of that obtainable from normal CuF<sub>2</sub>. Open circuit potential during stand, and capacity after stand were significantly improved, however. The average discharge potential of cells after 30 days of stand was higher than for cells which had no stand, with only a slight reduction in active material utilization.

The decomposed CuF<sub>2</sub>·2H<sub>2</sub>O appears to be reducible in the LiClO<sub>4</sub> propylene carbonate electrolyte, but its low solubility does not permit the normal

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<sup>10</sup>See page 41.

TABLE XXII  
 PERFORMANCE OF CELLS HAVING THERMALLY DECOMPOSED  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  CATHODES  
 AND LI ANODES IN  $\text{LiClO}_4$ -PC ELECTROLYTE

Cell No.	Theo. $\text{CuF}_2$ Cap., AH*	Initial O.C. Voltage	O.C. Stand Time, days	O.C. Voltage after stand	Discharge Time 2.0 VF, hours	Average Discharge Potential Volts	AH to 2.0VF	Percent Efficiency
1	3.96	3.52	0	----	129	2.85	1.84	47
2	4.05	3.52	0	----	136	2.33	1.58	39
3	4.33	3.52	0	----	148	2.32	1.72	40
4	3.96	3.52	0	----	119	2.30	1.37	35
5	4.08	3.52	9	3.42	<30	----	----	--
6	3.90	3.52	9	3.56	108	2.20	1.19	30
7	3.98	3.52	9	3.56	108	2.21	1.19	30
8	3.23	3.52	9	3.54	96	2.18	1.05	32
9	4.03	3.52	30	3.33	98	2.63	1.29	32
10	3.79	3.52	30	3.52	<12	----	----	--
11	3.97	3.53	30	3.33	104	2.77	1.44	36
12	3.73	3.52	30	3.53	43	2.27	.44	13

\*The equivalent weight for the material is assumed to be the same as for  $\text{CuF}_2(51)$ .

TABLE XXIII

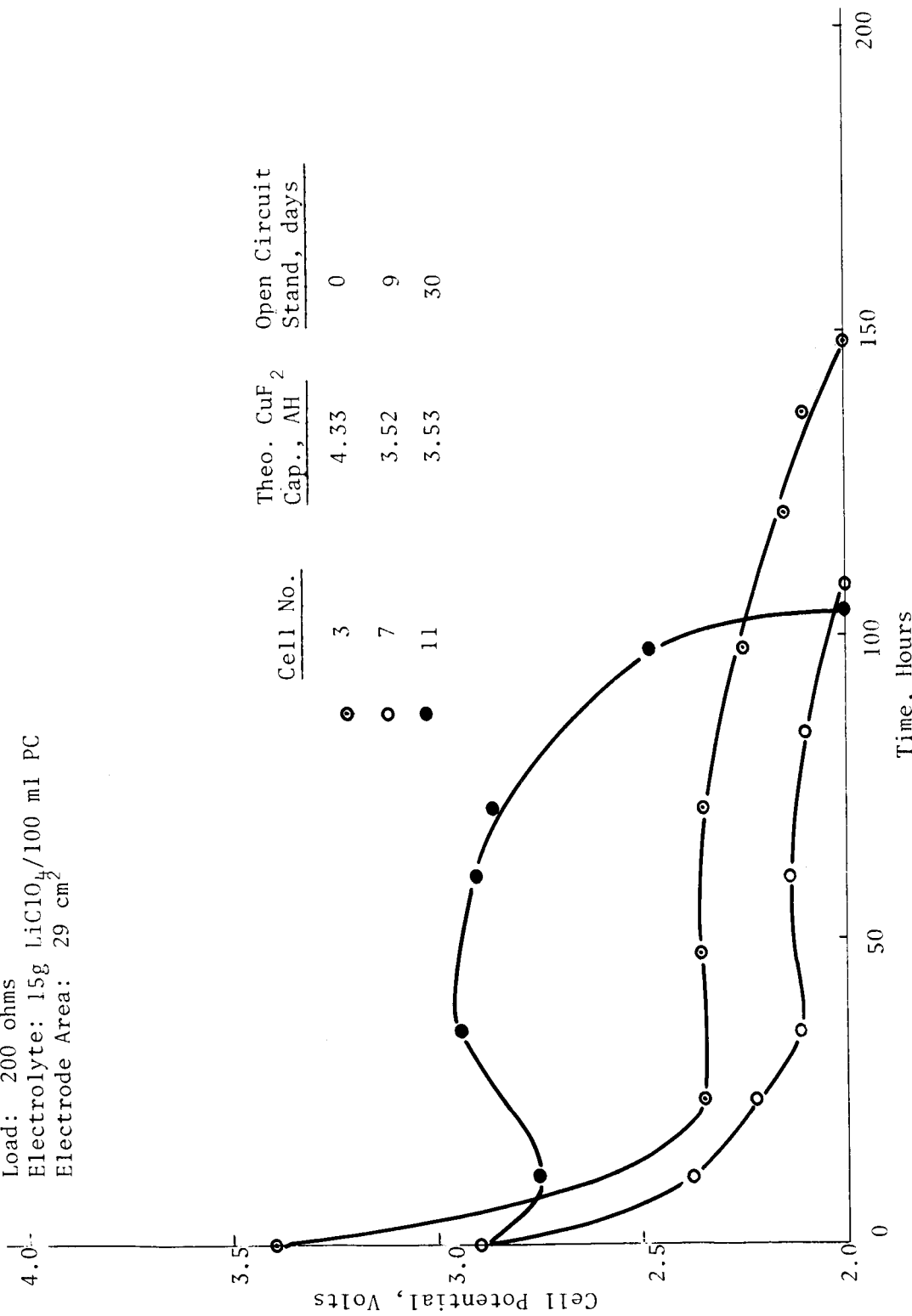
OPEN CIRCUIT POTENTIALS OF CELLS HAVING THERMALLY DECOMPOSED  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$

CATHODES AND LITHIUM ANODES IN  $\text{LiClO}_4$ -PC ELECTROLYTE

Temperature:  $35^\circ\text{C}$

Time on O.C., Days	Cell Numbers							
	5	6	7	8	9	10	11	12
0	3.52	3.52	3.52	3.52	3.52	3.52	3.53	3.52
3	3.59	3.59	3.59	3.58	3.59	3.59	3.60	3.58
4	3.58	3.58	3.58	3.57	3.58	3.58	3.59	3.57
5	3.58	3.57	3.58	3.56	3.57	3.57	3.58	3.56
6	3.57	3.56	3.57	3.55	3.56	3.57	3.57	3.56
7	3.56	3.56	3.56	3.54	3.55	3.56	3.56	3.55
9	3.42	3.56	3.56	3.54	3.55	3.56	3.56	3.55
11					3.52	3.55	3.42	3.54
12					3.51	3.53	3.37	3.53
13					3.51	3.53	3.36	3.50
18					3.50	3.50	3.30	3.52
19					3.50	3.52	3.40	3.52
20					3.45	3.52	3.42	3.52
25					3.35	3.53	3.45	3.52
26					3.37	3.55	3.37	3.52
30					3.33	3.52	3.33	3.53

LEC Test No. 640 - 18  
 Temperature: 35°C  
 Load: 200 ohms  
 Electrolyte: 15g LiClO<sub>4</sub>/100 ml PC  
 Electrode Area: 29 cm<sup>2</sup>

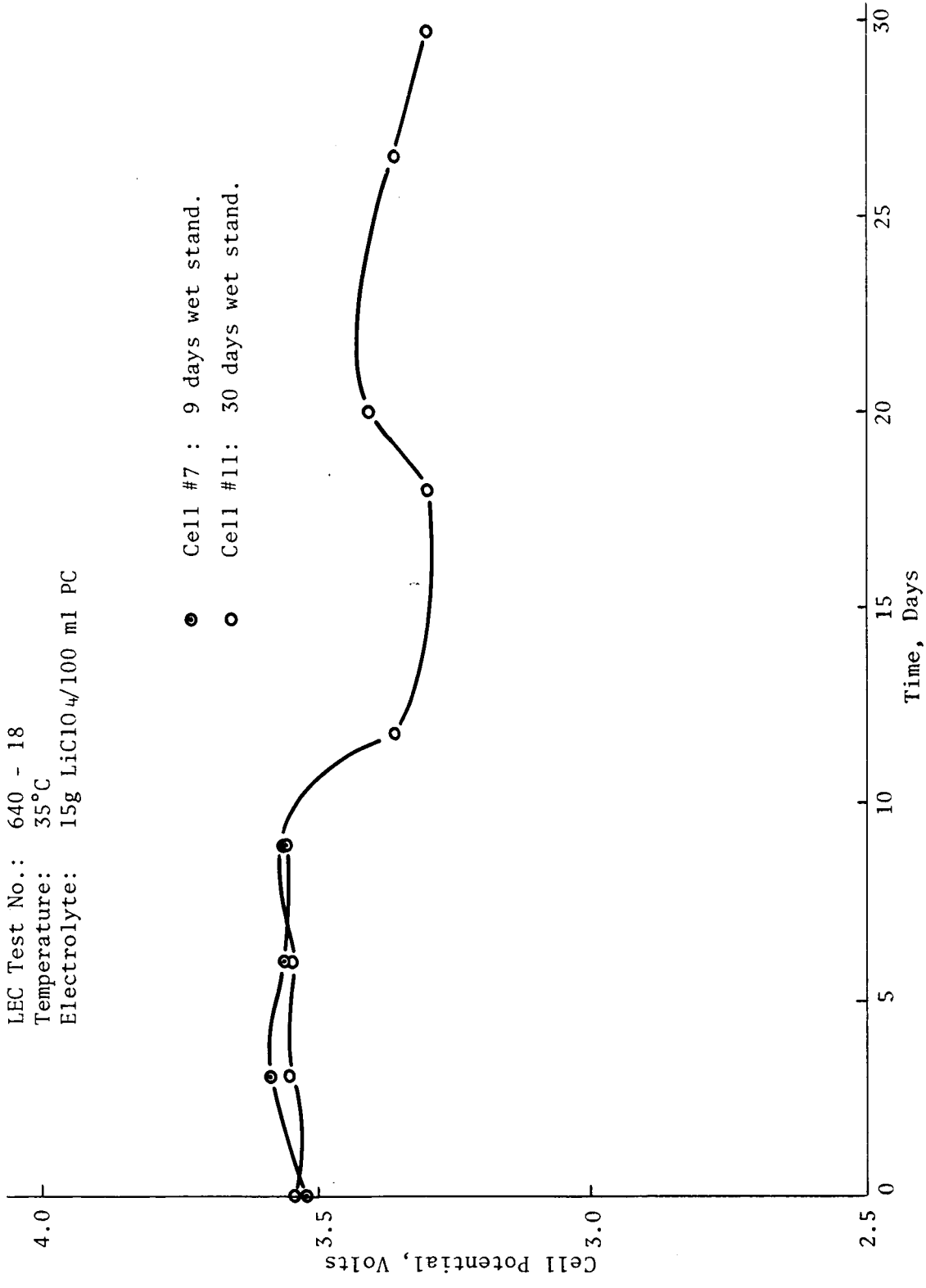


DISCHARGE PERFORMANCE OF CELLS WITH CuF<sub>2</sub> · 2H<sub>2</sub>O DECOMPOSITION PRODUCTS

FIGURE 19

LEC Test No.: 640 - 18  
Temperature: 35°C  
Electrolyte: 15g LiClO<sub>4</sub>/100 ml PC

● Cell #7 : 9 days wet stand.  
○ Cell #11: 30 days wet stand.



OPEN CIRCUIT POTENTIALS OF CELLS WITH CuF<sub>2</sub>·2H<sub>2</sub>O DECOMPOSITION PRODUCTS ON WET STAND

FIGURE 20



200 $\Omega$  discharge. The significantly better shelf life observed with this material can likewise be explained in terms of its lower solubility in the electrolyte solution. Further studies on this material are required to fully evaluate its properties and possible advantages over normal  $\text{CuF}_2$  as the active material of the cell.

### 2. 3. 3. Effect of $\text{CoF}_3$ , $\text{SbF}_3$ and $\text{MnF}_3$

Evaluation of additives to filter mat  $\text{CuF}_2$  electrodes was undertaken in order to study methods for improving shelf life of  $\text{CuF}_2$ -Li cells having propylene carbonate electrolyte. Since it had been demonstrated that presence of water is detrimental to shelf life, materials which are known to react with water were selected for addition to  $\text{CuF}_2$  during preparation of the electrodes. It was hoped that these additives would decompose the water released by  $\text{CuF}_2$  during stand, thus reducing its solubility in the electrolyte solution and improving capacity retention of the cells.

The additives selected for testing were  $\text{CoF}_3$  and  $\text{MnF}_3$  at a concentration of 4 grams/100 gram of  $\text{CuF}_2$ , and  $\text{SbF}_3$  at 6 grams/100 gram  $\text{CuF}_2$  (the concentration of additive being roughly proportional to its molecular weight). These were added to  $\text{CuF}_2$  prior to jar milling with graphite under heptane. The filter mat composition for construction of the electrodes was 100 parts  $\text{CuF}_2$ , 14 parts graphite, and 7 parts paper fiber, plus additive. Electrodes were prepared as described previously<sup>11</sup> by pressing 1.5 x 1.5 in. sections of the filter mat onto expanded silver and removing the residual heptane by vacuum drying. Three-electrode cells with outside lithium electrodes and MPR separation were constructed and tested for performance with  $\text{LiClO}_4$ -PC electrolyte (15 grams salt/100 ml solvent).

Six cells with each type additive, along with six having no additive, were constructed and tested. Two cells from each group were discharged thru 200 $\Omega$  at 35°C after one day of open circuit stand at 35°C; the remaining cells were discharged after stand periods of 8 and 14 days at 35°C.

Construction and discharge data for the cells are summarized in TABLE XXIV, page 61, while the open circuit potentials of cells during stand are listed in Table XXV, page 62. Voltage-time data for the best cell in each group are presented in Figures 21 to 24, pages 63 to 66.

<sup>11</sup> See appendix, Table A-9, page 140.

TABLE XXIV  
DISCHARGE PERFORMANCE OF  $\text{CuF}_2$ -Li CELLS CONTAINING ADDITIVES

Cell No.	Additive	Grams Additive 100g $\text{CuF}_2$	Theo. $\text{CuF}_2$ Cap., AH*	Stand Time @ +35°C days	Discharge Time to 2.5VF, hrs.	Average Discharge		AH to 2.5 VF	Cathode Eff., %
						Potential Volts	Time		
1-1	----	-	3.97	1	202	3.12	3.15	80	
1-2	----	-	3.96	1	202	3.11	3.14	79	
2-3	CoF <sub>3</sub>	4	4.08	1	187	3.05	2.86	70	
2-4	CoF <sub>3</sub>	4	3.97	1	177	3.04	2.69	68	
3-5	SbF <sub>3</sub>	6	4.12	1	144	2.95	2.12	52	
3-6	SbF <sub>3</sub>	6	3.89	1	132	2.84	1.87	48	
4-1	MnF <sub>3</sub>	4	3.84	1	157	3.00	2.56	61	
4-2	MnF <sub>3</sub>	4	3.74	1	190	3.03	2.88	77	
1-5	----	-	3.77	8	88	2.89	1.27	34	
1-6	----	-	3.66	8	104	2.94	1.53	42	
2-1	CoF <sub>3</sub>	4	3.88	8	86	2.83	1.22	31	
2-2	CoF <sub>3</sub>	4	3.63	8	40	2.95	0.59	16	
3-3	SbF <sub>3</sub>	6	4.13	8	0	----	----	--	
3-4	SbF <sub>3</sub>	6	3.70	8	0	----	----	--	
4-3	MnF <sub>3</sub>	4	3.63	8	84	2.83	1.19	33	
4-4	MnF <sub>3</sub>	4	3.80	8	118	2.91	1.72	45	
1-3	----	-	3.69	14	39	2.81	0.55	15	
1-4	----	-	3.66	14	0	----	----	0	
2-5	CoF <sub>3</sub>	4	3.70	14	0	----	----	0	
2-6	CoF <sub>3</sub>	4	3.93	14	41	2.76	0.57	14	
3-1	SbF <sub>3</sub>	6	3.84	14	0	----	----	0	
3-2	SbF <sub>3</sub>	6	4.13	14	0	----	----	0	
4-5	MnF <sub>3</sub>	4	3.07	14	35	2.73	0.48	16	
4-6	MnF <sub>3</sub>	4	4.22	14	1	----	----	--	

\* Based on  $\text{CuF}_2$  only.

TABLE XXV

OPEN CIRCUIT POTENTIALS OF  $\text{CuF}_2$ -Li CELLS CONTAINING ADDITIVES

Electrolyte: 15g  $\text{LiClO}_4/100$  ml PC  
 Temperature: 35°C

Cell No.	Additive	Open Circuit Potential														
		0 day	1 day	4 days	6 days	7 days	8 days	9 days	11 days	12 days	13 days	14 days				
1-1	----	3.69	3.63													
1-2	----	3.68	3.64													
2-3	$\text{CoF}_3$	3.73	3.71													
2-4	$\text{CoF}_3$	3.74	3.71													
3-5	$\text{SbF}_3$	3.68	3.58													
3-6	$\text{SbF}_3$	3.68	3.61													
4-1	$\text{MnF}_3$	3.74	3.66													
4-2	$\text{MnF}_3$	3.74	3.67													
1-5	----	3.69	----	3.35	3.35	3.35	3.35	3.35	3.35	3.35	3.30	3.30	3.30	3.30	3.30	3.30
1-6	----	3.67	----	3.38	3.34	3.34	3.34	3.34	3.34	3.34	3.25	3.25	3.25	3.25	3.25	3.25
2-1	$\text{CoF}_3$	3.63	----	3.37	3.30	3.30	3.28	3.28	3.28	3.28	3.20	3.20	3.20	3.20	3.20	3.20
2-2	$\text{CoF}_3$	3.71	----	3.42	3.32	3.32	3.22	3.22	3.22	3.22	3.30	3.30	3.30	3.30	3.30	3.30
3-3	$\text{SbF}_3$	3.67	----	3.13	2.66	2.66	2.70	2.70	2.70	2.70	2.50	2.50	2.50	2.50	2.50	2.50
3-4	$\text{SbF}_3$	3.67	----	3.21	2.80	2.80	2.61	2.61	2.61	2.61	2.35	2.35	2.35	2.35	2.35	2.35
4-3	$\text{MnF}_3$	3.72	----	3.31	3.24	3.24	3.26	3.26	3.26	3.26	3.20	3.20	3.20	3.20	3.20	3.20
4-4	$\text{MnF}_3$	3.73	----	3.32	3.21	3.21	3.17	3.17	3.17	3.17	3.10	3.10	3.10	3.10	3.10	3.10
1-3	----	3.64	----	3.41	3.33	3.33	3.31	3.31	3.31	3.31	3.30	3.30	3.30	3.30	3.30	3.30
1-4	----	3.65	----	3.42	3.30	3.30	3.24	3.24	3.24	3.24	3.05	3.05	3.05	3.05	3.05	3.05
2-5	$\text{CoF}_3$	3.73	----	3.38	3.30	3.30	3.30	3.30	3.30	3.30	3.20	3.20	3.20	3.20	3.20	3.20
2-6	$\text{CoF}_3$	3.71	----	3.40	3.23	3.23	3.01	3.01	3.01	3.01	0.85	0.85	0.85	0.85	0.85	0.85
3-1	$\text{SbF}_3$	3.67	----	3.19	2.63	2.63	2.94	2.94	2.94	2.94	2.85	2.85	2.85	2.85	2.85	2.85
3-2	$\text{SbF}_3$	3.67	----	3.13	2.88	2.88	2.87	2.87	2.87	2.87	2.85	2.85	2.85	2.85	2.85	2.85
4-5	$\text{MnF}_3$	3.70	----	3.53	3.25	3.25	3.20	3.20	3.20	3.20	3.15	3.15	3.15	3.15	3.15	3.15
4-6	$\text{MnF}_3$	3.70	----	3.34	3.17	3.17	3.13	3.13	3.13	3.13	3.15	3.15	3.15	3.15	3.15	3.15

CELLS PUT IN DISCHARGE AFTER 1 DAY OF WET STAND

WET STAND

CELLS PUT IN DISCHARGE AFTER 8 DAYS OF WET STAND

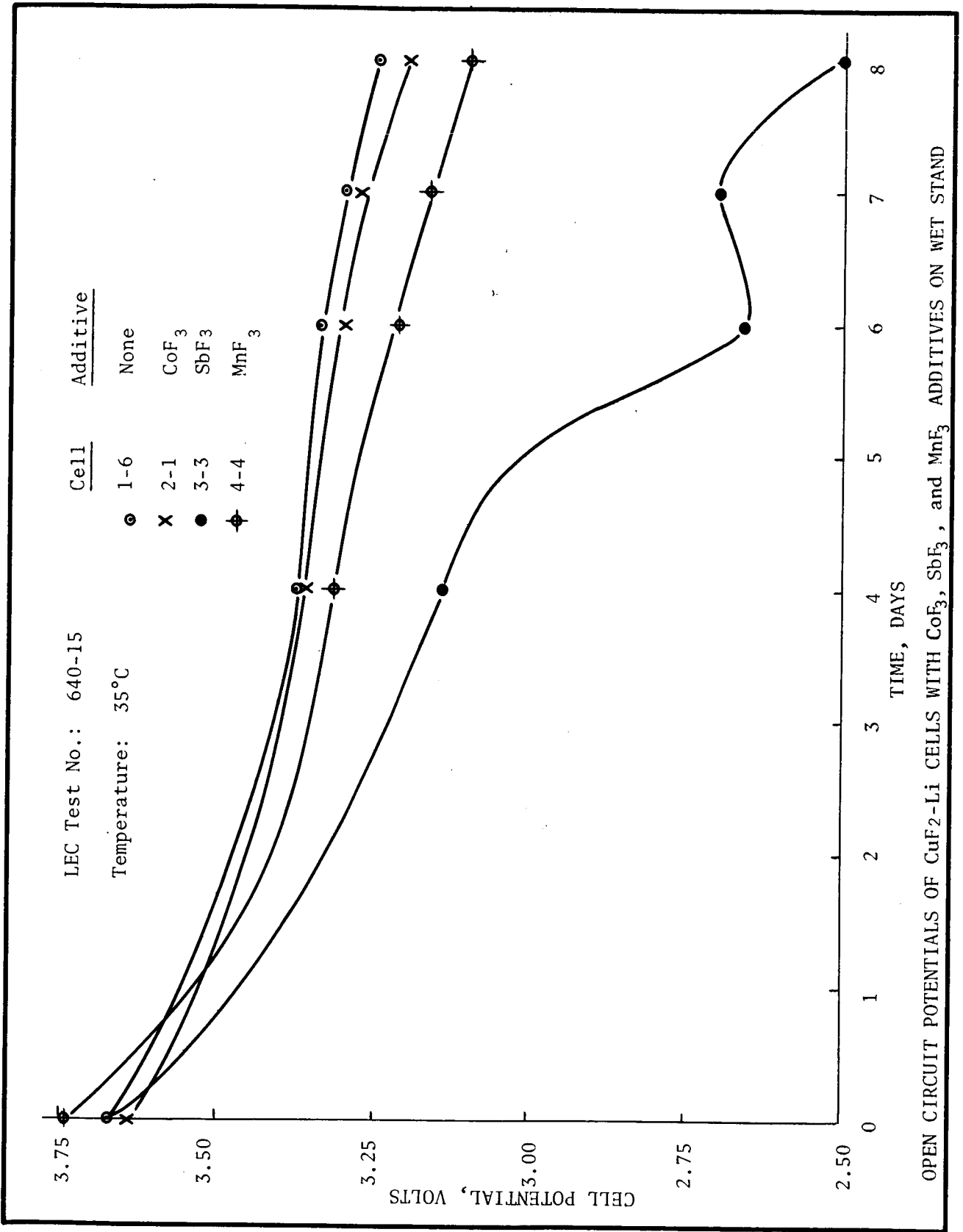


FIGURE 21

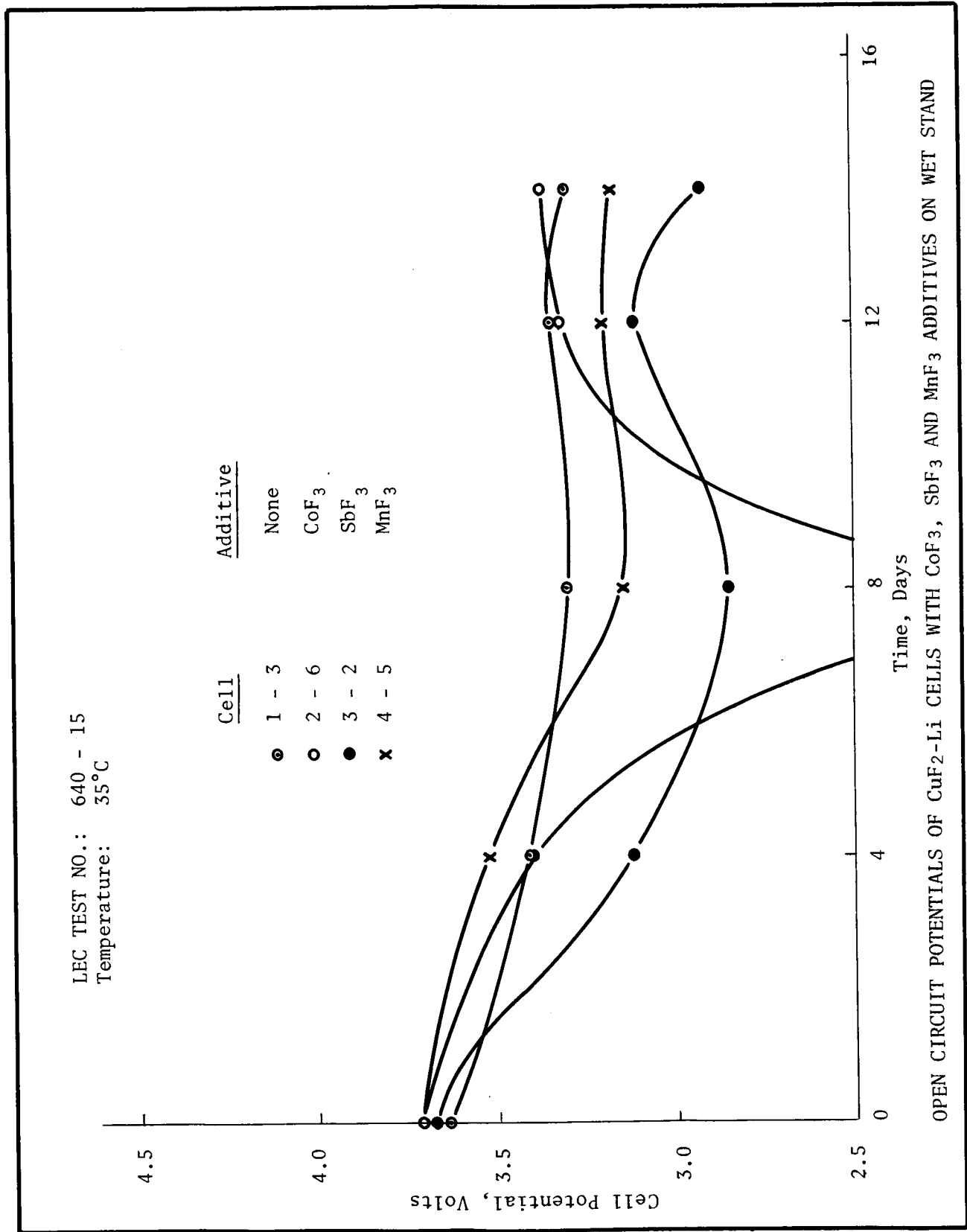


FIGURE 22

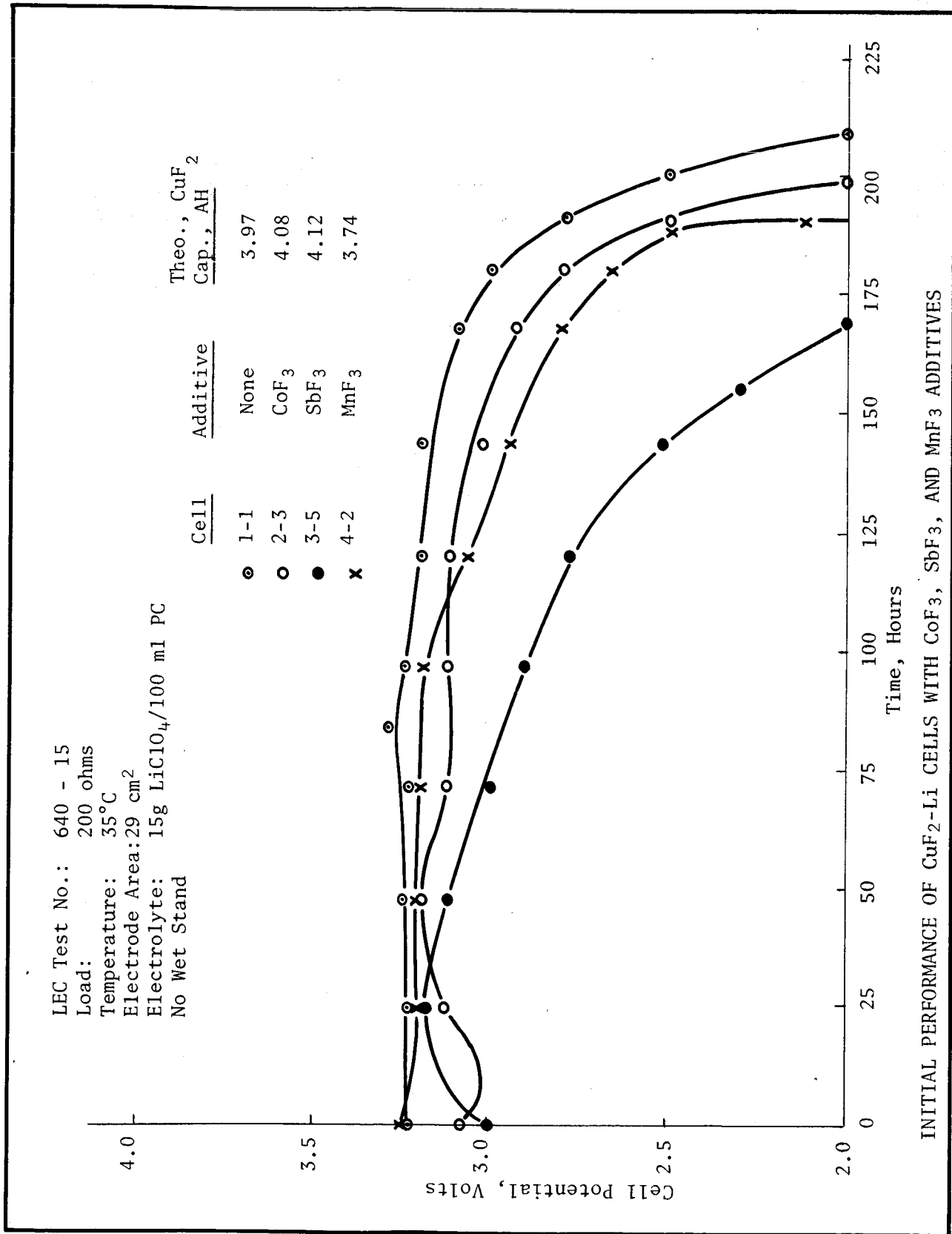


FIGURE 23

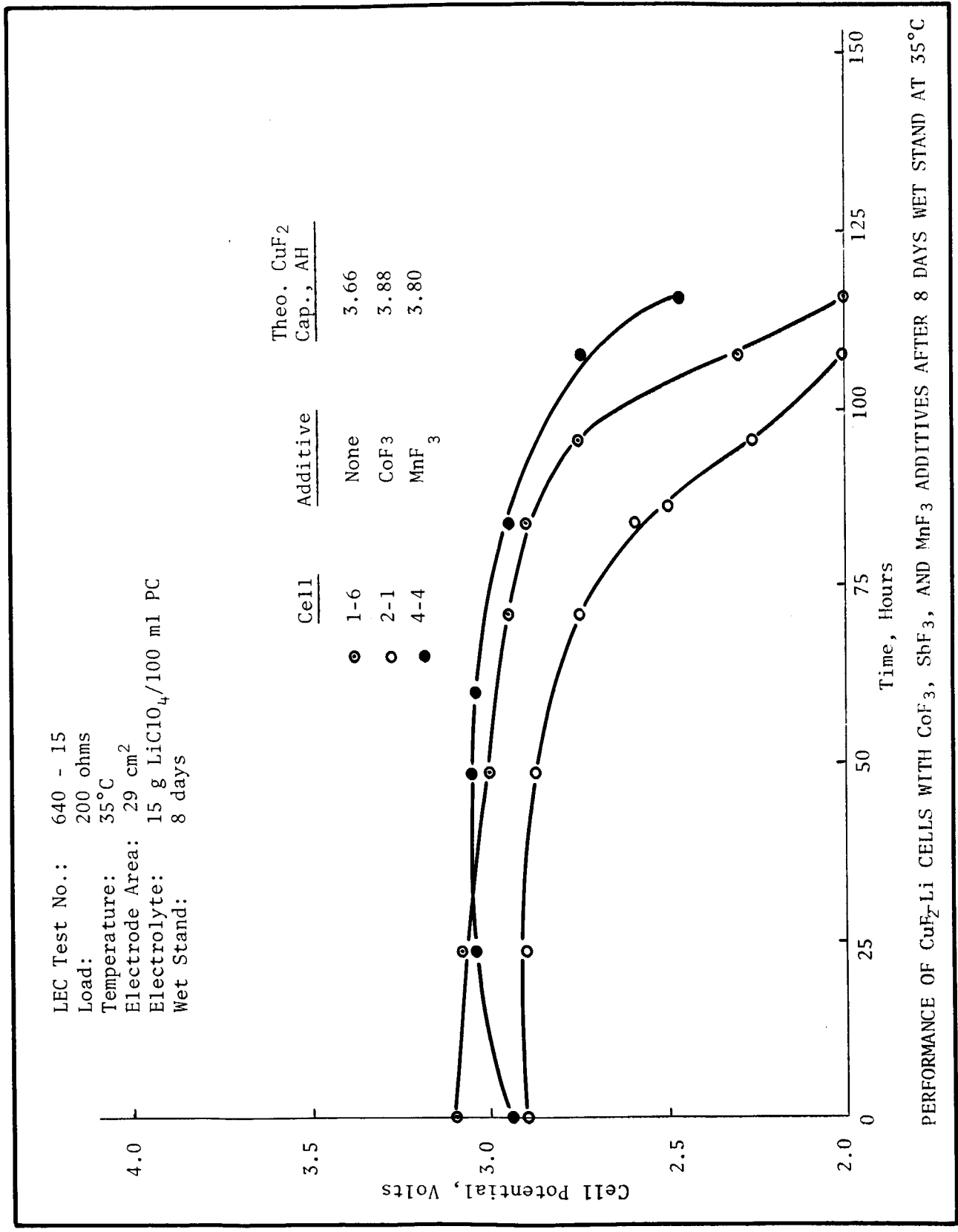


FIGURE 24

Addition of  $\text{SbF}_3$  had a clearly detrimental effect on both discharge capacity and capacity retention after stand. Addition of  $\text{CoF}_3$  and  $\text{MnF}_3$  appeared to have no significant effect on the characteristics of the cells. These cells suffered an average capacity loss of about 50 percent after 8 days stand at  $35^\circ\text{C}$ . After 14 days at the same temperature, only half of the cells had retained any capacity above a load potential of 2.5 volts. Inspection of the cells after discharge indicated that dissolution of the  $\text{CuF}_2$  had taken place, which appears to be the main cause of capacity loss during stand.

#### 2. 3. 4. Filter Mat $\text{CuF}_2$ Electrode Construction Studies

A series of cell discharge tests were performed to study the effect of filter mat composition and method of electrolyte addition on cell performance. The quantity of  $\text{CuF}_2$  per unit electrode area was held at approximately 1.8 gram  $\text{CuF}_2/\text{sq. in.}$ , while the weights of graphite and paper fiber were varied. Electrode and cell construction were as described previously.<sup>12</sup>

##### 2. 3. 4. 1. Ratio of $\text{CuF}_2$ To Additives

In this test series, cells were activated with electrolyte consisting of 15 grams of  $\text{LiClO}_4$  dissolved in 100 ml of propylene carbonate. The water content of the electrolyte solution as determined by Karl Fischer analysis was 140 ppm, while the  $\text{CuF}_2$  used for preparing the filter mat electrodes contained 1.2 percent of water as determined by X-ray analysis.

After activation with the electrolyte solution, the cells were allowed to stand on open circuit for four hours, and were then put in discharge at  $35^\circ\text{C}$  thru 200 or 100 ohm loads. Construction data and performance of the cells to a final voltage of 2.5 volts are presented in Tables XXVI and XXVII, pages 68 and 69. (The variation in theoretical  $\text{CuF}_2$  capacity was caused by non-uniformities in filter mat thickness). Volt-age-time curves for some typical discharges are shown in Figures 25 and 26, pages 70 and 71.

Inspection of the cells at the end of discharge showed that, in a number of cells the  $\text{CuF}_2$  electrode matrix had not been completely penetrated by the electrolyte solution. This condition was more prevalent in cells which had a high weight ratio of graphite to paper fiber in the  $\text{CuF}_2$

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<sup>12</sup> See page 41.



TABLE XXVI  
 FILTER-MAT CuF<sub>2</sub> ELECTRODE TESTS, 200-OHM DISCHARGE

Cell No.	Additive grams/100g CuF <sub>2</sub>		Theo. Cap., AH	Electrolyte Volume, cc	Average Discharge Potential	A-min/gram Positive Electrode	CuF <sub>2</sub> Efficiency %
	Graphite	Paper Fiber					
5-1	2	2	4.42	5.0	3.01	16.7	57
5-3	2	2	4.13	6.5	3.05	16.3	53
6-1	4	2	3.92	6.0	3.13	20.6	72
6-3	4	2	4.54	5.5	3.10	19.4	67
7-1	8	2	3.75	6.0	3.11	18.0	65
7-3	8	2	3.76	5.5	3.10	18.9	65
8-1	14	2	3.92	6.0	3.11	18.1	69
8-3	14	2	3.80	7.5	2.82	15.1	58
9-1	4	4	5.05	5.5	----	----	--
9-3	4	4	3.67	4.0	3.10	17.3	61
10-1	8	4	4.34	6.5	3.00	17.8	63
10-3	8	4	4.75	5.5	3.17	15.6	57
11-1	14	4	3.90	6.5	3.14	18.9	73
11-3	14	4	3.41	7.0	3.14	19.6	76
12-1	20	4	4.44	6.5	3.12	17.9	72
12-3	20	4	4.13	6.5	3.18	20.1	81
13-1	4	8	4.35	6.0	3.14	18.9	69
13-3	4	8	5.03	6.5	3.08	18.5	67
14-1	8	8	4.13	6.0	3.11	19.1	72
14-3	8	8	3.70	5.5	3.12	20.6	78
15-1	14	8	4.19	7.0	3.13	20.3	81
15-3	14	8	3.26	5.0	3.00	15.2	61
16-1	20	8	3.98	7.0	3.03	14.2	59
16-3	20	8	4.28	5.0	3.05	9.5	40

Electrode Area: 29 cm<sup>2</sup>  
 Electrolyte: 15g LiClO<sub>4</sub>/100 ml PC  
 Temperature: 35°C

TABLE XXVII

FILTER-MAT CuF<sub>2</sub> ELECTRODE TESTS, 100-OHM DISCHARGE

Cell No.	Additive grams/100g CuF <sub>2</sub>		Theo. Cap., AH	Electrolyte Volume, cc	Average Discharge Potential	A-min/gram Positive Electrode	CuF <sub>2</sub> Efficiency, %
	Graphite	Paper Fiber					
5-2	2	2	4.45	5.5	2.79	15.5	53
5-4	2	2	3.55	5.5	2.69	13.2	45
6-2	4	2	4.16	5.5	2.81	17.5	61
6-4	4	2	4.10	5.5	2.69	16.9	59
7-2	8	2	3.76	5.5	2.81	17.9	65
7-4	8	2	4.00	5.0	2.84	16.3	59
8-2	14	2	3.94	5.0	2.92	8.2	31
8-4	14	2	3.71	5.0	2.88	14.0	53
9-2	4	4	4.61	6.0	2.90	15.6	55
9-4	4	4	3.29	5.0	2.84	16.7	61
10-2	8	4	3.39	5.0	3.02	14.4	53
10-4	8	4	3.77	6.5	2.90	17.3	63
11-2	14	4	4.17	5.5	3.00	13.1	50
11-4	14	4	3.67	5.5	2.88	14.0	54
12-2	20	4	3.86	5.0	2.97	12.6	51
12-4	20	4	4.47	7.0	2.91	12.0	48
13-2	4	8	4.85	6.0	2.67	6.1	22
13-4	4	8	4.31	6.0	2.72	13.9	51
14-2	8	8	3.38	5.0	2.94	13.7	52
14-4	8	8	3.52	6.0	2.82	14.9	57
15-2	14	8	3.58	5.5	2.92	11.0	44
15-4	8	8	4.18	6.0	2.78	14.8	59
16-2	20	8	4.23	5.0	-----	-----	--
16-4	20	8	4.28	7.0	2.88	12.4	51

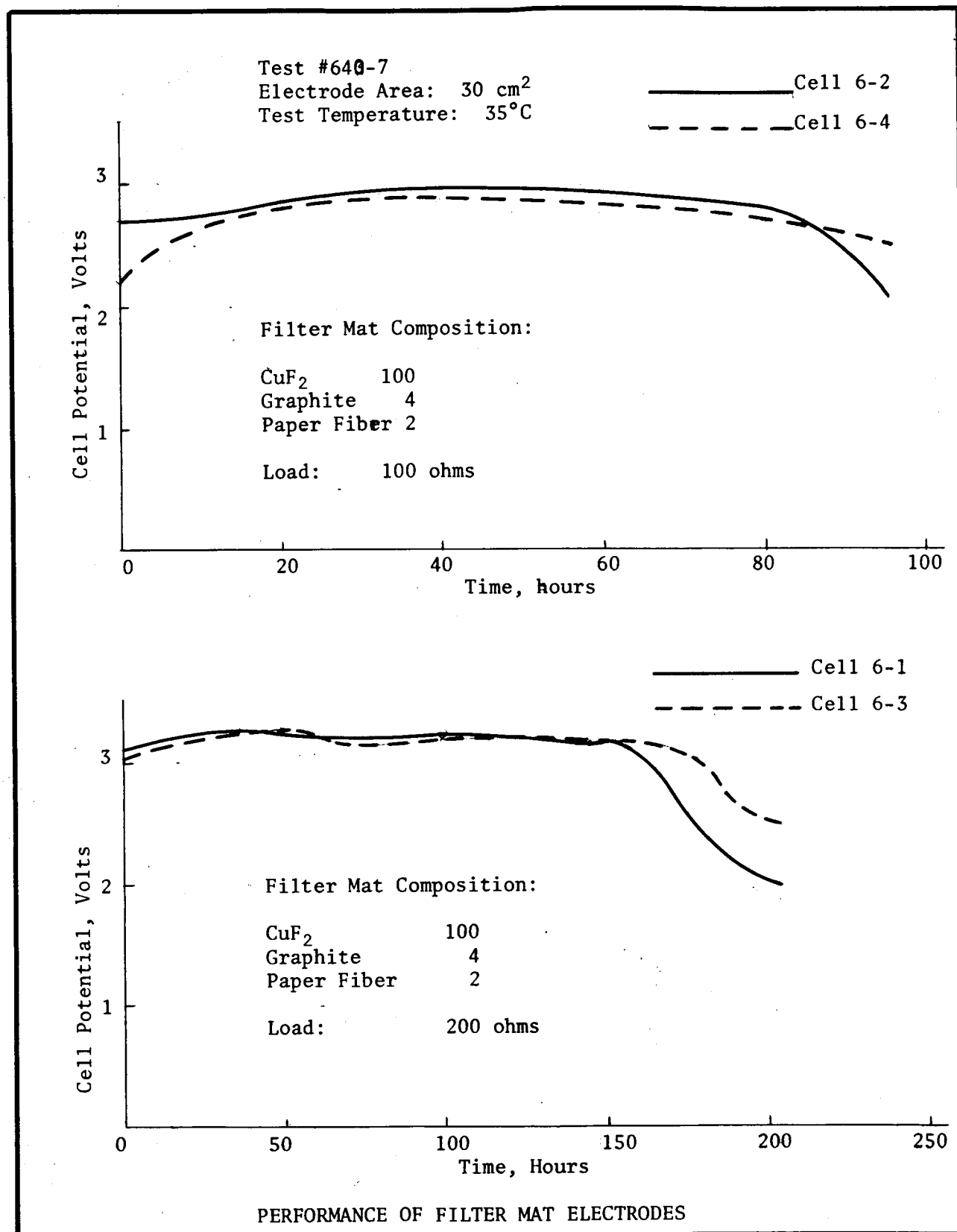


FIGURE 25

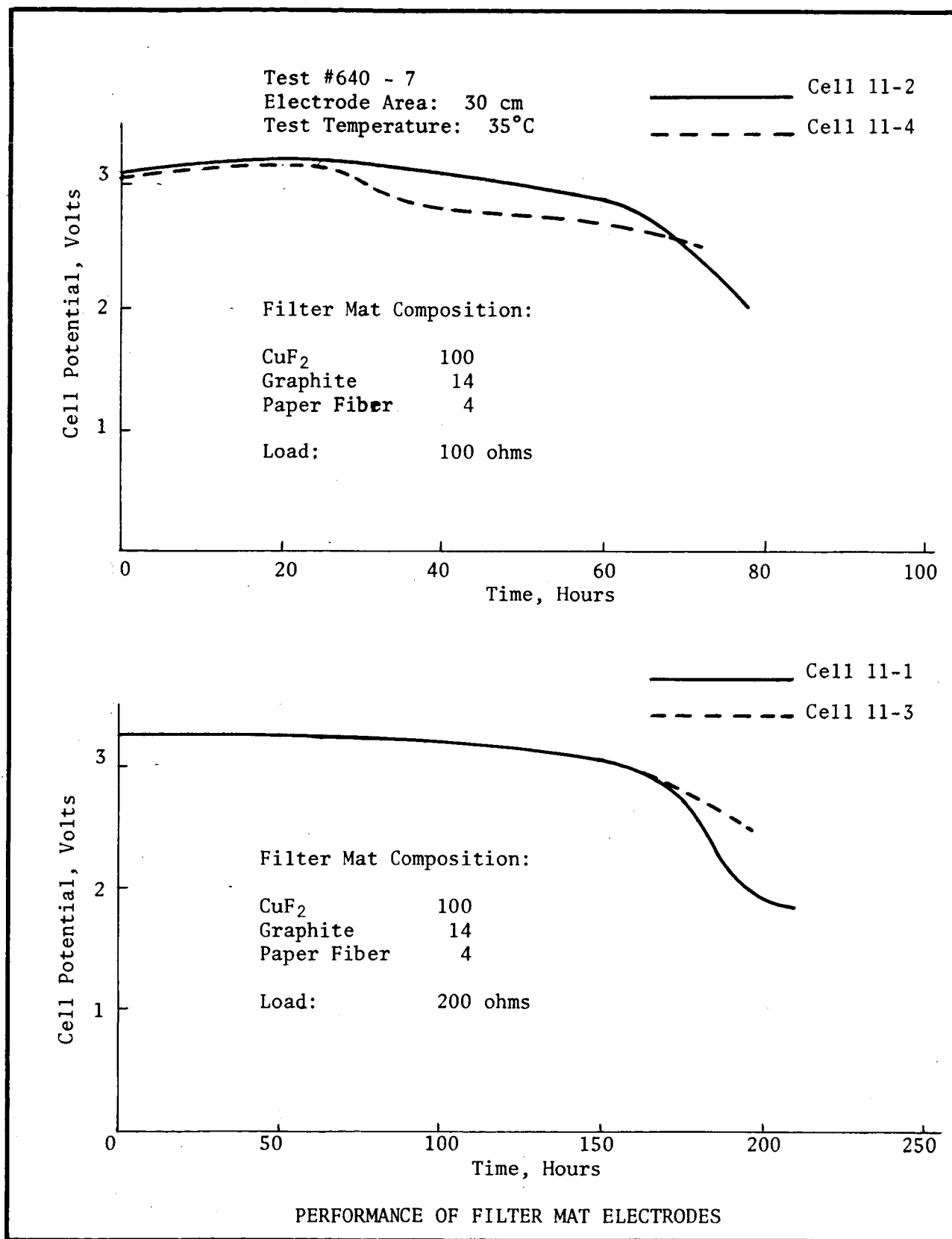


FIGURE 26

electrode matrix. The variation in electrolyte volume figures presented in Tables XXVI and XXVII, probably reflects the poor wetting properties of the graphite and probably affected the discharge performance of some cells.

With the 200 $\Omega$  discharge loads (ca. 0.5 mA/cm<sup>2</sup>) efficiency of the CuF<sub>2</sub> electrode was as high as 81 percent to a final cell voltage of 2.5 volts, while with 100 $\Omega$  load the highest efficiency figure recorded was 65%. Optimum fiber concentration appeared to be in the range of 4 to 8 grams per 100g of CuF<sub>2</sub>, and the best graphite level was in the range of 8 - 20 grams per 100g of CuF<sub>2</sub>. However, some efficient discharges did occur with cells having additive levels outside the above described ranges.

#### 2. 3. 4. 2. Effect of Vacuum Impregnation

To study the effect of cathode wetting on cell performance, several cathode compositions and vacuum impregnation of cells with the electrolyte were studied.

In this series, four test cells for each positive electrode composition were constructed and tested. The filter mat electrodes were prepared as described previously, and the graphite and paper pulp concentrations were varied over the range of 4 - 16 and 2 - 8 grams/100g CuF<sub>2</sub>(0.5% H<sub>2</sub>O), respectively. The test cells had the usual sandwich construction with one filter mat CuF<sub>2</sub> electrode, and two lithium slab electrodes separated by 0.03 in. microporous rubber.

After addition of the electrolyte (15g LiClO<sub>4</sub>/100 ml PC, 50 ppm water), two cells in each group were placed in a desiccator and maintained under vacuum until no further gassing from the electrodes and separators could be observed. The vacuum was then released, and the electrolyte levels in the cells were adjusted to the previous height. The remaining two cells in each group were filled by the normal procedure. Discharges were then started at a constant current of 21 mA and a temperature of 35°C. A summary of construction and discharge data for the cells is given in Table XXVIII, page 73 and 74. Electrolyte volume for cells 1-1 thru 3-4 was not obtained because leaks in the polyethylene envelopes caused an undetermined amount of loss during filling.

Considerable variation in CuF<sub>2</sub> reduction efficiency among replicate cells was encountered over the entire composition range. The highest efficiencies were obtained with cells having the highest graphite content (16g/100g CuF<sub>2</sub>). However, increasing the paper fiber content appeared to affect the performance adversely, which may be an indication that this material (S & S filter paper pulp, acid washed) causes some contamination in the cell. It may be possible to replace some of the filter paper pulp with another, preferably conductive, fibrous material (such as graphite fibers).

TABLE XXVIII

EFFECT OF ADDITIVE CONCENTRATION ON PERFORMANCE OF  $\text{CuF}_2$  ELECTRODES

Electrode Area:  $29 \text{ cm}^2$  Electrolyte:  $15\text{g LiClO}_4/100 \text{ ml PC}$   
 Temperature:  $35^\circ\text{C}$  Load:  $21 \text{ mA}$

Cell No.	Grams		% $\text{CuF}_2$ in mix	Theo. $\text{CuF}_2$ Cap., AH	Electrolyte Volume, cc	Time to 2.5 VF Hours	Average Potential to 2.5VF, Volts	Cap. to 2.5VF, AH	$\text{CuF}_2$ Reduc. Eff., %
	Additive/100g $\text{CuF}_2$ Graphite	Paper Fiber							
1-1	4	2	94	3.80	---	0	---	---	---
1-2	4	2	94	3.68	---	0	---	---	---
1-3	4	2	94	4.08	---	138**	2.73	2.90	71
1-4	4	2	94	3.96	---	138**	2.85	2.90	73
2-1	8	2	91	3.82	---	109	2.82	2.29	60
2-2	8	2	91	4.03	---	150	3.00	3.15	78
2-3	8	2	91	3.96	---	96	2.94	2.02	51
2-4	8	2	91	3.92	---	56	2.78	1.18	30
3-1	16	2	85	4.00	---	150	3.08	3.15	79
3-2	16	2	85	3.36	---	134	3.01	2.82	84
3-3	16	2	85	4.16	---	160	2.97	3.36	81
3-4	16	2	85	3.68	---	119	3.00	2.50	68
4-1	4	4	93	3.83	8.8*	84***	2.59	1.76	46
4-2	4	4	93	4.15	7.7*	<12	---	---	---
4-3	4	4	93	3.92	6.5	89	2.91	1.87	48
4-4	4	4	93	3.97	6.5	128	2.87	2.69	68
5-1	8	4	89	3.85	7.5*	138	2.89	2.90	75
5-2	8	4	89	4.30	7.7*	90	2.83	1.89	44
5-3	8	4	89	4.12	6.5	165	2.99	3.27	79
5-4	8	4	89	3.57	6.5	135	2.92	2.84	80

\* Vacuum impregnated.

\*\* Load voltage below 2.5V for first 12 hours.

\*\*\* Load voltage below 2.5V at 24 hours.

TABLE XXVIII (Continued)

EFFECT OF ADDITIVE CONCENTRATION ON PERFORMANCE OF CuF<sub>2</sub> ELECTRODES

Cell No.	Grams Additive/100g CuF <sub>2</sub> Graphite Paper Fiber	% CuF <sub>2</sub> in mix	Theo. CuF <sub>2</sub> Cap., AH	Electrolyte Volume, cc	Time to 2.5 VF, Hours	Average Potential		CuF <sub>2</sub> Reduc. Eff., %	
						Volts	Cap. to 2.5VF, AH		
6-1	16	4	83	4.52	9.6*	165	2.93	3.22	71
6-2	16	4	83	3.72	8.2*	0	-----	-----	--
6-3	16	4	83	3.28	6.5	139	2.91	2.92	89
6-4	16	4	83	3.21	6.5	123	3.01	2.58	81
7-1	4	8	89	3.69	6.0*	71	2.89	1.49	40
7-2	4	8	89	3.78	6.0*	92	2.84	1.93	51
7-3	4	8	89	4.45	7.0	138**	2.89	2.84	64
7-4	4	8	89	3.85	6.6	95**	2.73	1.99	52
8-1	8	8	86	4.38	7.0*	94***	2.75	1.97	45
8-2	8	8	86	4.45	7.0*	95	2.93	1.99	45
8-3	8	8	86	3.62	6.5	98	3.01	2.06	57
8-4	8	8	86	4.18	7.0	98	2.98	2.06	49
9-1	16	8	81	4.18	7.5*	89	2.87	1.87	45
9-2	16	8	81	4.27	7.5*	106	3.09	2.23	56
9-3	16	8	81	3.96	7.0	<36	-----	-----	--
9-4	16	8	81	4.07	6.5	45	2.90	0.95	23

\*Vacuum impregnated.

\*\*Load voltage below 2.5V for first 12 hours.

\*\*\*Load voltage below 2.5V at 24 hours.

Vacuum impregnation of the cells during activation increased the total volume of electrolyte absorbed, but in most groups of cells, a decrease rather than the expected increase in capacity was observed. This may be at least partially due to disruption of the filter mat cathode structure, since some gassing was always observed upon application of vacuum.

### 2. 3. 5. Pasted CuF<sub>2</sub> Electrode Tests

In order to develop an alternate CuF<sub>2</sub> electrode construction method - one which does not require the use of cellulose fibers - some tests with pasted CuF<sub>2</sub> electrodes were conducted.

CuF<sub>2</sub> and graphite or carbon black were micropulverized together for 15 sec. in a "Hi-Speed" blender. The binder was cellulose acetate dissolved in 90% ethyl acetate - 10% ethanol mixture, or polystyrene dissolved in toluene. The binder solution was added to the dry mix until a stiff paste resulted, which was then applied to expanded silver grids cut to 1.5 x 1.5 in. size. After drying the plates under vacuum, 3-plate test cells were built and tested as described before.

#### 2. 3. 5. 1. Effect of Binder and Conductor

In this test, eight cells with various cathode compositions were constructed and tested. The cells were activated with LiClO<sub>4</sub>/PC electrolyte, 15g solute/100 ml solvent, and discharged at 20 mA (0.7 mA/cm<sup>2</sup>) and 35°C after an activated stand of 4 hours. Cathode composition and discharge performance for these cells are shown in Table XXIX, page 76.

Carbon black gave better discharge performance than graphite, and polystyrene gave better results than cellulose acetate. The CuF<sub>2</sub> content in this electrode composition was 95%, which is higher than the 83% commonly used in filter mat preparation. Since the discharge efficiency was equally good, the pasted electrode construction would appear to offer a weight advantage over the filter mat construction. A disadvantage may be the more difficult wetting of these electrodes with the electrolyte solution.

#### 2. 3. 5. 2. Effect of Argon Drying

Four cells were constructed and tested to evaluate the effect of argon drying of cathodes after the normal vacuum drying. The paste composition for these cells was

CuF <sub>2</sub>	100
Graphite	10
Cellulose Acetate	1



TABLE XXIX

PERFORMANCE OF PASTED  $\text{CuF}_2$  ELECTRODES

Electrolyte: 15g  $\text{LiClO}_4/100$  ml PC  
 Current: 20 mA (0.7 mA/cm<sup>2</sup>)  
 Temperature: 35°C  
 Stand Time: 4.0 Hours

Cell No.	Grams of Additive/100 grams of $\text{CuF}_2$		Theo. $\text{CuF}_2$ Cap., AH	Hours to 2.5 VF	Cap. to 2.5 VF, AH	Average Discharge Potential, Volts	% Cathode Efficiency		
	Graphite*	Carbon Black**							
1	5	-	0.8	---	3.26	54.1	1.08	2.80	33
2	5	-	0.8	---	3.17	52.4	1.04	2.72	33
3	-	5	0.8	---	3.81	55.9	1.12	2.83	40
4	-	5	0.8	---	2.64	80.8	1.61	3.06	61
5	5	-	---	0.4	2.77	62.6	1.25	2.54	45
6	5	-	---	0.4	2.94	65.4	1.31	2.88	45
7	-	5	---	0.4	2.65	92.0	1.84	2.98	69
8	-	5	---	0.4	2.52	98.8	1.98	3.03	79

\* Air-Spun Graphite, The Joseph Dixon Crucible Co.

\*\* Conductex SC, Columbian Carbon Co.

\*\*\* 2% Solution in 90% ethyl acetate - 10% ethanol.

\*\*\*\*1% Solution in toluene.

and discharge performance thru 200 $\Omega$  loads at 35°C is shown in Table XXX.

Drying of the electrodes at 130°C before construction of cells appeared to improve the capacity for this group of cells. The effect that this may have on wet shelf life should be worth studying in future work.

TABLE XXX

PERFORMANCE OF PASTED CuF<sub>2</sub> ELECTRODES AFTER ARGON DRYING

Load: 200 $\Omega$ (0.5 mA/cm <sup>2</sup> ) Temperature: 35°C Electrolyte: 15g LiClO <sub>4</sub> /100 ml PC						
<u>Cell No.</u>	<u>Cathode Drying</u>	<u>Theo. CuF<sub>2</sub> Cap., AH</u>	<u>Discharge Time, 2.5 VF, Hours</u>	<u>Average Discharge Potential, Volts</u>	<u>AH to 2.5 VF</u>	<u>Efficiency, Percent</u>
1	16 hrs., 130°C	3.88	188	3.12	2.93	76
2	16 hrs., 130°C	4.04	192	3.14	3.01	75
3	16 hrs., 24°C	3.86	170	3.14	2.67	69
4	16 hrs., 24°C	4.07	156	2.99	2.33	57

2. 3. 5. 3. Effect of Sulfur

Thin-pasted CuF<sub>2</sub> electrodes containing sulfur were tested with Li-anodes in PC-LiClO<sub>4</sub> electrolyte. A dry mix having the composition

CuF <sub>2</sub>	20 g
Dixon Graphite	2 g
Sulfur (sublimed)	1 g

was ground for 15 seconds in the "Hi-Speed" blender. A 1% solution of polystyrene in toluene was used to prepare a paste; the amount of polystyrene added by this solution was about 0.1g/20g of CuF<sub>2</sub>. Electrodes were pasted to a thickness of about 0.03 inches on expanded silver and dried

overnight at hard vacuum. Three-plate cells were constructed using 0.03 in. MPR separation. Results of the discharge test are shown in Table XXXI.

Although comparable cells without sulfur were not tested in this series, addition of this material to the  $\text{CuF}_2$  paste appears to produce no significant effect on cell performance. This is probably due to the relative insolubility of sulfur in the organic electrolyte.

TABLE XXXI

PERFORMANCE OF  $\text{CuF}_2$  ELECTRODES WITH SULFUR

Temperature: 35°C  
 Electrolyte: 15g  $\text{LiClO}_4$ /100 ml PC  
 Load: 20 mA (0.7 mA/cm<sup>2</sup>)

<u>Cell No.</u>	<u>Theo. Cathode Capacity</u>	<u>Active Stand Time, (Hrs.)</u>	<u>Discharge Time to 2.5 VF, (Hours)</u>	<u>Average Discharge Potential, Volts</u>	<u>AH to 2.5 VF</u>	<u>Cathode Eff., %</u>
1	1.26	138	0	----	0	0
2	1.05	138	0.16	----	0	0
3	1.22	72	12.2	2.56	0.25	20
4	1.07	72	20.5	2.75	0.41	38
5	1.10	24	26.8	2.84	0.54	49
6	1.15	24	32.9	2.87	0.66	57
7	1.01	1	36.9	3.15	0.74	73
8	1.13	1	34.9	3.17	0.70	62

2. 3. 6. Performance of  $\text{CuF}_2$ -Li Cells At Various Discharge Rates

In order to characterize the performance capabilities of the low-rate  $\text{CuF}_2$ -Li system, discharge performance of cells having the usual filter-mat electrode construction (14 grams of graphite and 7 grams of paper fiber per 100 grams of  $\text{CuF}_2$ ) was determined at various discharge loads. The electrolyte was 15g  $\text{LiClO}_4$ /100 ml of propylene carbonate, and microporous rubber separation and slab lithium electrodes were employed as before. The geometric electrode area of the three-plate (1  $\text{CuF}_2$  electrode, 2 Li electrodes) cell was 29 cm<sup>2</sup>. Discharges were conducted at 35°C thru resistive loads of 100, 200, 500 and 1000 ohms. The construction and discharge data

are summarized in Table XXXII, and voltage-time curves for the best cell at each discharge rate are presented in Figure 27, page 80.

In terms of  $\text{CuF}_2$  reduction efficiency, the best performance was obtained from cells discharged thru 200 ohm loads (ca. 250 hour discharge); the highest reduction efficiency in this group (best of three cells) was 73% at an average discharge potential of 3.04 volts to a cut-off voltage of 2.5 V. With 100 ohm loads (ca. 100 hour discharge), the best efficiency was 58 percent at 2.90 V average discharge potential. With lower discharge rates, the performance decreased, the best-of-three-cells figures being 47 percent efficiency at 3.20 V average thru 500 ohm load (ca. 400 hour discharge), and 23 percent efficiency at 3.14 V average thru 1000 ohm load (ca. 400 hour discharge).

Inspection of discharged cells showed copper-colored deposits on the lithium, particularly in the cells which were discharged thru 1000 $\Omega$ . Dissolution of  $\text{CuF}_2$  was again evident in this test series, and probably contributed to the decreased performance of the cells with increasing discharge time.

TABLE XXXII

PERFORMANCE OF  $\text{CuF}_2$ -Li CELLS AT VARIOUS DISCHARGE RATES

(LEL Test No. 640-16)

Electrolyte: 15g  $\text{LiClO}_4$ /100 ml PC  
 Electrode Area: 29  $\text{cm}^2$   
 Temperature: 35°C

Cell No.	Theo. $\text{CuF}_2$ Cap., AH	Load, $\Omega$	Time to 2.5 VF, Hours	Average Discharge Potential, Volts	Cap. to 2.5VF, AH	Eff., %
1	6.13	1000	192	3.11	0.60	10
2	5.98	1000	360	3.18	1.14	10
3	5.95	1000	432	3.14	1.35	23
4	5.67	500	432	3.14	2.68	47
5	5.92	500	360	3.07	2.21	37
6	5.52	500	408	3.20	2.62	47
7	5.89	200	172	2.89	2.49	42
8	5.33	200	258	3.04	3.90	73
9	5.42	200	247	3.04	3.72	69
10	5.42	100	108	2.90	3.14	58
11	5.24	100	79	2.79	2.20	42
12	6.15	100	17	----	----	--

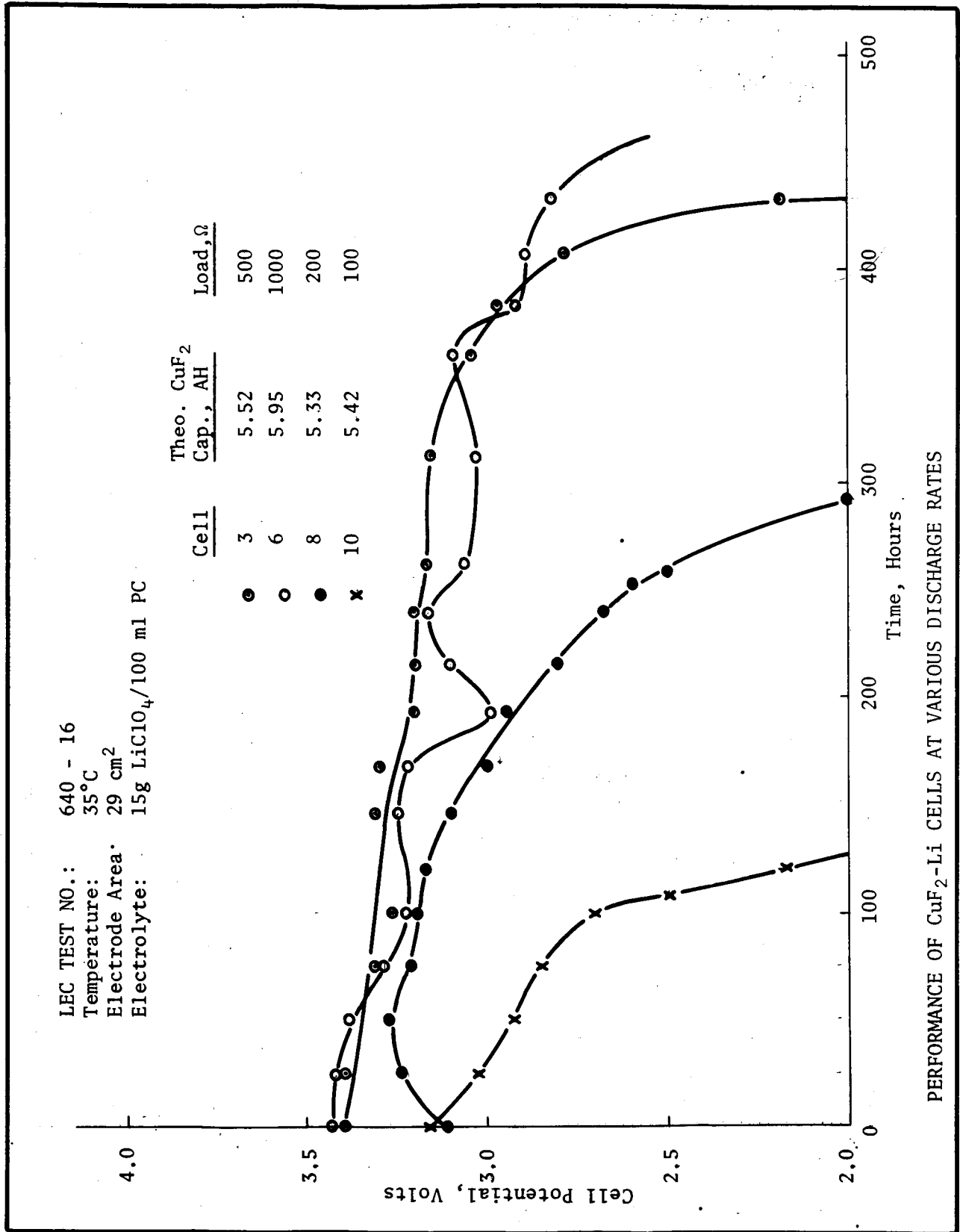


FIGURE 27

### 2. 3. 7. CuF<sub>2</sub> Electrode Construction Tests

It appeared desirable to evolve an alternate CuF<sub>2</sub> electrode construction method which would not require incorporation of cellulose fibers, since these may be reactive with some of the solvents to be evaluated in cell tests (possibly DMSO). For this reason, construction of electrodes by adding Microthene FN 500 polyethylene powder to CuF<sub>2</sub> and graphite (or carbon black) was studied.

Small batches of CuF<sub>2</sub>, graphite and Microthene FN 500 (USI Chemical) were dry-blended in a micro-pulverizer. The charge was then transferred to a 1.5 in. square steel compression mold which was placed in a hydraulic press, with platens preheated to 400°C. After 15 minutes (to allow the mold to reach 400°C), 5000 lbs of force were applied for 30 seconds. Since no mold release was used, initial attempts resulted in cathodes which stuck fast to the mold faces. This difficulty was eliminated by applying adhesive-backed Teflon film to the mold base and plunger face.

Twelve cells listed in Table XXXIII, page 82, were built with CuF<sub>2</sub> electrodes prepared by the above method. Three-plate lithium-anode test cells were built with mixes 1 - 4, while two-plate cells were constructed for the remaining compositions. The cells were activated with 15g LiClO<sub>4</sub>/100 ml PC electrolyte, and discharged at 1.0 (mixes 1 - 4) or 0.67 (mixes 5 - 8) mA/cm<sup>2</sup> at 35°C.

The highest CuF<sub>2</sub> utilization efficiency was obtained with mix #6 (72 and 85% to 2.5 VF); which is about equivalent to the best results obtained with filter-mat construction. The dry press method, therefore, appears to be suitable for construction of CuF<sub>2</sub> electrodes.

### 2. 3. 8. Effect of LiClO<sub>4</sub> Concentration

The effect of LiClO<sub>4</sub> concentration in PC on cell performance and wet stand capabilities was studied at concentrations of 10 and 20 grams of solute per 100 ml of solvent. The CuF electrodes were prepared by the filter mat technique and had the composition

CuF <sub>2</sub>	100
Graphite	14
Paper Fiber	7

TABLE XXXIII

COMPOSITION OF HOT-PRESSED CuF<sub>2</sub> ELECTRODES

<u>Cell No.</u>	<u>CuF<sub>2</sub></u>	<u>C. B.</u>	<u>Graphite</u>	<u>Binder</u>	<u>C. D. mA/cm<sup>2</sup></u>	<u>Cathode Eff., %</u>
1	10	1	---	0.2	1.0	38
2	10	1	---	0.1	1.0	16
3	10	0.5	---	0.1	1.0	16
4	10	0.5	---	0.05	1.0	42
5	9	---	0.9	0.18	.67	68
6	9	---	0.9	0.18	.67	75
7	9	---	0.9	0.088	.67	85
8	9	---	0.9	0.088	.67	72
9	9	0.9	---	0.088	.67	70
10	9	0.9	---	0.088	.67	63
11	9	0.44	---	0.088	.67	67
12	9	0.44	---	0.088	.67	70

Three-plate test cells with Li negatives and 0.03 in. MPR were constructed and were assembled in groups of three cells in hermetically sealed glass jars. Construction and discharge data for these cells are summarized in Table XXXIV, page 83.

Before stand, discharge capacity was about equal with both electrolyte concentrations. After wet stand at 0°C, the lower concentration gave markedly better results. This may be explained in terms of lower reaction rates between LiClO<sub>4</sub> and CuF<sub>2</sub> in these cells.

### 2. 3. 9. Effect of Solute on Capacity

Since the lack of shelf life of the CuF<sub>2</sub>-Li system appeared to be the result of chemical action of the solute on CuF<sub>2</sub>, cell performance tests with solutes other than LiClO<sub>4</sub> were conducted. Although shelf life tests were of major interest, only initial capacity studies could be performed within the available time period.

Electrolyte salts for which compatibility tests with CuF<sub>2</sub> and Li in PC solution had been performed (see Section 2. 1.; Electrolyte Studies) were

TABLE XXXIV

EFFECT OF  $\text{LiClO}_4$  CONCENTRATION ON CELL PERFORMANCE

Cell No.	$\text{LiClO}_4$ conc. g/100 ml PC	Theo. $\text{CuF}_2$ Cap., AH	Initial O.C.V.	O.C. stand, days at $0^\circ\text{C}$	Discharge		Average Discharge Potential Volts	AH to 2.5 VF	Eff., %
					Time to 2.5 VF Hours	Volts			
1	10	3.66	3.58	--	133	3.10	2.66	73	
2	10	3.06	3.58	--	79	2.91	1.58	52	
3	10	3.19	3.58	--	119	2.82	2.38	75	
4	20	2.90	3.55	--	108	2.96	2.16	75	
5	20	2.92	3.55	--	90	2.90	1.80	62	
6	20	3.21	3.55	--	120	2.93	2.40	75	
13	10	4.10	3.59	10	148.5	3.04	2.97	73	
14	10	3.51	3.59	10	135.5	3.04	2.71	77	
15	10	3.98	3.59	10	141	2.99	2.82	71	
16	20	3.80	3.50	10	100	2.82	2.00	54	
17	20	2.62	3.55	10	80.5	2.91	1.61	62	
18	20	2.58	3.55	10	87.5	2.95	1.75	60	
25	10	4.00	3.59	24	<1	-----	-----	--	
26	10	3.12	3.59	24	29.5	2.74	.59	19	
27	10	3.44	3.59	24	99.5	2.80	1.99	58	
28	20	2.87	3.59	24	<1	-----	-----	--	
29	20	3.71	3.58	24	<1	-----	-----	--	
30	20	3.68	3.35	24	<1	-----	-----	--	

Temperature:  $35^\circ\text{C}$ Current: 20 mA ( $0.7 \text{ mA/cm}^2$ )



selected for these tests. The electrolyte solutions were prepared with lithium-dried and distilled propylene carbonate at a concentration of 1.0 mol solute/liter of solvent. Some of the solutions were prepared by a double decomposition reaction between the corresponding salts to yield the insoluble  $\text{KClO}_4$ <sup>13</sup> and the desired salt in solution. These solutions were, therefore, saturated with respect to  $\text{KClO}_4$  and are designated in the tables with the suffix "m".

The  $\text{CuF}_2$  electrodes were prepared using the filter mat technique and had the composition

$\text{CuF}_2$ (0.7% $\text{H}_2\text{O}$ )	100
Graphite	14
Paper Fiber	7

Three-plate  $\text{CuF}_2$ -Li cells were constructed, activated with the corresponding electrolyte solutions, and discharged at 35°C thru 200Ω loads (0.5 mA/cm<sup>2</sup>). Construction and discharge data for these cells are presented in Table XXXV, page 85, and voltage-time data for some discharges are shown in Figures 28 and 29, pages 86 and 87.

Of the electrolytes tested in this series, only  $\text{KPF}_6$  and  $\text{LiPF}_6$  produced consistently poor discharge performance. With the other electrolytes, rather poor replication occurred, but with each of these electrolytes at least one cell gave  $\text{CuF}_2$  reduction efficiency of over 70%. This indicates that a high solubility of  $\text{CuF}_2$  in the electrolyte is not required for good reduction efficiency, since some of the salts in this test (e.g.  $\text{NaClO}_4$ ) showed very low tendency to react with  $\text{CuF}_2$  in direct compatibility tests (see Section 2. 2. 3.). The effect of  $\text{CuF}_2$  solubility on the wet shelf life of cells remains to be studied.

### 2. 3. 10. Cell Performance With Various Solvents

As a further attempt to correlate the results of electrolyte compatibility and cell discharge data,  $\text{CuF}_2$ -Li cells with various electrolyte solvents were built and discharged.

Propylene carbonate (PC), dimethylsulfoxide (DMSO), acetic anhydride (AA), N-nitroso dimethylamine (NDA), nitromethane (NM), and methyl acetate (MA) were the solvents selected for this test series.

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<sup>13</sup> Precipitated  $\text{KClO}_4$  was weighed and the stoichiometric quantity was recovered.

TABLE XXXV  
EFFECT OF SOLUTE ON  $\text{CuF}_2$ -Li CELL PERFORMANCE IN PC

Cell No.	Solute	Elec'lyte water content		Specif. Condc. $\text{mho/cm} \times 10^3$	Electrolyte Volume cc	Theo. $\text{CuF}_2$ Capa. AH	Dischg. Time to 2.5 VF, Hours	Average Potential to 2.5 VF, Volts	Average Current to 2.5 VF	$\text{CuF}_2$ Cap. to 2.5 VF, AH	$\text{CuF}_2$ Reduc. Eff., %
		$\mu\text{g/ml sol'n}$	$\text{mho/cm} \times 10^3$								
1	$\text{LiClO}_4$	90	5.4	8.8	4.49	3.55	223	3.01	15.1	3.37	75.1
2	$\text{LiClO}_4$	90	5.4	7.4	4.76	3.60	247	2.99	15.0	3.70	77.8
3	$\text{NaClO}_4$	72	5.6	8.6	4.20	3.55	234	2.99	15.0	3.51	83.5
4	$\text{NaClO}_4$	72	5.6	8.4	5.06	3.59	242	3.09	16.0	3.88	76.7
5	KPF <sub>6</sub>	97	7.8	9.2	4.88	3.53	5	2.74	13.7	0.07	1.4
6	$\text{KAsF}_6$	61	8.1	9.4	4.28	3.45	100	2.83	14.2	1.42	33.1
7	$\text{LiBF}_4$	129	2.9	8.9	4.83	3.55	197	3.02	15.1	2.98	61.7
8	$\text{LiPF}_6(\text{m})$	105	6.4	6.9	4.90	3.53	5	2.97	14.9	0.07	1.4
9	$\text{LiAsF}_6(\text{m})$	260	6.2	6.6	4.89	3.52	253	3.06	15.3	3.87	79.2
10	$\text{NaAsF}_6$	160	8.2	6.3	4.89	3.48	181	2.87	14.4	2.60	53.2
11	KPF <sub>6</sub>	97	7.8	7.2	4.84	3.51	7	2.71	13.6	0.09	2.0
12	$\text{KAsF}_6$	61	8.1	7.5	4.41	3.50	233	3.03	15.2	3.54	80.4
13	$\text{LiBF}_4$	129	2.9	8.0	4.24	3.60	207	3.01	15.1	3.12	73.7
14	$\text{LiPF}_6(\text{m})$	105	6.4	7.6	4.36	3.49	6	2.77	13.9	0.08	1.7
15	$\text{LiAsF}_6(\text{m})$	260	6.2	9.0	4.37	3.58	105	3.18	15.9	1.67	46.7
16	$\text{NaAsF}_6$	160	8.2	8.6	4.36	3.50	226	3.12	15.6	3.52	80.9
17	$\text{NaAsF}_6(\text{m})$	---	---	8.3	4.90	3.56	261	3.11	15.6	4.07	83.2

Electrode Area: 29  $\text{cm}^2$ 

Temperature: 35°C

Load: 200 ohms

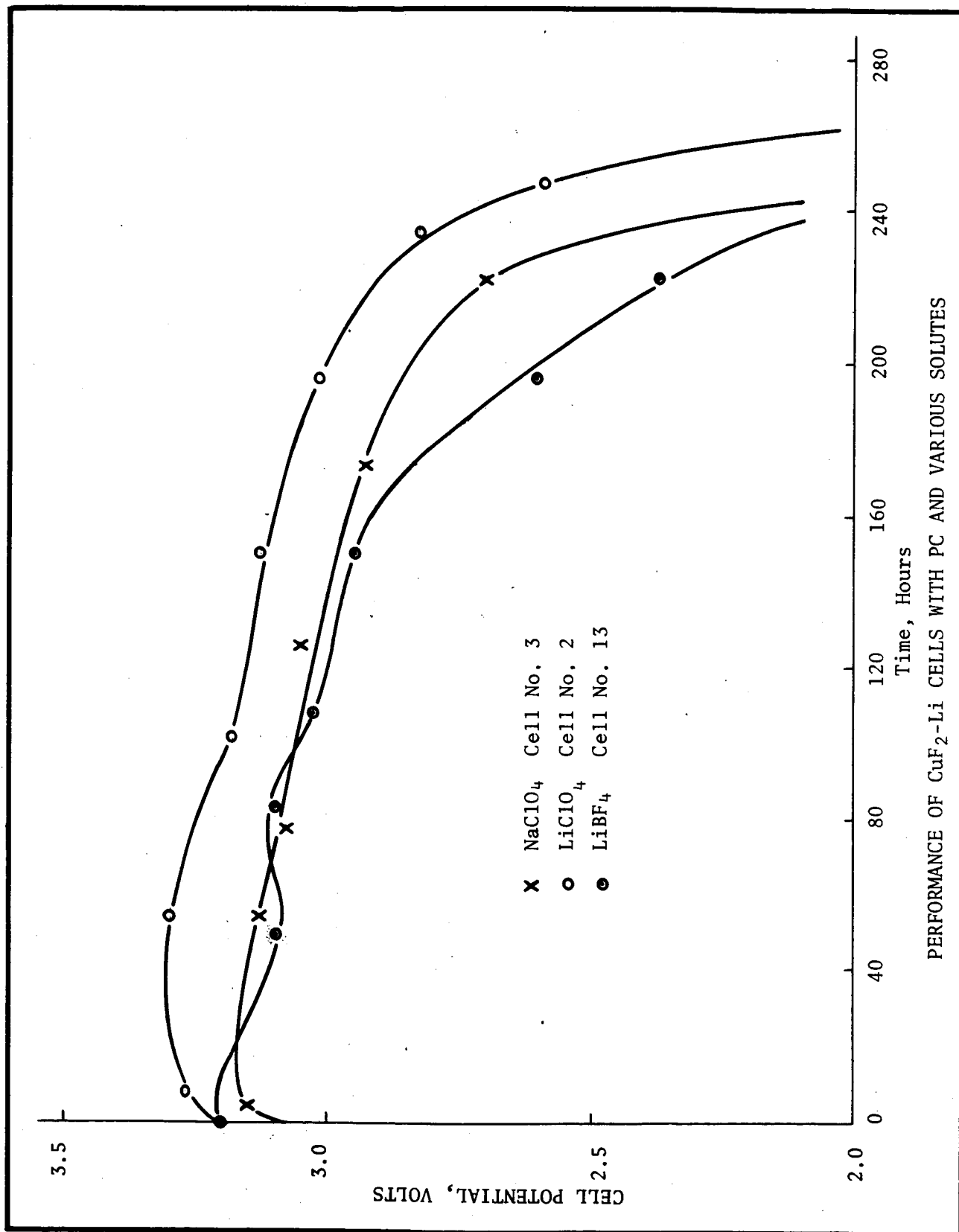


FIGURE 28

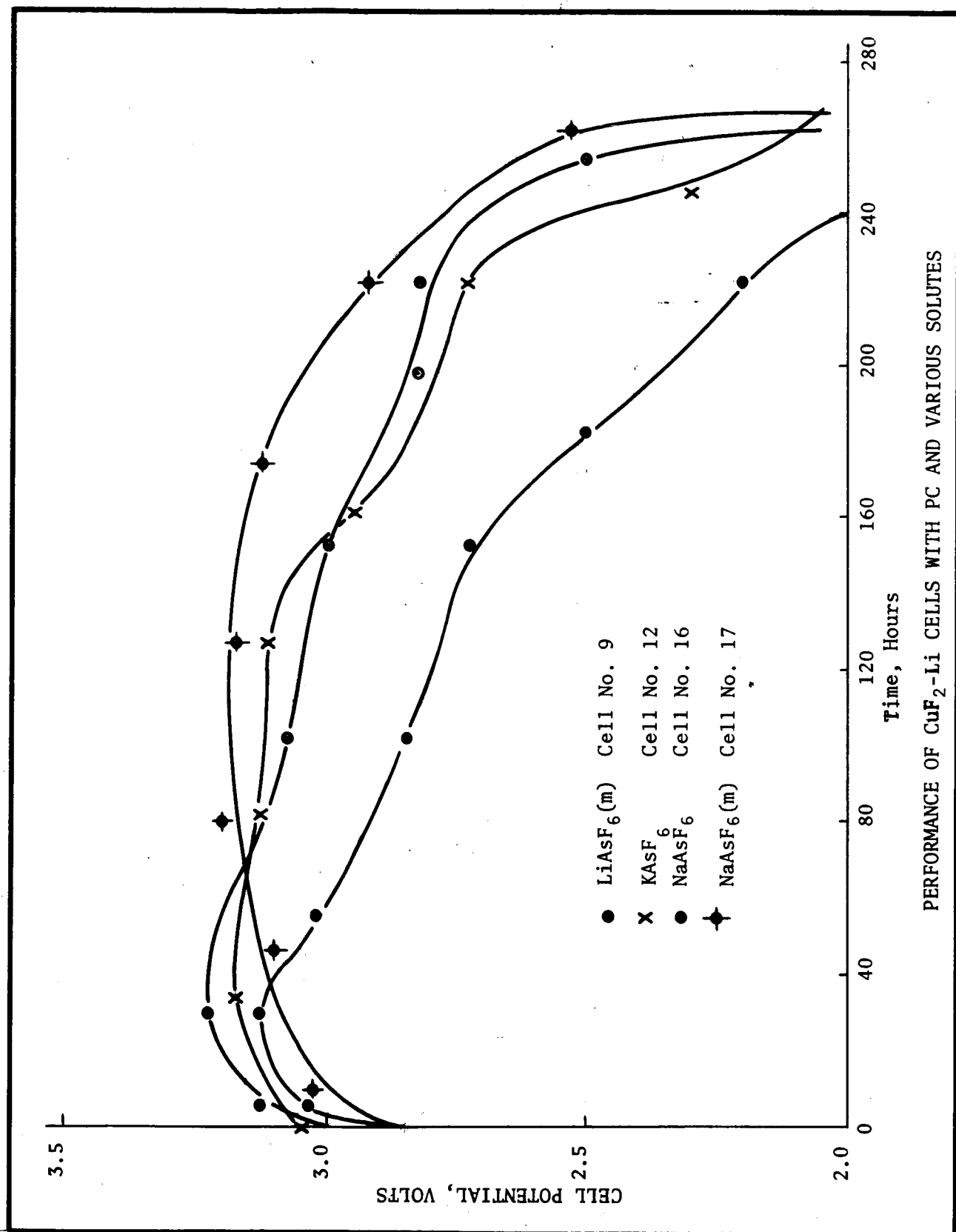


FIGURE 29

The solvents were lithium treated and distilled as described for propylene carbonate. Nitromethane was filtered after lithium treatment rather than distilled because of the potential explosion hazard. The solutes  $\text{LiClO}_4$ , and  $\text{KAsF}_6$  were selected for these tests. Cell construction and discharge conditions were as described in the previous section.

Results of the discharge tests for these cells are shown in Table XXXVI, page 89. In all, results of these discharges were disappointing in that only the "standard" cells - those with  $\text{LiClO}_4/\text{PC}$  electrolyte gave the expected performance (70 - 80%  $\text{CuF}_2$  utilization). The reason for the poor performance of the other cells could not be determined, and no conclusions about the significance of these results can therefore be drawn.

### 2. 3. 11. Cell Tests With $\text{NaClO}_4$ -PC Electrolyte

Comparative cell tests with  $\text{LiClO}_4$  and  $\text{NaClO}_4$  electrolyte solutions in propylene carbonate were performed. The salts were dried under hard vacuum at  $110^\circ\text{C}$  for 16 hours and 1 molar solutions were prepared in lithium-dried, redistilled PC. Karl Fischer analysis showed 52 and 55 ppm  $\text{H}_2\text{O}$  for the  $\text{LiClO}_4$  and  $\text{NaClO}_4$  electrolyte, respectively.

Filter-mat  $\text{CuF}_2$  electrodes having the composition

$\text{CuF}_2$	160g
Graphite	16g
Paper Fiber	4g

were prepared. Three-plate cells with lithium anodes and MPR separation were constructed under argon and activated with the electrolyte. Three cells with each electrolyte were discharged immediately at 20 mA and  $35^\circ\text{C}$ , while the remaining cells were given a 5-day O. C. stand at  $35^\circ\text{C}$  before being discharged at the same load and temperature.

Construction and discharge data for the cells are shown in Table XXXVII, page 90.

Voltage-time data for the best of three cells in each group are plotted in Figure 30, page 91.

Although the wet stand properties of the cells with both electrolytes were poor, replacing of the lithium ion with sodium did appear to increase the residual capacity after stand. These results, although inconclusive, indicate the possibility of using Na or K electrolytes with the  $\text{CuF}_2$ -Li cells for better shelf life characteristics.

TABLE XXXVI

CuF<sub>2</sub>-Li CELL TESTS WITH VARIOUS SOLVENTS

Cell No.	Solvent	Solute	Electrolyte water µg/ml Sol'n	Specific Conduc. mho/cm	CuF <sub>2</sub> Cap. AH	Average Discharge Potential to 2.0 VF	Cap. to 2.0 VF, AH	Cathode Eff., %
1	PC	LiClO <sub>4</sub>	117	4.3x10 <sup>-3</sup>	5.41	3.03	4.07	76
2	"	"	"	"	5.33	3.11	3.74	70
3	"	KAsF <sub>6</sub>	150	7.82x10 <sup>-3</sup>	5.23	*	----	----
4	"	"	"	"	4.08	*	----	----
5	DMSO	LiClO <sub>4</sub>	109	1.1x10 <sup>-2</sup>	5.16	2.5	.01	0.1
6	"	"	"	"	2.18	2.5	.01	0.5
7	"	KAsF <sub>6</sub>	110	1.2x10 <sup>-2</sup>	4.89	2.5	.03	0.7
8	"	"	"	"	4.35	2.70	.13	3.1
9	AA	LiClO <sub>4</sub>	150	7.7x10 <sup>-3</sup>	4.72	2.34	.35	7.4
10	"	"	"	"	4.38	2.60	.16	3.7
11	"	KAsF <sub>6</sub>	114	1.6x10 <sup>-2</sup>	4.72	2.2	.13	2.9
12	"	"	"	"	5.38	2.66	.20	3.8
13	"	**LiClO <sub>4</sub>	495	1.0x10 <sup>-2</sup>	4.27	2.24	.02	0.5
14	"	"	"	"	4.17	2.54	.38	9.1
15	NDA	"	99	1.5x10 <sup>-2</sup>	4.58	2.49	.15	3.2
16	"	"	"	"	5.23	*	----	----
17	"	KAsF <sub>6</sub>	146	2.1x10 <sup>-2</sup>	5.38	2.73	.48	9.0
18	"	"	"	"	4.71	2.31	.28	6.1
19	NM	LiClO <sub>4</sub>	241	7.3x10 <sup>-3</sup>	5.64	2.33	.23	4.1
20	"	"	"	"	4.79	2.74	.89	18.6
21	"	KAsF <sub>6</sub>	121	1.0x10 <sup>-2</sup>	4.62	2.02	.48	10.5
22	"	"	"	"	4.50	2.37	.60	13.5
23	MA	LiClO <sub>4</sub>	---	----	5.37	2.61	.49	9.2
24	"	"	---	----	4.53	2.74	.20	9.1
25	"	KAsF <sub>6</sub>	---	----	4.80	*	----	----
26	"	"	---	----	4.91	2.68	.64	13.4

\*Cells immediately dropped below cut-off of 2.0V.

\*\*Purified by recrystallization in AA.

TABLE XXXVII

EVALUATION OF NaClO<sub>4</sub> IN PC

Discharge Condition: +35°C, 20 mA (0.7 mA/cm<sup>2</sup>)  
 Stand Condition: +35°C

Cell No.	Electrolyte	O. C., Stand, Time, Days	Theo. CuF <sub>2</sub> Capa., AH	Discharge Time to 2.5 VF, Hours	Cap. to 2.5 VF, AH	Eff., %
1	NaClO <sub>4</sub>	0	5.08	75.0	1.50	30
2	"	0	5.04	115.5	2.31	46
3	"	0	4.67	135.0	2.70	58
4	"	5	5.50	<1	----	--
5	"	5	5.10	<1	----	--
6	"	5	3.71	<1	----	--
7	LiClO <sub>4</sub>	0	4.38	134.0	2.68	61
8	"	0	5.31	94.0	1.89	36
9	"	0	4.18	135.0	2.70	65
10	"	5	5.60	<1	----	--
11	"	5	4.30	<1	----	--
12	"	5	4.70	<1	----	--

2. 3. 12. Ag<sub>2</sub>O<sub>2</sub>-Li Cell Tests

Since the solubility of CuF<sub>2</sub> in LiClO<sub>4</sub>-PC electrolyte appeared to contribute adversely to the wet stand capability of the CuF<sub>2</sub>-Li cells, self-discharge tests with cells having Ag<sub>2</sub>O<sub>2</sub> instead of CuF<sub>2</sub> in the positive electrode were performed. Silver oxide was chosen for these tests because it was presumed to have a very low solubility in the electrolyte, thus allowing evaluation of the remaining cell construction for wet stand capability without the complication of a dissolved species (Cu<sup>++</sup>) attacking the lithium electrode from solution.

The Ag<sub>2</sub>O<sub>2</sub> electrodes were prepared by the filter-mat technique. The composition of the filter-mat was:

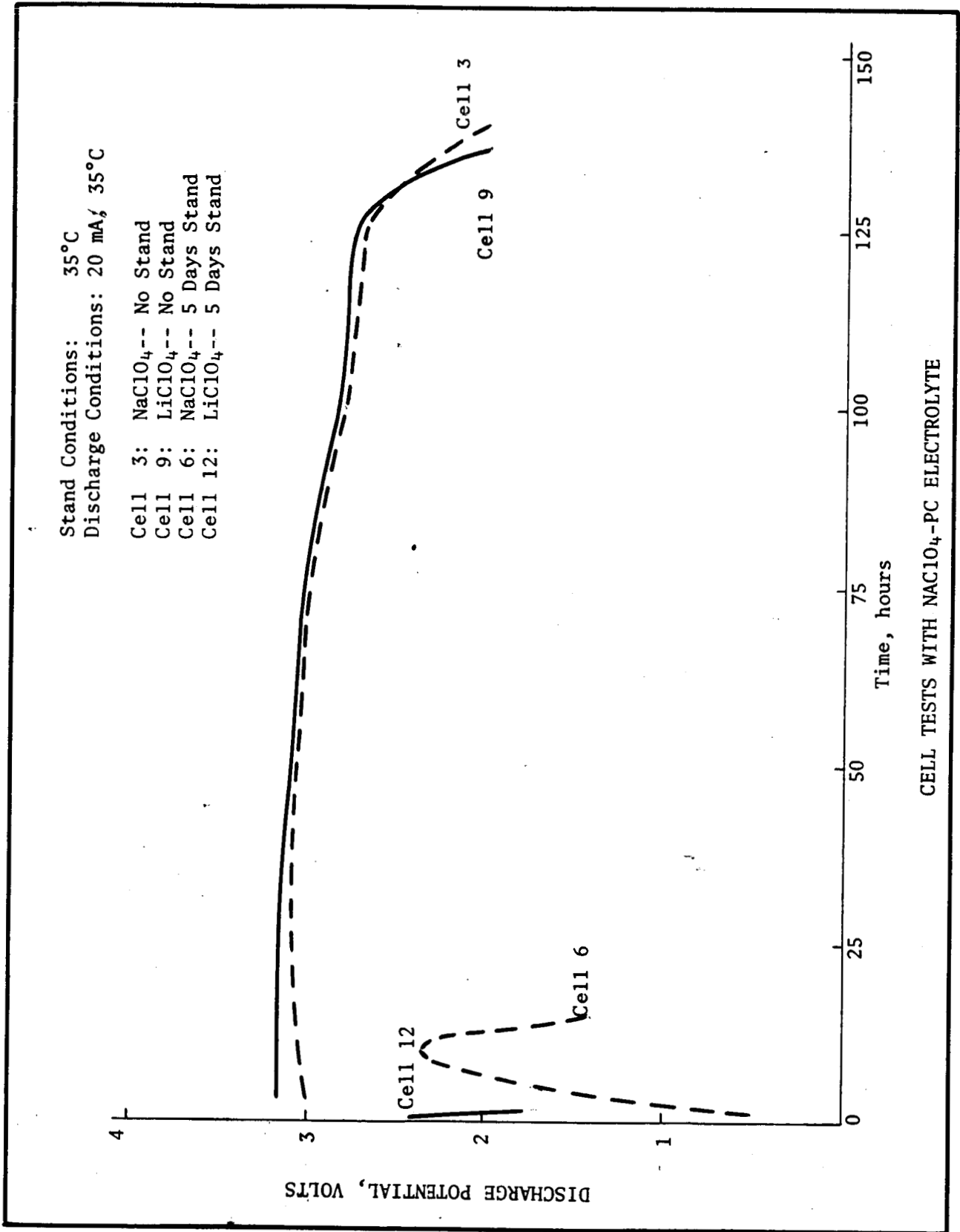


FIGURE 30



Ag <sub>2</sub> O <sub>2</sub>	83
Graphite	7
Paper Fiber	3

X-ray analysis of the Ag<sub>2</sub>O<sub>2</sub> showed the material to contain more than 99 percent of divalent silver.

Three-plate test cells with microporous rubber separation and lithium anodes were constructed and activated with 1.5 M LiClO<sub>4</sub>-PC electrolyte. Some cells were put in discharge thru 200 ohms at 35°C, while the remaining cells were allowed to stand on open circuit at the same temperature before discharge was started.

Construction data and discharge results are summarized in Table XXXVIII, page 93. Cathode reduction efficiencies of over 40% were obtained both with and without O. C. stand, but reproducibility of performance was erratic. The cells which had only polyethylene envelope seals (Cell Nos. 1- 6) appeared dry after the 2-week stand, indicating electrolyte loss.

Additional cells with Ag<sub>2</sub>O<sub>2</sub> active material were constructed and tested. These cells had polyethylene-coated cellulose rather than paper fibers in the cathode mix. Performance of these cells was poor.

It did not appear at the conclusion of these tests that Ag<sub>2</sub>O<sub>2</sub> will yield energy densities as high as CuF<sub>2</sub> does. Its only advantage may be a better wet shelf life potential, which may warrant further studies of this material in future work.

TABLE XXXVIII  
 PERFORMANCE OF Ag<sub>2</sub>O<sub>2</sub>-Li CELLS WITH LiClO<sub>4</sub>-PC ELECTROLYTE

Cell No.	Stand Time, Days	Theoretical Ag <sub>2</sub> O <sub>2</sub> Capa. AH	Hours to 2.5 VF	Capacity to 2.5 VF AH	Average Discharge Potential Volts	Cathode Eff., %	Remarks
1	--	2.90	86	1.25	2.89	43	1
2	--	2.75	92	1.14	2.48	42	1
3	14	2.88	4	----	----	--	1
4	14	2.62	30	0.41	2.75	16	1
5	28	2.66	3	----	----	--	1
6	28	2.44	3	----	----	--	1
7	--	2.61	<12	----	----	--	2
8	--	2.34	<12	----	----	--	
9	11	2.69	74	1.12	2.89	42	
10	11	3.09	65	1.13	2.91	37	
11	11	2.92	78	1.13	2.90	39	
12	11	2.38	--	----	----	--	2,3

Discharge Temperature: 35°C

Stand Temperature: 35°C

Load: 200 ohms

Electrode Area: 29 cm<sup>2</sup>

- 1 Cells sealed in polyethylene envelopes.  
 2 Cells sealed in glass jars.  
 3 Broken terminals at 18.5 hours.

### 3. HIGH RATE BATTERY STUDY

#### 3. 1. Electrolyte Studies

To obtain sufficiently high current density for high energy cell performance at the 1 to 10 hour discharge rate, electrolytes having sufficient conductance and low viscosity are required. Under the previous contract (NAS 3-6004) of this program, the methyl formate-LiClO<sub>4</sub> electrolyte was tested for use with the CuF<sub>2</sub>-Li couple. In this work, the maximum conductivity of the MF-LiClO<sub>4</sub> electrolyte was found to be  $26 \times 10^{-3} \text{ohm}^{-1} \text{cm}^{-1}$  at a concentration of 30g solute/100 ml of solvent. The stability of this electrolyte in the presence of Li and CuF<sub>2</sub> electrodes appeared adequate for reserve-activated cells. Because no other electrolyte appeared to present equally good promise for use in high rate CuF<sub>2</sub>-Li cells, nearly all of the work on the present contract was performed for the development of cells using the MF-LiClO<sub>4</sub> electrolyte system.

#### 3. 1. 1. Lithium Stability Tests

Attempts to improve the stability of the MF-LiClO<sub>4</sub> electrolyte included agitation of the solvent with powdered lithium. However, a gas producing reaction made this method difficult and dangerous to apply. An attempt was made to apply the lithium treatment method by preceding it with drying the solvent with CaO and distillation in order to remove most of the moisture before the introduction of Li powder into the solvent. Methyl acetate was also included in the investigation because of earlier indications that this solvent may have superior stability to lithium compared to MF.

The solvents were agitated for 3 days with 5g of CaO/100 ml of solvent, filtered, and distilled rejecting the first and last tenth of the distillate. The solvents were then agitated for 3 days with 1g of Li powder/100 ml of solvent, filtered, and distilled rejecting the 1st 10 - 20% of the solvent.

Lithium perchlorate solutions were prepared from methyl acetate and methyl formate in concentrations of 25 and 50g of solute/100 ml of solvent. Strips of bright lithium ribbon were placed in these solutions and the lithium stabilities were compared with those of the untreated solvents. The observations from these tests are listed in the Appendix, Table A-10.

The lithium treatment improved stability of the MF electrolyte, but appeared to be of no consequence with the methyl acetate. Lithium stability did not appear to be affected by solute concentration in this test.

### 3. 1. 2. CuF<sub>2</sub> Stability Tests

Copper fluoride solubility tests in solvents treated as described in the previous section were conducted as described in Section. 2. 1. 3. 1. Forty ml of the electrolyte were agitated with 1.0g of CuF<sub>2</sub> for a period of 8 days. At the end of this period, samples of the solution were withdrawn and Cu II content was determined colorimetrically results of these analyses are shown in Table XXXIX.

TABLE XXXIX  
SOLUBILITY OF CuF<sub>2</sub> IN MA AND MF ELECTROLYTES

<u>Solvent</u>	<u>Treatment</u>	<u>g LiClO<sub>4</sub>/100 ml solvent</u>	<u>Cu<sup>++</sup>, ppm</u>
MA	CaO	25	31
MA	CaO	50	75
MA	CaO-Li	25	140
MA	CaO-Li	50	145
MF	CaO	25	170
MF	CaO	50	123
MF	CaO-Li	25	70
MF	CaO-Li	50	105
MA	None	25	33
MF	None	25	150

The above analyses did not show any clear effect from the lithium treatment of either solvent. Solubility of CuF<sub>2</sub> was low in either solvent compared to other electrolyte systems tested in this program.

### 3. 2. Positive Limited Cell Studies

Because of the relatively low current densities available with organic electrolytes (compared to aqueous systems), a thin-plate  $\text{CuF}_2$ -Li cells is needed for efficient discharge at the 1 - 10 hour rate. Since little difficulty was visualized in producing thin lithium electrodes (0.015 in. sheet is available commercially), work on this program was aimed at developing thin, efficient  $\text{CuF}_2$  electrodes.

#### 3. 2. 1. Pasted Electrode Composition Study

Electrodes were prepared by pasting a mixture of  $\text{CuF}_2$ , graphite, and cellulose acetate wetted with 90% ethyl acetate - 10% ethyl alcohol solution onto expanded silver grids. The resulting electrodes had a thickness of about 0.025 in. and an area of about 30 cm<sup>2</sup> (1.5 x 1.5 in.) when assembled with two negative electrodes in three-plate cells. To insure positive limitation, the lithium electrodes had a combined theoretical capacity of about 4 ampere hours compared to 0.5 - 1.0 ampere hour in the  $\text{CuF}_2$  electrode. The "standard" separation in these cells was 0.02 in. thick glass fiber mat, and 50g  $\text{LiClO}_4$ /100 ml methyl formate was employed as the electrolyte. The cells had polyethylene outside cases, and were placed between blocks for lateral support. The cell components, an assembled cell, and a number of cells assembled for discharge are pictured in Figures 31 to 33, pages 97 and 98.

Discharge tests were performed at current densities of 5 - 15 mA/cm<sup>2</sup>. Test temperature was generally -15°C in order to minimize solvent loss during discharge. Some typical voltage-time curves for these discharges are presented in Figures 34 and 35, pages 99 and 100. A summary of construction and discharge data is given in the Appendix, Table A-10, page 141.

To a final cell voltage of 2.0 volts, electrochemical efficiencies in the range of 50 - 70% were obtained for the  $\text{CuF}_2$  electrodes. The initial and average discharge potential of the cells increased with increasing graphite content of the paste. As expected, increasing the current density from 10 to 15 mA/cm<sup>2</sup> decreased the discharge potential; however, the electrochemical efficiency was not significantly affected over the current density range of 5.0 to 15.0 mA/cm<sup>2</sup>. Increasing the thickness of the electrodes from 0.025 in. to 0.050 in. decreased both the discharge potential and the electrochemical efficiency. Lithium perchlorate added to the paste in amounts of 3.0 to 12.0g/100g of  $\text{CuF}_2$  showed no noticeable effect on the discharge properties of the electrodes.

It may be seen from the tabulation of cell construction data that the theoretical capacity of 1.5 x 1.5 x 0.025 in.  $\text{CuF}_2$  electrodes increases as the graphite content in the paste is decreased, while the electrolyte

Figure 31

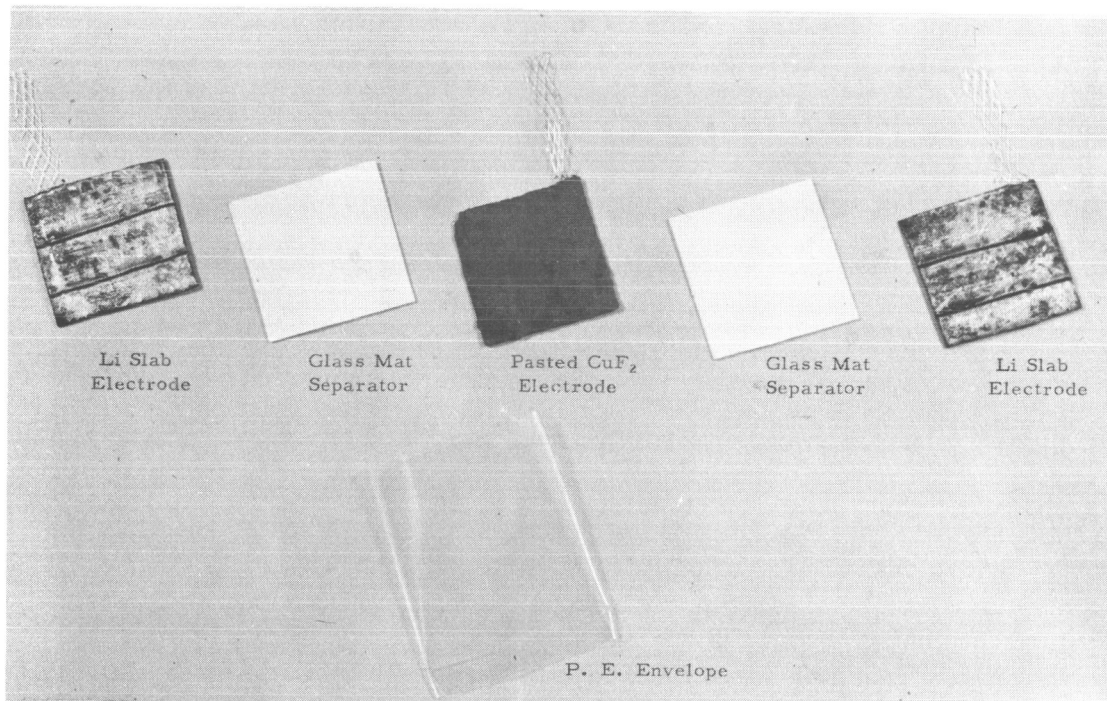
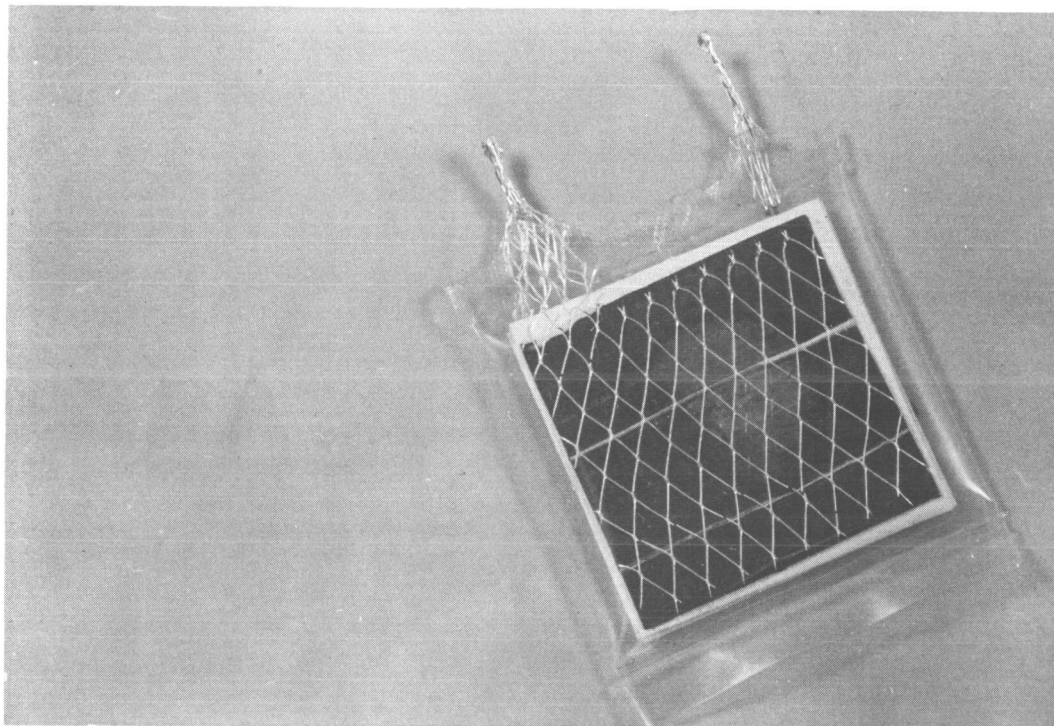
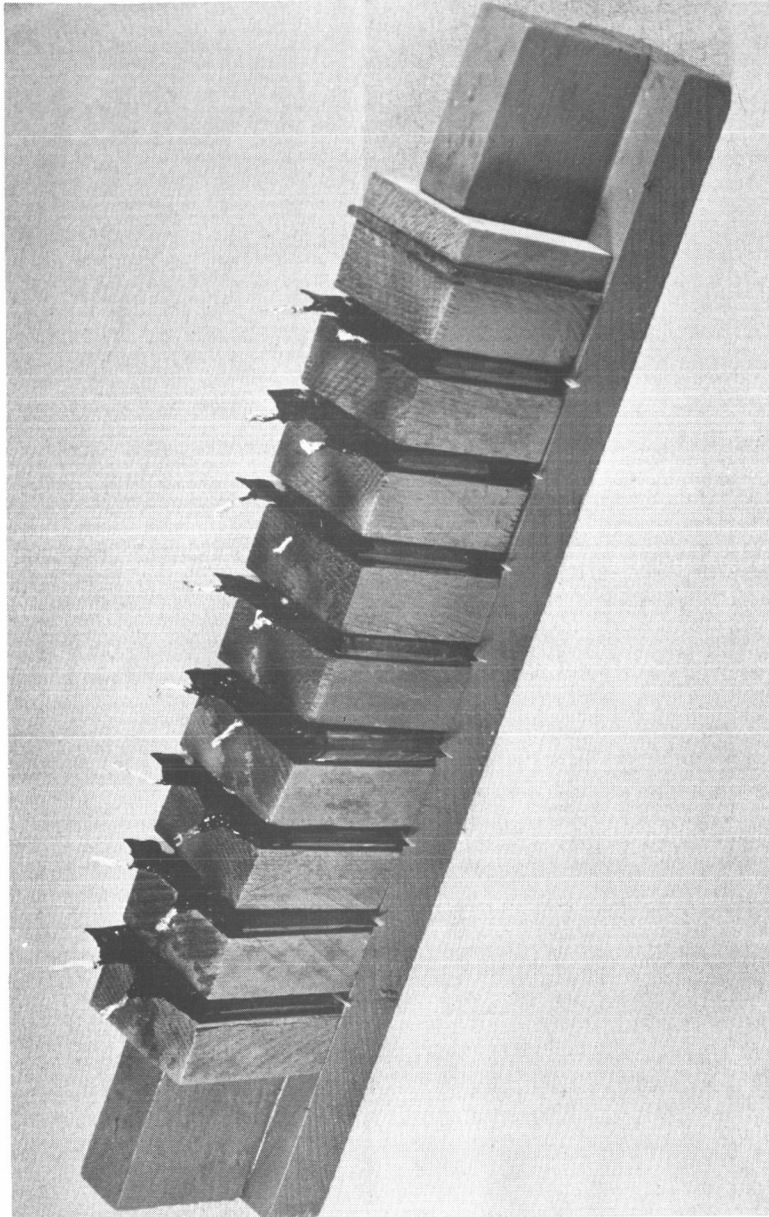
Pasted  $\text{CuF}_2$  Electrode Test  
Cell Components

Figure 32

Pasted  $\text{CuF}_2$  Electrode Test Cell



Cell Discharge Rack

Figure 33

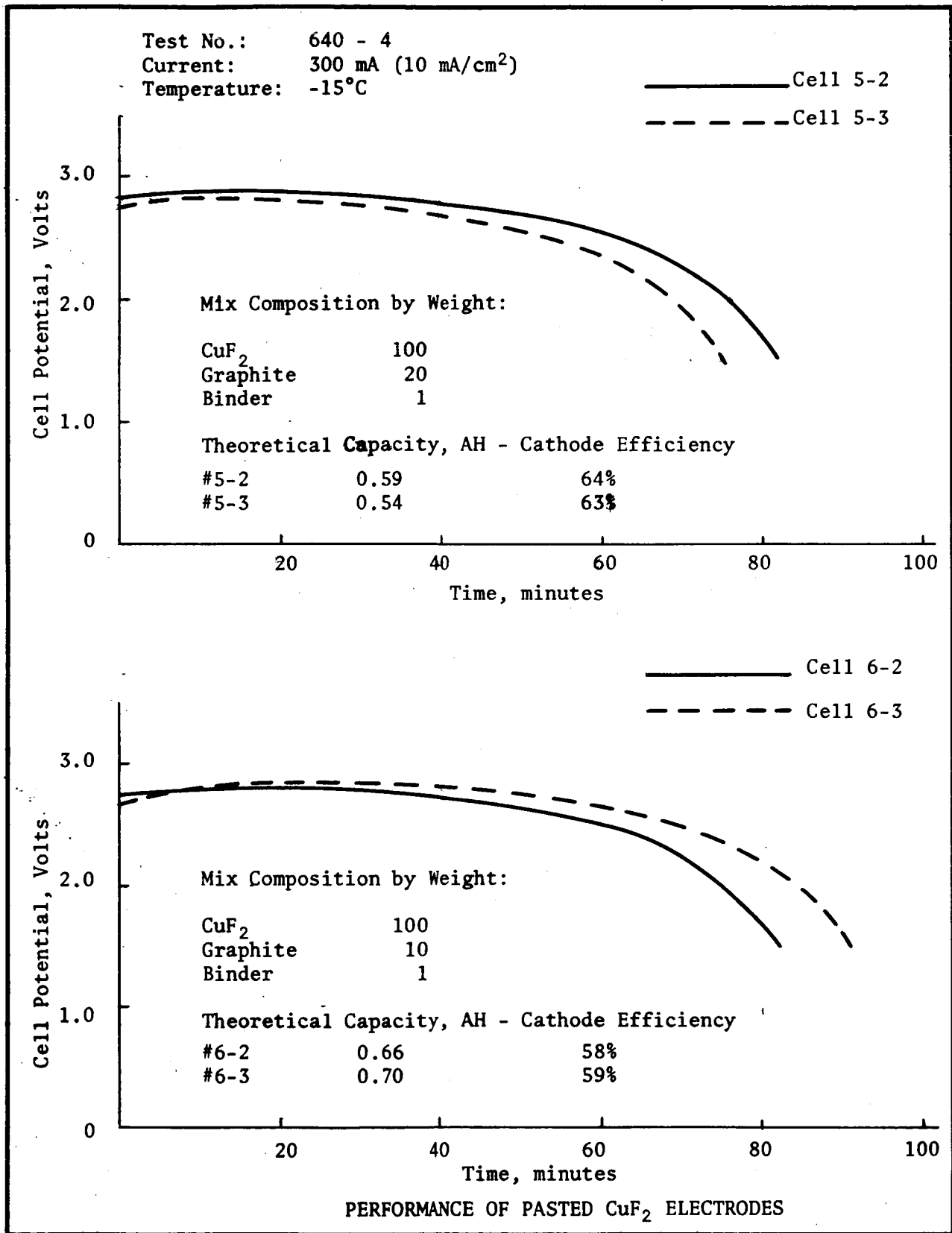


FIGURE 34



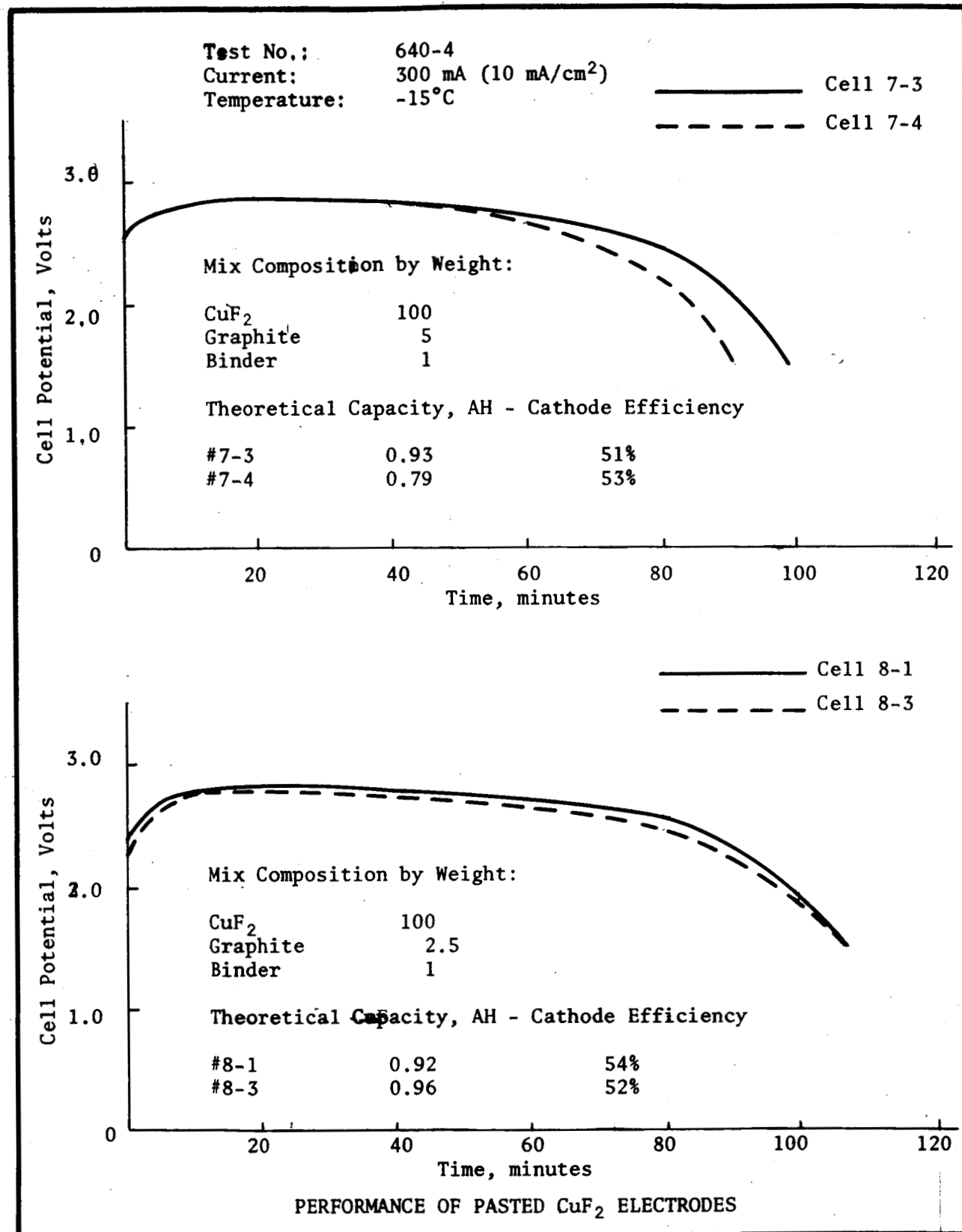


FIGURE 35

volume required for the cell remains essentially the same. Therefore, the theoretical energy density of the cell changes with  $\text{CuF}_2$  electrode composition. This has to be considered, in addition to the efficiency of  $\text{CuF}_2$  utilization, in the evaluation of the mix composition. In these tests, one gram of cellulose acetate and 10 - 20 grams of graphite per 100 grams of  $\text{CuF}_2$  represented an optimum composition range for the discharge rates employed.

### 3. 2. 2. Conductive Material

To evolve  $\text{CuF}_2$  electrodes for high energy density, high rate cells, the ratio of active to inactive material in the electrodes must be high. For electrodes operating at relatively high current densities, this may not be achieved at the expense of conductivity of the matrix. Thus, additives which lend good conductance when added in small concentrations, are desired for such electrodes.

Three conductive materials were compared in cell tests with Dixon air spun graphite, which had been used in most cell tests. The conductors evaluated were Conductex SC and SA-40-220 (Columbian Carbon Company) and alkaline battery type nickel flake (Electric Storage Battery Company).

Pasted  $\text{CuF}_2$  electrodes were prepared as described in Section 3. 2. 1. The mix composition was 20 grams  $\text{CuF}_2$  (Lot 7,  $\text{H}_2\text{O}$  content ca. 1.5%), 1 gram conductive material, and 0.2 gram cellulose acetate. After blending the dry components in a micronizer blender, pastes were prepared using the 10% alcohol - 90% ethyl acetate pasting solvent, and pasted onto expanded metal. After vacuum drying of the electrodes, three-plate cells with two lithium electrodes and glass fiber separation were assembled, activated with  $\text{LiClO}_4/\text{MF}$  electrolyte (50g salt/100 ml solvent), and discharged at 10 mA/cm<sup>2</sup> at -15°C. Construction data and discharge results for the cells are listed in Table XL, page 102, and voltage-time data for the best of the three cells in each group are plotted in Figure 36, page 103.

In this test series, the cells which had carbon black in the  $\text{CuF}_2$  paste mix gave better discharge performance than those with either graphite or nickel flake at the same concentration. Cell performance replication was comparatively poor, except for cells which had nickel flake additive. Also, the poor performance of cells having graphite conductor had not been characteristic to this paste composition in earlier tests. However, the best cells with carbon black additive gave  $\text{CuF}_2$  reduction efficiencies as high as 65% at the ca. 2 hour discharge rate. Since the active material in these electrodes is in the order of 80 - 90% including the weight of the silver grid, high energy densities should be possible with this electrode construction.

TABLE XI  
CONDUCTIVE MATERIAL EVALUATION

Discharge Current: 300 mA/cell (10 mA/cm<sup>2</sup>)  
 Temperature: -15°C

Cell No.	Conductive Material*	Dry paste Wt., gms	CuF <sub>2</sub> Capacity AH	Open Circuit Potential	Discharge Potential		Capacity to 2.0 VF AH	Cathodic Eff., %
					Initial	Average		
A-1	Conductex SC <sup>1</sup>	2.33	.997	3.56	2.86	2.70	.616	61.8
A-2	Conductex SC	2.75	1.205	3.54	2.95	2.71	.777	64.4
A-3	Conductex SC	2.60	1.131	3.55	2.06	2.08	.087	7.7
B-1	SA-40-220 <sup>2</sup>	2.54	1.101	3.53	3.09	2.74	.717	65.0
B-2	SA-40-220	2.45	1.056	3.53	3.09	2.74	.693	65.6
B-3	SA-40-220	2.10	.931	3.53	2.89	2.61	.516	55.5
C-1	Graphite <sup>3</sup>	2.60	1.131	3.45	Rev.	----	----	----
C-2	Graphite	2.59	1.126	3.55	2.64	2.64	.087	7.7
C-3	Graphite	2.70	1.180	3.54	2.66	2.32	.351	29.7
D-1	Ni Flake <sup>4</sup>	3.00	1.330	3.52	2.96	2.65	.562	48.6
D-2	Ni Flake	2.71	1.185	3.51	2.92	2.57	.567	48.0
D-3	Ni Flake	3.00	1.330	3.46	3.02	2.62	.642	48.2

\* 5 grams/100 g CuF<sub>2</sub>

<sup>1</sup> Columbian Carbon Company

<sup>2</sup> Columbian Carbon Company

<sup>3</sup> Dixon Airspun

<sup>4</sup> E. S. B. Company, Alkaline Battery Division.

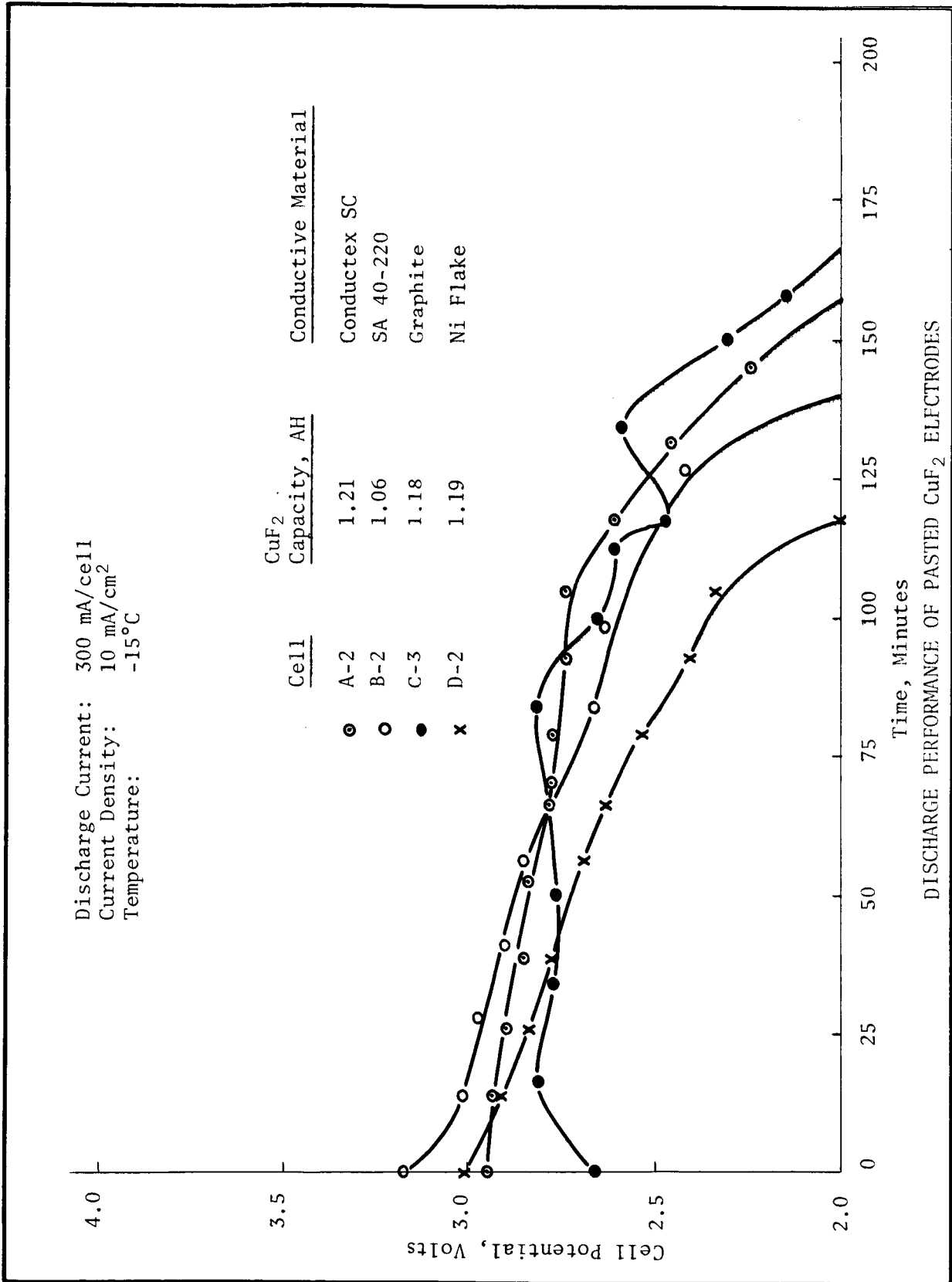


FIGURE 36

### 3. 2. 3. Effect of CuF<sub>2</sub> Water Content On Discharge Performance

Since the water content of CuF<sub>2</sub> was known to affect its solubility in the organic electrolytes, tests were performed to evaluate the effect of CuF<sub>2</sub> water content on discharge performance of the positive electrode.

Three-plate cells with pasted CuF<sub>2</sub> and sheet lithium electrodes were constructed as previously described. The CuF<sub>2</sub> electrodes were about 0.040 in. thick and had a theoretical capacity of about 1.0 AH. The paste composition was 100 parts CuF<sub>2</sub>, 10 parts graphite, and 1 part cellulose acetate, with 10 percent ethyl alcohol - 90 percent ethyl acetate as the pasting solution. A glass fiber mat, 0.02 in. thick, was used for electrode separation. Discharge tests were performed at 300 mA (10 mA/cm<sup>2</sup>) at -15°C in LiClO<sub>4</sub>-methyl formate electrolyte (50g salt/100 ml solvent), and the results obtained with the various materials are shown in Table XLI, page 105.

Performance of the cells can be related directly to the amount of water contained by the CuF<sub>2</sub> used to prepare the electrodes. Material from Lot 7 performed as expected from previous tests when the water content was above one percent. However, after argon stream drying to a water content below 0.3 percent, cell polarization was sufficiently severe to reverse polarity of the cells upon closing of the discharge circuit. Material from Lot 9, which had a water content of about 0.4 percent as received from the manufacturer, gave equally poor results.

The results indicate that completely dehydrated CuF<sub>2</sub> is too insoluble in the LiClO<sub>4</sub>-MF electrolyte to allow discharge at 10 mA/cm<sup>2</sup>. A water content of one percent seems to be required for discharge at the 1 - 10 hour rate. For a reserve-activated system, this water content does not appear to be prohibitively high.

### 3. 2. 4. Discharge Performance With CuF<sub>2</sub>·2H<sub>2</sub>O Active Material

To evaluate possible methods of manipulating the discharge properties of the CuF<sub>2</sub> electrodes, tests with CuF<sub>2</sub>·2H<sub>2</sub>O as an additive to CuF<sub>2</sub> were performed. The pasted positive electrodes, and 3-plate cells were prepared as described in Section 3. 2. 1. Discharge tests were performed at 10 mA/cm<sup>2</sup> and -15°C; results of the discharge tests are tabulated in Table XLII, page 106.

The CuF<sub>2</sub>- CuF<sub>2</sub>·2H<sub>2</sub>O mixture produced electrodes having about the same discharge characteristics as have been observed with electrodes made from CuF<sub>2</sub> as received from the manufacturer and having an equivalent total water

TABLE XLI

DISCHARGE PERFORMANCE OF DRIED  $\text{CuF}_2$  IN MF- $\text{LiClO}_4$  CELLS

Electrolyte: 50g  $\text{LiClO}_4$ /100 ml MF  
 Current: 300 mA (10 mA/cm<sup>2</sup>)  
 Temperature: -15°C

Cell No.	CuF <sub>2</sub> Treatment	% H <sub>2</sub> O by X-Ray	CuF <sub>2</sub> Capacity		Open Circuit Potential	Discharge Potential		Capacity to 2.0 VF AH	Cathodic Eff., %
			AH	AH		Initial	Average		
1	Lot 9B, untreated	0.4	.982	1.90	3.55	1.90	2.72	.455	46.3
2	Lot 9B, untreated	0.4	1.08	-----	3.50	-----	-----	.051	4.7
3	Lot 9B, untreated	0.4	1.11	-----	3.56	-----	-----	-----	-----
4	Lot 7, 16 hours, vacuum, room temp.	1.5	1.05	2.71	3.57	2.71	2.73	.732	69.7
5	Lot 7, 16 hours, vacuum, room temp.	1.5	0.910	3.00	3.54	3.00	2.75	.615	67.7
6	Lot 7, 16 hours, vacuum, 70°C	1.5	0.873	2.97	3.55	2.97	2.69	.555	63.7
7	Lot 7, 16 hours, vacuum, 70°C	1.2	0.925	2.56	3.50	2.56	2.68	.615	66.5
8	Lot 7, 16 hours, vacuum, 70°C	1.2	0.934	Rev.	0.02	Rev.	-----	-----	-----
9	Lot 7, 16 hours, vacuum, 70°C	1.2	1.00	2.91	3.55	2.91	2.70	.663	66.3
10	Lot 7, 23 hrs, argon sweep, 152°C	<0.3	0.958	Rev.	3.56	Rev.	-----	-----	-----
11	Lot 7, 23 hrs, argon sweep, 152°C	<0.3	0.934	Rev.	3.57	Rev.	-----	-----	-----
12	Lot 7, 23 hrs., argon sweep, 152°C	<0.3	0.967	Rev.	3.57	Rev.	-----	-----	-----

TABLE XLII

PERFORMANCE OF  $\text{CuF}_2$  and  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  IN  $\text{LiClO}_4/\text{MF}$  ELECTROLYTE

Electrolyte: 50g  $\text{LiClO}_4/100$  ml MF  
 Current: 300 mA (10 mA/cm<sup>2</sup>)  
 Temperature: -15°C

Cell No.	Active Material	% Water	$\text{CuF}_2$ Capacity AH	Open Circuit Potential	Discharge Potential		Capacity to 2.0 VF AH	Cathodic Eff., %
					Initial	Average		
1	95% $\text{CuF}_2$ , 5% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	1.3*	1.23	3.61	2.91	2.69	0.845	68.7
2	95% $\text{CuF}_2$ , 5% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	"	0.998	3.61	2.98	2.76	0.702	70.4
3	95% $\text{CuF}_2$ , 5% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	"	1.07	3.61	2.54	2.42	0.475	44.4
4	100% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	26	1.01	1.50	Rev.	-----	-----	-----
5	100% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	"	0.89	3.63	2.94	2.76	0.520	66.9
6	100% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	"	0.97	3.63	2.94	2.76	0.558	65.3

\*Calculated.

content (ca. 2 percent). Electrodes made from 100 percent  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  gave similar discharge potential and electrochemical efficiency as the  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ - $\text{CuF}_2$  mixture.

The above results further demonstrate that (1) water in the range of 1 - 2 percent may be necessary for rapid discharge of  $\text{CuF}_2$ , and (2) the water may be present as an impurity in the original  $\text{CuF}_2$ , or it may be added in the form of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ .

### 3. 2. 5. Effect of Electrolyte Concentration

To determine the best  $\text{LiClO}_4$  concentration for the MF electrolyte, a series of 3-plate test cells were built and discharged. Concentrations over the range of 20 to 70g  $\text{LiClO}_4$ /100 ml MF were used, and the cells were discharged at 20, 8.3 and 3.0mA/cm<sup>2</sup> (600, 250, and 90 mA).

#### 3. 2. 5. 1. "Open" Cells at -15°C

Electrodes and cells were prepared as described in Section 3. 2. 1. The positive paste composition was  $\text{CuF}_2$ -100 parts; graphite - 10 parts; cellulose acetate - 1 part. The discharge tests were performed at -15°C to minimize loss of methyl formate by evaporation.

Results of these discharge tests are summarized in Table XLIII, page 108 to 110. For the discharge conditions used, an optimum electrolyte concentration of 50 - 60g  $\text{LiClO}_4$ /100 ml MF is indicated.

#### 3. 2. 5. 2. Hermetically Sealed Cells At Room Temperature

To study the effect of room temperature and hermetic sealing on the performance of the  $\text{CuF}_2$ -Li system in methyl formate, a series of test cells were built and discharged in glass compatibility tubes. The tubes had an I. D. of about 1.0 in. and a volume of ca. 85 ml, and were equipped with terminal plates for connections to the electrodes.

The lithium electrodes were prepared by pressing a strip of 1/2 x 1/16 inch ribbon onto expanded silver support. The  $\text{CuF}_2$  electrodes were made by pasting a mix having the composition

$\text{CuF}_2$ (1.5% $\text{H}_2\text{O}$ )	19
Graphite	2
Cellulose Acetate	0.2

onto expanded silver. The cross-sectional area of both electrodes was 6.0 cm<sup>2</sup>. Separation was provided by 0.02 inch thick glass filter-mat.



TABLE XLIII  
EFFECT OF  $\text{LiClO}_4$  CONCENTRATION ON  $\text{CuF}_2$ -Li CELL

PERFORMANCE IN METHYL FORMATE											
Current: 600 mA (20 mA/cm <sup>2</sup> ) Temperature: -15°C											
Cell No.	Theo. $\text{CuF}_2$ Capacity AH	Electrolyte Conc. g $\text{LiClO}_4$ /100 ml MF	Electrolyte Volume	Time to 2.0 VF Hours	AH to 2.0 VF	Average Discharge Potential to 2.0 VF	Cathodic Eff., %				
1	1.24	20	3.4	0.62	0.37	2.26	30				
2	1.17	20	5.0	0.57	0.34	2.23	29				
3	1.12	30	5.0	0.61	0.37	2.14	33				
4	1.12	30	4.2	0.59	0.36	2.46	32				
5	1.07	40	4.9	0.79	0.48	2.46	44				
6	1.17	40	4.2	0.84	0.51	2.40	43				
7	1.08	50	4.3	0.98	0.59	2.42	55				
8	1.21	50	4.2	1.11	0.67	2.43	55				
9	1.10	60	4.1	1.05	0.63	2.29	57				
10	1.16	60	4.3	1.08	0.65	2.24	56				
11	1.29	70	4.0	0.19	0.11	2.08	8.5				
12	1.29	70	4.1	0.14	0.08	2.10	6.7				

TABLE XLIII (Continued)  
 EFFECT OF  $\text{LiClO}_4$  CONCENTRATION ON  $\text{CuF}_2$ -Li CELL

PERFORMANCE IN METHYL FORMATE

Current: 250 mA ( $8.3 \text{ mA/cm}^2$ )  
 Temperature:  $-15^\circ\text{C}$

Cell No.	Theo. $\text{CuF}_2$ Capacity AH	Electrolyte Conc. g $\text{LiClO}_4$ /100 ml MF	Electrolyte Volume	Time to 2.0 VF Hours	AH to 2.0 VF	Average Discharge Potential	Cathodic Eff., %
1	1.04	20	5.0	1.34	0.34	2.55	32
2	1.31	20	5.0	1.73	0.43	2.52	33
3	1.14	30	5.0	2.20	0.55	2.49	48
4	1.12	30	5.0	2.17	0.54	2.60	48
5	1.16	40	5.0	2.42	0.61	2.62	52
6	1.10	40	5.0	2.41	0.60	2.70	55
7	1.17	50	5.0	3.29	0.82	2.70	70
8	1.20	50	5.0	3.49	0.87	2.65	73
9	1.18	60	5.0	3.57	0.89	2.58	76
10	1.10	60	5.0	3.15	0.79	2.56	72
11	1.15	70	5.0	3.16	0.79	2.31	69
12	1.21	70	4.8	2.50	0.63	2.22	52

TABLE XLIII (Continued)  
 EFFECT OF  $\text{LiClO}_4$  CONCENTRATION ON  $\text{CuF}_2$ -Li CELL

PERFORMANCE IN METHYL FORMATE

Current: 90 mA ( $3 \text{ mA/cm}^2$ )  
 Temperature:  $-15^\circ\text{C}$

Cell No.	Theo. $\text{CuF}_2$ Capacity AH	Electrolyte Conc. g $\text{LiClO}_4$ /100 ml MF	Electrolyte Volume	Time to 2.0 VF Hours	AH to 2.0 VF	Average Discharge Potential to 2.0 VF	Cathodic Eff., %
1	1.20	20	5.2	1.77	0.16	2.64	13
2	1.17	20	5.0	1.77	0.16	2.58	14
3	1.09	30	5.0	3.01	0.27	2.29	25
4	1.12	30	5.0	3.01	0.27	2.35	24
5	1.21	40	5.0	5.17	0.47	2.64	38
6	1.22	40	5.0	4.15	0.37	2.67	31
7	1.15	50	3.0	5.87	0.53	2.70	46
8	1.20	50	2.8	6.60	0.59	2.67	49
9	1.35	60	3.5	9.26	0.83	2.67	62
10	1.20	60	4.0	7.58	0.68	2.71	57
11	1.22	70	3.0	1.43	0.13	2.34	11*
12	1.29	70	4.0	0.29	0.84	2.66	65

\* Cell failed to absorb electrolyte. Separator dry and clean at post-discharge examination.

The electrodes and separation were assembled into 3-plate cells between glass slides held together by rubber bands. About 0.5 in. of the glass mat separation was allowed to be exposed below the bottom of the glass slides. The assembly was then lowered into the glass compatibility tube containing 5 ml of electrolyte solution, allowing the exposed separation to dip into the liquid; the tubes were then sealed.

Cell discharges were performed at 35°C and current densities of 20, 8.6 and 3.2 mA/cm<sup>2</sup>. An open circuit stand time of 15 - 20 minutes was allowed for the cathode and separation to become fully wet with the electrolyte. Results of the discharge are summarized in Table XLIV, pages 112 to 114, and selected voltage-time data have been plotted in Figures 37 to 39, pages 115 to 117.

Both discharge potential and electrochemical efficiency of the CuF<sub>2</sub> electrode were higher in these tests than had been obtained in the envelope cells at -15°C. The electrolyte concentration of 50g LiClO<sub>4</sub>/100 ml MF appeared to be the best compromise over the discharge rate range tested. Lower electrolyte concentrations performed better at the lower discharge rate (10 - 15 hour rate), while the higher rates (ca. 1 - 2 hour rates) appeared to benefit from higher LiClO<sub>4</sub> concentration.

The pressure in all tubes remained below 5 psig during the discharge, indicating that internal pressure should not present a problem with methyl formate batteries at ambient temperatures. In a separate test at 74°C, the vapor pressure above the 50g LiClO<sub>4</sub>/100 ml MF electrolyte was found to be 10 psig.

### 3. 3. Seven-Plate Cell Tests

To study the problems associated with scaling up the 3-plate test cells used for cathode studies to cells having 4 - 5 AH capacity and more nearly balanced Li and CuF<sub>2</sub> theoretical capacities, 7-plate cells were constructed and tested.

Copper fluoride electrodes were made by applying paste having the following composition

CuF <sub>2</sub>	44.0 g
Dixon Graphite	4.4 g
Cellulose Acetate (2% solution in 90 ethyl acetate/10 ethyl alcohol)	0.44 g

to silver grids in a 1.5 x 2 x 0.03 in. polypropylene mold.

TABLE XLIV  
 EFFECT OF  $\text{LiClO}_4$  CONCENTRATION ON SEALED  $\text{Li-CuF}_2$

CELL PERFORMANCE IN METHYL FORMATE

Current: 250 mA (20 mA/cm<sup>2</sup>)  
 Temperature: 35°C

Cell No.	g $\text{LiClO}_4$ 100 ml, MF	Electrolyte $\text{H}_2\text{O}$ , ppm	CuF <sub>2</sub> Capacity AH	Discharge Potential		Cap. to 2.0 VF, AH	Electrochemical Efficiency %
				Initial	Average		
1	20	2110	.78	2.72	2.66	.33	42
2	20	2110	.77	2.79	2.53	.35	46
3	30	1770	.77	2.63	2.34	.32	42
4	30	1770	.74	2.76	2.49	.47	63
5	40	3100	.72	2.64	2.52	.33	47
6	40	3100	.86	2.77	2.50	.35	40
7	50	1130	.73	2.85	2.59	.38	52
8	50	1130	.78	2.85	2.65	.40	53
10	60	3300	.87	2.65	2.35	.30	35
11	60	3300	.75	2.65	2.48	.36	49
12	70	1700	.65	2.65	2.42	.34	53
13	70	1700	.79	2.58	2.38	.31	40
14	80	1200	.86	2.50	2.29	.22	26
15	80	1200	.89	2.20	2.27	.16	18
16	90	490	.94	0	0	0	0
17	90	490	.75	0	0	0	0

TABLE XLIV (Continued)  
 EFFECT OF LiClO<sub>4</sub> CONCENTRATION ON SEALED Li-CuF<sub>2</sub>  
 CELL PERFORMANCE IN METHYL FORMATE

Current: 104 mA (8.6 mA/cm<sup>2</sup>)  
 Temperature: 35°C

Cell No.	g LiClO <sub>4</sub> / 100 ml, MF	Electrolyte H <sub>2</sub> O, ppm	CuF <sub>2</sub> Capacity AH	Discharge Potential		Cap. to 2.0 VF, AH	Electrochemical Efficiency %
				Initial	Average		
20	20	2110	.80	2.94	2.55	.16	58
21	20	2110	.79	2.96	2.54	.46	58
22	30	1770	.79	2.96	2.67	.54	69
23	30	1770	.84	3.03	2.76	.60	71
24	40	3100	.72	3.05	2.78	.58	81
25	40	3100	.77	3.06	2.80	.62	81
26	50	1130	.69	3.02	2.69	.54	78
27	50	1130	.71	3.04	2.71	.59	83
28	60	3300	.75	2.88	2.66	.51	68
29	60	3300	.77	2.85	2.67	.57	74
30	70	1700	.80	2.77	2.60	.51	65
31	70	1700	.72	2.70	2.64	.46	64
32	80	1200	.66	2.57	2.50	.49	74
33	80	1200	.64	2.56	2.60	.36	56
34	90	490	.74	2.43	2.53	.54	74
35	90	490	.66	2.48	2.54	.43	65

TABLE XLIV (Continued)  
 EFFECT OF  $\text{LiClO}_4$  CONCENTRATION ON SEALED  $\text{Li-CuF}_2$

CELL PERFORMANCE IN METHYL FORMATE

Current: 38 & 42 mA (3.2 & 3.5 mA/cm<sup>2</sup>)\*  
 Temperature: 35°C

Cell No.	g $\text{LiClO}_4$ / 100 ml, MF	Electrolyte $\text{H}_2\text{O}$ , ppm	$\text{CuF}_2$ Capacity AH	Discharge Potential		Cap. to 2.0 VF, AH	Electrochemical Efficiency %
				Initial	Average		
36	20	2110	.76	3.00	2.66	.53	70
37	20	2110	.89	3.00	2.68	.64	72
38	30	1770	.71	3.02	2.78	.53	74
39	30	1770	.71	3.04	2.76	.64	74
40	40	3100	.85	3.14	2.77	.53	72
41	40	3100	.93	3.18	2.87	.52	70
42	50	1130	.72	3.18	2.77	.61	67
43	50	1130	.91	3.20	2.92	.65	66
44	60	3300	.77	3.12	2.92	.48	46
45	60	3300	.79	3.16	2.92	.60	55
46	70	1700	.83	3.02	2.89	.35	48
47	70	1700	.81	2.90	2.91	.43	53
48	80	1200	.83	2.64	2.94	.35	42
49	80	1200	.68	2.28	2.75	.33	49
50	90	490	.94	1.80	2.58	.38	41
51	90	490	.82	2.30	2.83	.38	46

\*Cells 36 -39 were discharged at 42 mA. Remaining cells were discharged at 38 mA.

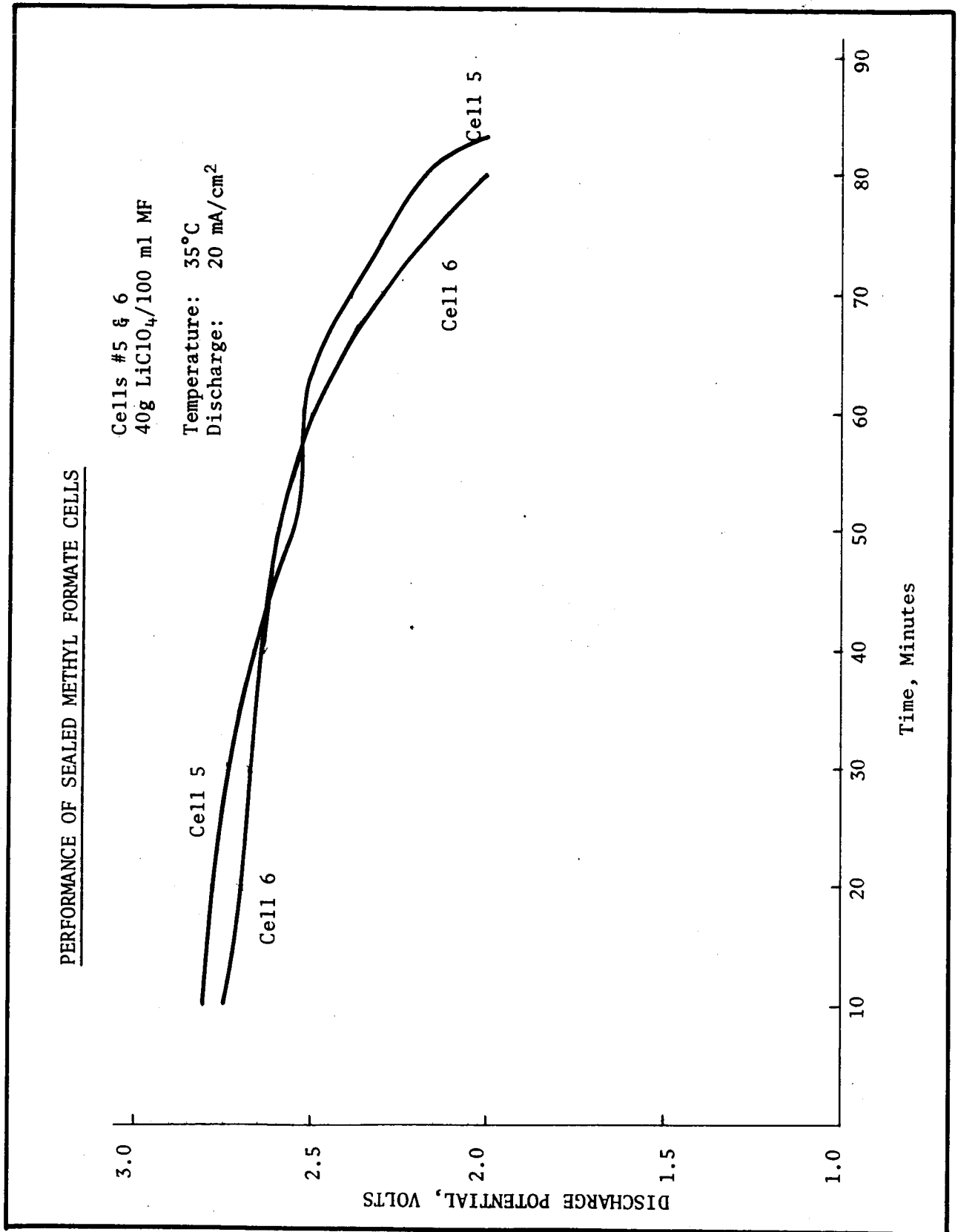
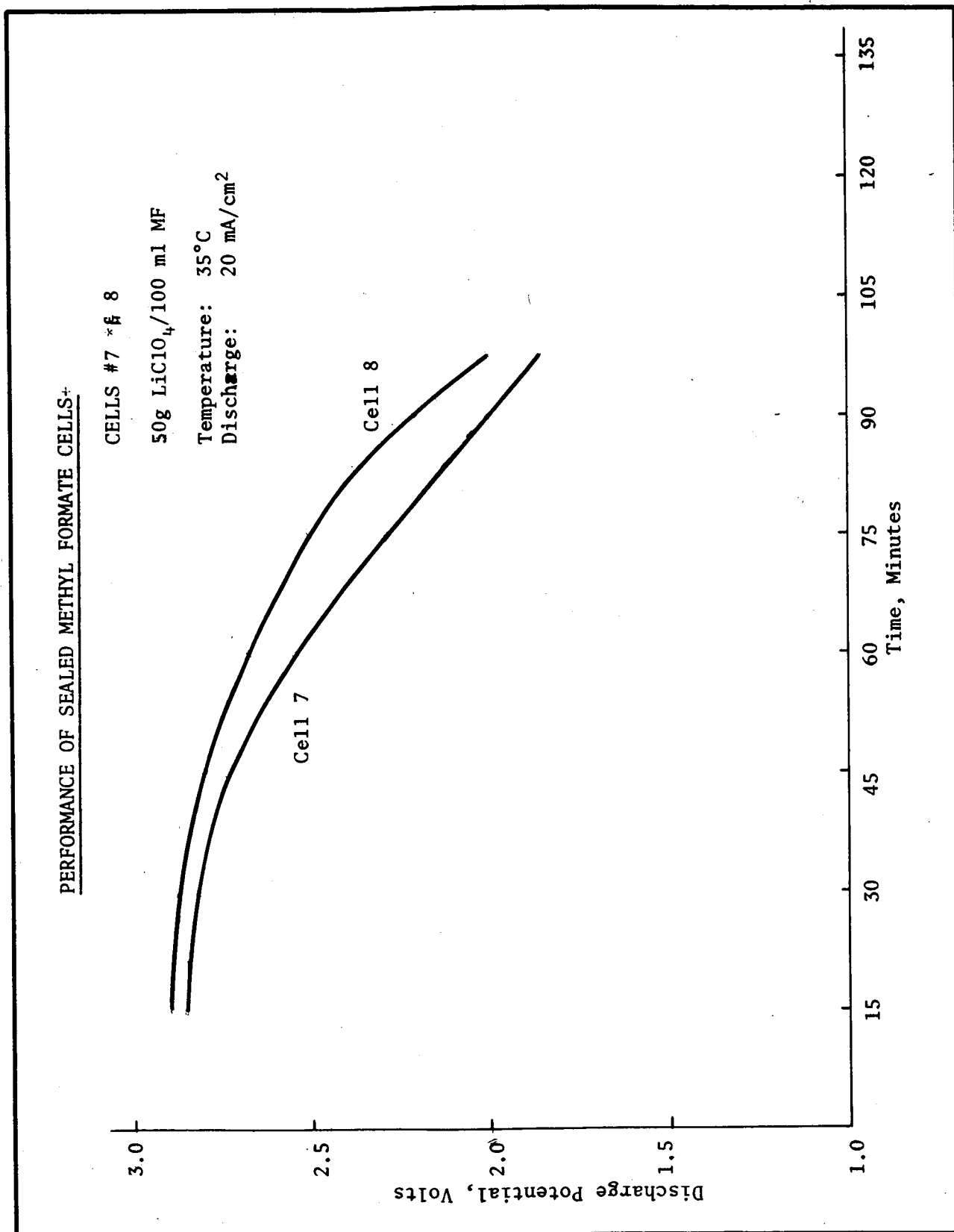


FIGURE 37





FIGURES 38

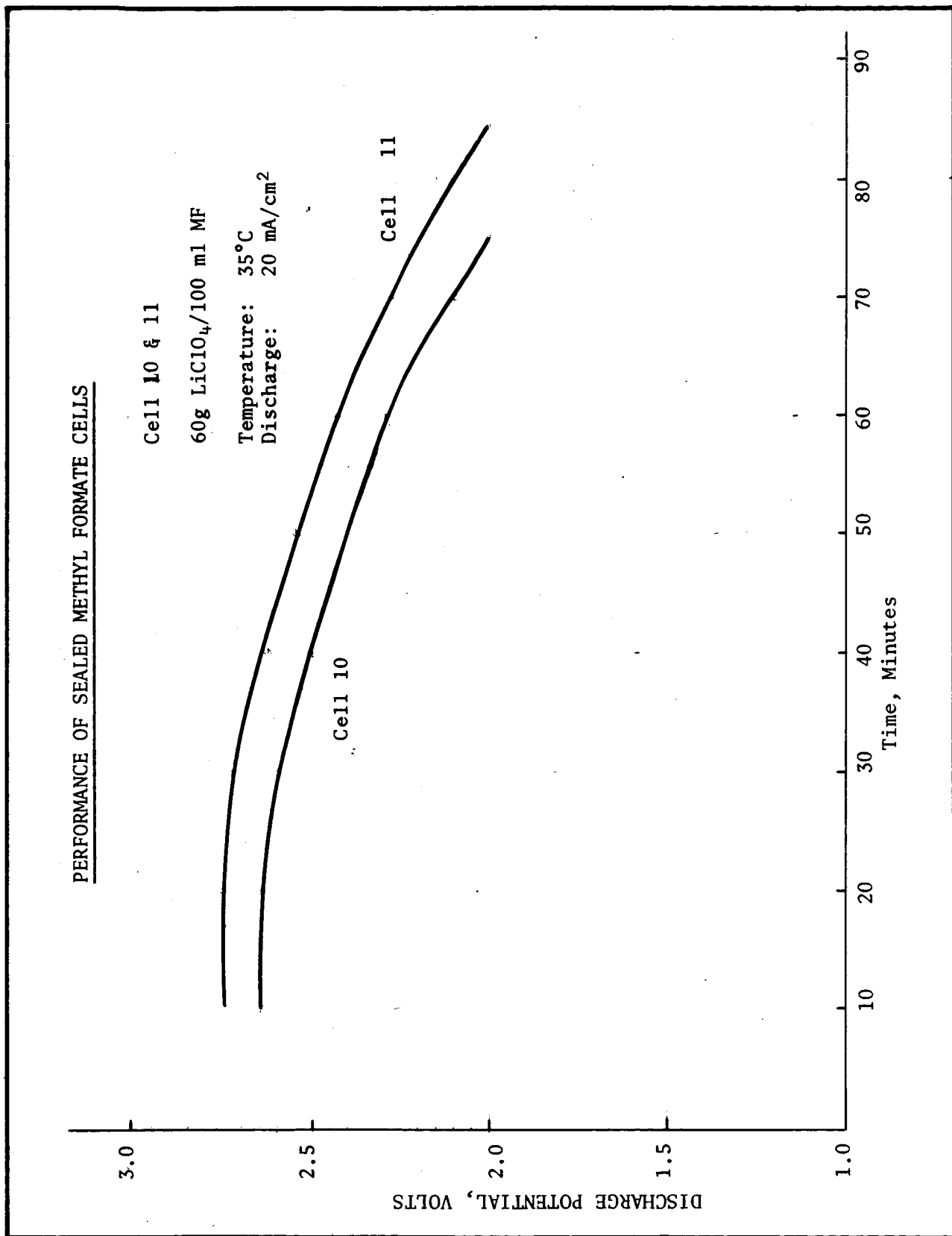


FIGURE 39

Dry ingredients were ground in the "Hi-Speed" mixer after which the resin solution was added to make the paste. The plates were dried under hard vacuum overnight before cell assembly. Anodes were fabricated by pressing 2 x 1.5 x 0.015 in. lithium sheets onto one or both sides of 1.5 x 2 in. expanded silver grids. Two single-sided and two double-sided anodes were made for assembly in the 7-plate cell configuration.

Three cells were assembled with three cathodes, two double anodes, and two single anodes per cell so that each cathode surface faced an anode surface. The plates were separated by 0.02 in. thick glass filter mat and sealed in 2 in. wide polyethylene envelopes.

The cells were assembled in a wooden test rack enclosed in a polyethylene bag. The assembly was placed in -12°C freezer three hours prior to activation with 50g LiClO<sub>4</sub>/100 ml MF electrolyte, pre-cooled to -12°C.

Two cells were activated after one day of storage under argon, and after 15 minutes of wet stand discharged through resistive loads of 2.74 or 3.53 ohms. The third cell was stored at room temperature under argon for a period of four weeks, at which time it was activated and discharged under the same conditions as cell #1 (2.74 ohms at -12°C).

Results of the discharges and construction data are presented in Table XLV, page 118. Voltage-time curves for the three cells are given in Figure 40, page 119.

The results obtained with these cells are about equivalent to those obtained with the 3-plate elements in previous tests. No scale-up problems appear to exist for building 4 - 5 AH cells with the present construction. Also, the cells appear to be storable under argon prior to activation for at least the 4-week period used in this test.

TABLE XLV  
PERFORMANCE OF SEVEN-PLATE CELLS

Cell No.	Dry Stand Time	Theo. Capa. AH	Discharge		Average Discharge Potential	AH to 2.0 VF	Cathodic Eff., %
			Time to 2.0 VF (hours)	Load $\Omega$			
1	1 day	5.42	3.96	2.74	2.51	3.63	67
2	1 day	5.46	5.07	3.53	2.62	3.76	69
3	28 days	5.33	3.68	2.74	2.35	3.09	58

Electrolyte: 50g LiClO<sub>4</sub>/100 ml MF  
Electrode Area: 116 cm<sup>2</sup>  
Temperature: -15°C

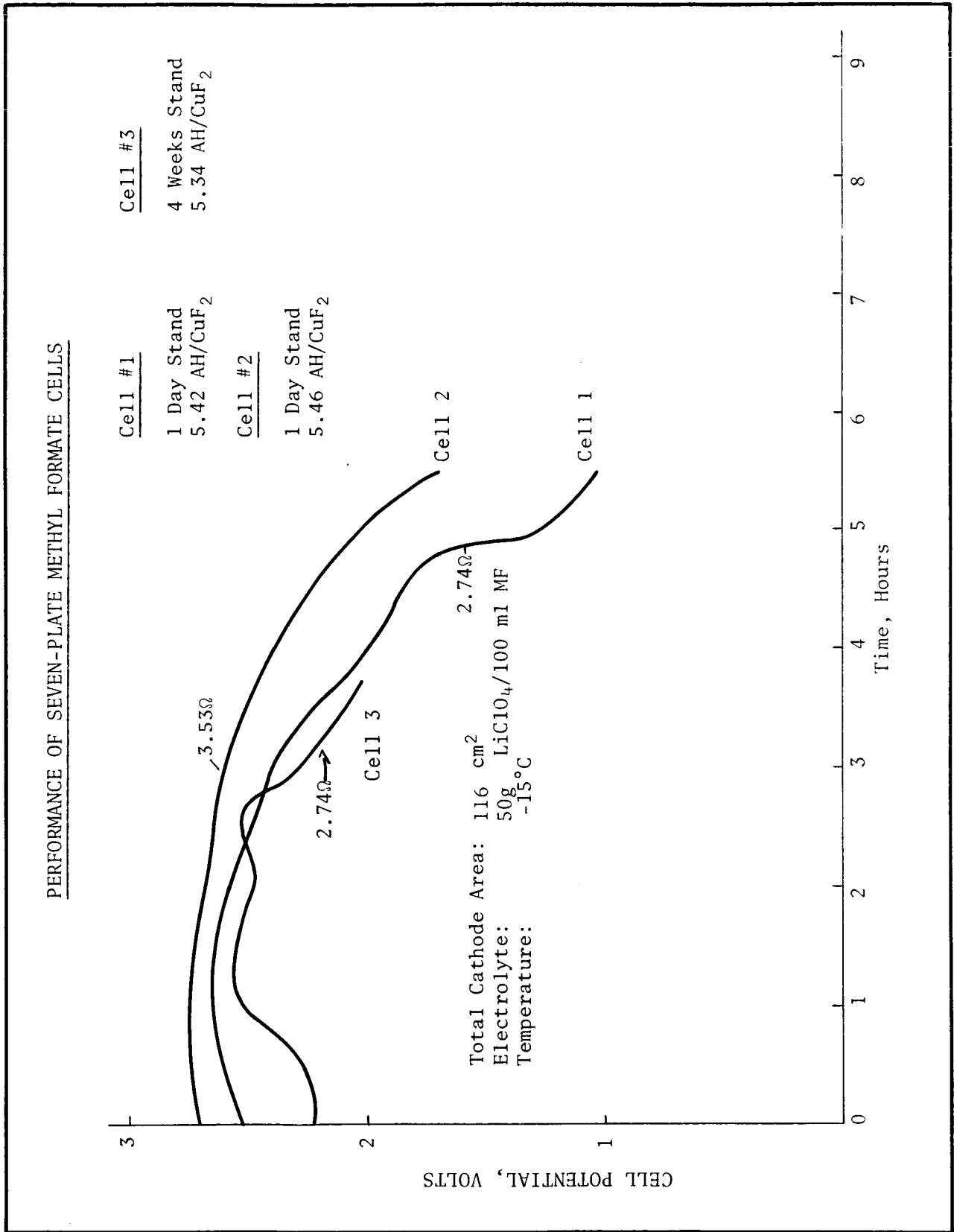


FIGURE 40

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APPENDIX

TABLE A-1

LITHIUM STABILITY IN PROPYLENE CARBONATE SOLUTIONS (+25°C)

Exposure Time (hrs.)	H <sub>2</sub> O = 710 ppm No Solute	H <sub>2</sub> O = 1900 ppm 15g LiClO <sub>4</sub> /100 ml	H <sub>2</sub> O = 390 ppm No Solute	H <sub>2</sub> O = 390 ppm 15g LiClO <sub>4</sub> /100 ml
10	Li surfaces black.	Tarnishing of cut Li.	No visible attack.	No visible attack.
25	No further changes.	Film covering shiny Li; Gelatinous material in the liquid.	Cut Li is blackened.	No visible attack.
100	Same	Heavy gelatinous material in liquid.	Cut Li black; degreased surface blackened	No visible attack.
300			Degreased Li completely black.	No attack on shiny Li, however, amorphous surface is now white.
500			Li completely black; and curling.	No further changes.

TABLE A-2

## LITHIUM STABILITY IN PROPYLENE CARBONATE SOLUTIONS (+25°C)

Exposure Time (hrs.)	H <sub>2</sub> O = 710 ppm No Solute	H <sub>2</sub> O = 660 ppm 15g LiClO <sub>4</sub> /100 ml	H <sub>2</sub> O = 180 ppm No Solute	H <sub>2</sub> O = 190 ppm 15g LiClO <sub>4</sub> /100 ml
10	Cut surfaces black; degreased surfaces tarnishing.	No visible attack.	Li tarnishing.	No visible attack.
25	Translucent film covering most of the Li; white gelatinous material in liquid.	No visible attack.	Cut surfaces black.	No visible attack.
100	White material increasing. Dull and curling.	Tarnishing of cut surfaces and white gelatinous material in liquid.	Degreased Li black.	No visible attack.
300	No change.	No change.	2/3 of degreased Li black.	No visible attack.
500			Li completely black and curling; white, gelatinous material in liquid.	No visible attack.

TABLE A-3

LITHIUM STABILITY IN PROPYLENE CARBONATE SOLUTIONS (+35°C)

Time, Hours	Propylene Carbonate purified by distillation alone.		Propylene Carbonate purified by lithium treatment & distillation.	
	No Solute H <sub>2</sub> O + (25 ± 20)ppm	1M LiClO <sub>4</sub> H <sub>2</sub> O = 175 ppm	No Solute H <sub>2</sub> O <25ppm	1M LiClO <sub>4</sub> H <sub>2</sub> O = 150 ppm
15	Cut Li surfaces tarnished.	No attack.	Li surface tarnished.	No attack.
45	Li surface black.	No attack.	Same	No attack.
70	No changes.	No attack.	No changes.	No attack.
160	No changes.	No attack.	Same	No attack.
210	No changes.	Li slightly tarnished.	Same	Cut Li surface tarnishing.
330	Gelatinous mate- rial in bottom of tube.	Gelatinous material in bottom of tube.	Same	Same
540	Same	No change.	Same	Trace of gela- tinous material in bottom of tube.
1250	Gelatinous mate- rial & some crys- talline white material in bottom of tube; liquid turbid. Li surfaces black.	All surfaces dulled; gela- tinous mate- rial in bottom of tube.	Li surface dulled & tarnished; gelatinous material in bottom of tube.	Some gelatinous material in bottom of tube; liquid phase clear & colorless; cut sur- face very shiny.



TABLE A-4

LITHIUM STABILITY TESTS IN 1.0 M PROPYLENE CARBONATE

<u>Solution</u>	<u>Time, Days</u>	<u>Lithium</u>	<u>Solutions</u>
LiClO <sub>4</sub>	7	Bright	Clear
	14	Bright	Clear
	21	Dull	Clear
NaClO <sub>4</sub>	7	Black growth	White gel ppt.
	14	Black growth	Brown gel ppt.
	21	Brown & black growth	Voluminous ppt.
KPF <sub>6</sub>	7	Etched	Clear
	14	Etched	Clear
	21	Dull	Clear
KAsF <sub>6</sub>	7	Etched	Clear
	14	Black	Clear
	21	Black	Clear
LiBF <sub>4</sub> (m) <sup>1</sup>	7	Dull black	Clear, pale yellow
	14	Dull black	Clear, pale yellow
	26	Dull black	Clear, pale yellow
LiPF <sub>6</sub> (m) <sup>1</sup>	7	Dull black	Clear, pale yellow
	14	Dull black	Clear, pale yellow
	26	Black	Clear, pale yellow
LiAsF <sub>6</sub> (m) <sup>1</sup>	7	Dull black	Clear
	14	Dull black	Clear
	26	Dull black	Clear
NaAsF <sub>6</sub> (m) <sup>1</sup>	7	Dull black, gassing	Clear, white ppt.
	14	Dull black, yellow growth	Clear, white ppt.
	26	Dull black, yellow growth	Clear, white ppt.
LiBF <sub>4</sub> (F) <sup>2</sup>	7	Bright	Clear
	14	Bright	Clear
	26	Bright	Clear
LiBF <sub>4</sub> (F) <sup>2</sup>	7	Bright	Clear
	14	Bright	Clear
	26	Bright	Clear

<sup>1</sup> Metathetical preparation.

<sup>2</sup> Supplied by Foote Mineral Co.

TABLE A-5

LITHIUM STABILITY IN VARIOUS ELECTROLYTES

<u>Electrolyte</u> *	<u>Time, Days</u>	<u>Lithium</u>	<u>Solution</u>
LiClO <sub>4</sub> /PC	7	Bright	Clear
	14	Dull	Clear
	21	Dull & Black	Clear
KAsF <sub>6</sub> /PC	7	Bright	Clear
	14	Dull	Clear
	21	Dull & Black	Clear
LiClO <sub>4</sub> /DMSO	7	Bright	Clear
	14	Dull & Black	Clear
	21	Dull & Black	Clear
KAsF <sub>6</sub> /DMSO	7	Bright	Clear
	14	Dull	Clear
	21	Dull	Clear
LiClO <sub>4</sub> /AA	7	Gray deposits	Clear, white ppt.
	14	Gray deposits	Clear, white ppt.
	21	Gray deposits	Clear, white ppt.
KAsF <sub>6</sub> /AA	7	Dull	Clear
	14	Gray deposits	Clear, white ppt.
	21	Gray deposits	Clear, white ppt.
LiClO <sub>4</sub> /NNDA	7	Dull	Clear
	14	Flesh colored deposits	Clear
	21	Flesh colored deposits	Clear
KAsF <sub>6</sub> /NNDA	7	Dull	Clear
	14	Dull & Black	Clear
	21	Dull & Black	Clear
LiClO <sub>4</sub> /NM	7	Decomposed	Dark brown ppt.
	14	Decomposed	Dark brown ppt.
	21	-----	-----
KAsF <sub>6</sub> /NM	7	Black, coating	Clear
	14	Black, coating	Clear
	21	Black, coating	Clear

\* 1 mole of salt/L of solvent.

TABLE A-5(A)

## LITHIUM STABILITY IN METHYL FORMATE

Exposure Time	CaO Treated	
	25g LiClO <sub>4</sub> /100 ml H <sub>2</sub> O: 350 ppm	50g LiClO <sub>4</sub> /100 ml H <sub>2</sub> O: 350 ppm
11 days	Untreated 25g LiClO <sub>4</sub> /100 ml Pressure buildup. Li coated with white film, solution yellow and turbid.	Sol'n light yellow. Li strip covered with white crystalline material. Sol'n clear yellow. Li strip covered with white flocculant material.
14 days	Li completely covered with a thick white film. Sol'n brownish-yellow and turbid.	Li completely covered with white film. Sol'n clear, light yellow. Sol'n clear, yellow, brown tinge. Some flocculant white material on bottom of test tube.
17 days	Sol'n & Li one solid white mass.	Heavy white film on Li surfaces. Sol'n light brown. Heavy white film on Li surface.
48 days	Sol'n & Li strip one white solid mass.	Sol'n light yellow. Li strip covered with flocculant white material. Sol'n black. Li black viscous mass.

TABLE A-5(A) (Continued)

LITHIUM STABILITY IN METHYL FORMATE

Exposure Time	CaO-Li Treated	
	<u>25g LiClO<sub>4</sub>/100 ml, H<sub>2</sub>O:500 ppm</u>	<u>50g LiClO<sub>4</sub>/100 ml, H<sub>2</sub>O:350 ppm</u>
11 days	Sol'n dark brownish black. Li surface covered with yellowish brown gel.	Sol'n dark brown. Li strip grey. No gel.
14 days	Li covered with a brown gel. Sol'n dark brown.	Sol'n almost black. Li covered with fine hairlike crystals.
17 days	Sol'n black viscous mass. Li covered with black gelled mass.	Sol'n black, viscous mass. Li covered with black gel.
48 days	Li covered with brown gel. Sol'n black.	Sol'n & Li strip black gel.

TABLE A-5(B)

LITHIUM STABILITY IN METHYL ACETATE

Exposure Time	CaO Treated	
	25g LiClO <sub>4</sub> /100 ml H <sub>2</sub> O: 800 ppm	50g LiClO <sub>4</sub> /100 ml H <sub>2</sub> O: 1000 ppm
11 days	Untreated 25g LiClO <sub>4</sub> /100 ml Sol'n clear light brownish yellow, Li surface clean & bright.	Sol'n light clear yellow. Li surface bright, very slight white film on surface.
14 days	Li clean & bright. Sol'n clear light yellow.	Sol'n color same. Li clean & bright. Gel on bottom of test tube.
17 days	Li clean & bright. Sol'n clear light yellow.	Sol'n color unchange. White film on surface of Li. Gel on bottom of tube.
48 days	Sol'n light brown, Li covered with white film, white ppt. on bottom of test tube.	Sol'n yellowish brown, Li unchanged, white film on surface, gel on bottom of tube.

TABLE A-5(B) (Continued)  
LITHIUM STABILITY IN METHYL ACETATE

Exposure Time	CaO-Li Treated	
	25g LiClO <sub>4</sub> /100 ml; H <sub>2</sub> O: 3100 ppm	50g LiClO <sub>4</sub> /100 ml; H <sub>2</sub> O: 3700ppm
11 days	Sol'n light brownish yellow. Li etched & bright below surface of liquid. White film on surface of Li above sol'n, some white particles suspended in sol'n.	Sol'n light, clear yellow Li surface bright, very slight white film on surface.
14 days	Sol'n clear, same color Li bright with some flaky. Crystalline particles on surface.	Some yellow spots on surface of Li, also a fine white film. Sol'n bright opaque.
17 days	Li covered with white film. Sol'n light brown. Gell in suspension & on bottom of test tube.	Li covered with white film. Yellow spots on Li surface. Gel on bottom of test tube.
48 days	Sol'n light brown, Li grey-white with gel clinging to surface. Gel on bottom of tube.	Li covered with fine white film, small amount of gel on bottom of tube. Li not heavily attacked.

TABLE A-5(C)

LITHIUM STABILITY TESTS IN 1.0 M SOLUTIONS

<u>Solution</u>	<u>Time</u>	<u>Observation</u>
LiClO <sub>4</sub> /PC	1 day 19 days	Li bright, electrolyte clear. No change in appearance.
LiClO <sub>4</sub> /MA	1 day 19 days	Li bright, solution clear. Stopper popped, Li strip corroded.
KClO <sub>4</sub> /PC (sat.)	1 day 19 days	Li bright, solution clear. Li 40% black, solution has yellow tinge.
KClO <sub>4</sub> /MA (sat.)	1 day 19 days	Li bright, solution clear. Li 90% black, sol'n water white.
NaClO <sub>4</sub> /PC	1 day 19 days	Li bright, solution clear. One side of Li black, other side covered with bubbles. Ppt. on bottom of test tube.
NaClO <sub>4</sub> /MA	1 day 19 days	Li bright, sol'n clear. Gel part- icles on Li surface & tube surface Li tarnished.
KPF <sub>6</sub> /PC	1 day 19 days	Li bright, sol'n clear. Li tarnished on fifth day, solution clear. No change to 19 days.
KPF <sub>6</sub> /MA	1 day 19 days	Li tarnished, sol'n clear. After 3 days, Li completely black; 5 days some ppt; & no change from 5 days to 19 days.
LiBr/PC	1 day 19 days	Li bright, sol'n clear. Li bright, no attack, sol'n water white, cloudy.
LiBr/MA	1 day 19 days	Li bright, sol'n clear. White coating on Li in 2 days; Li covered with gel particles in 3 days; white crystals on Li in 8 days. Sol'n color light yellow.

TABLE A-5(D)  
 COMPATIBILITY OF VARIOUS ELECTROLYTES WITH METALLIC LITHIUM

<u>Solute</u>	<u>Solvent</u>	<u>15 Minutes</u>	<u>3-1/2 Hours</u>	<u>24 Hours</u>
KClO <sub>4</sub>	PC	No effect.	Tarnishing slightly.	No noticeable change.
KClO <sub>4</sub>	BL	No effect.	Tarnishing slightly.	Li moderately tarnished.
KClO <sub>4</sub>	DMSO	No effect.	No noticeable change.	No noticeable change.
KClO <sub>4</sub>	AN	Gel adhering to cut area.	Yellow gel; Li badly corroded.	Solid yellow gel in tube.
KClO <sub>4</sub>	NM	Cut area dark.	No noticeable change.	Black coating on Li.
KPF <sub>6</sub>	B1	No effect.	Li dark above liquid.	Black coating on Li.
KPF <sub>6</sub>	DMSO	No effect.	No noticeable change.	No noticeable change.
KPF <sub>6</sub>	AN	Cut area dark.	Yellow gel; Li badly corroded.	Solid yellow gel in tube.
KPF <sub>6</sub>	NM	Scraped area dark; bright area gray.	No noticeable change.	Li black with yellow coating on sides.
LiBr	PC	No effect.	No noticeable change.	No noticeable change.
NaBr	PC	No effect.	No noticeable change.	Li tarnishing slightly.
KBr	PC	No effect.	No noticeable change.	Li tarnishing slightly.
KF•2H <sub>2</sub> O	PC	Bubbles on Li surface.	Li turning slightly black.	White powdery surface on Li.
KAlF <sub>6</sub>	PC	Cut area dark, rest of strip slightly tarnished.	Li turning black.	Li deep black.



TABLE A-5(D) (Continued)  
COMPATIBILITY OF VARIOUS ELECTROLYTE WITH METALLIC LITHIUM

<u>Solute</u>	<u>Solvent</u>	<u>15 Minutes</u>	<u>3-1/2 Hours</u>	<u>24 Hours</u>
None	NM	Cut area; slightly tarnished.	No noticeable change.	Li moderately tarnished.
None	AN	Yellow gel on cut surface.	Liquid bubbling. Yellow spots.	Yellow gel in tube.
None	DMSO	No effect.	No noticeable change.	No noticeable change.
None	MA	Cut area black; bubbling.	Deep grey coating, bubbling.	Li grey-white.
None	BL	No effect.	Scraped area slightly dark.	Li grey.
None	PC	No effect.	No noticeable change.	Cut area dark.
None	AN*	Yellow gel on Li surface.	Liquid gassing.	Yellow gel.

\* Treated with molecular sieve.

TABLE A-5(E)

CuF<sub>2</sub> SOLUBILITY IN METHYL ACETATE SOLUTIONS

<u>Solute</u>	<u>Time, Days, <math>\mu\text{g/ml}</math> [Cu<sup>++</sup>]</u>			
	<u>7</u>	<u>14</u>	<u>21</u>	<u>28</u>
LiClO <sub>4</sub>	331	384	511	692
NaClO <sub>4</sub>	76	115	96	115
KPF <sub>6</sub>	403*	1410	640	896
KAsF <sub>6</sub>	64	96	160	83
KBF <sub>4</sub>	<19*	<32	<32	<32
LiAsF <sub>6</sub> (m) <sup>1</sup>	128	128	224	237
NaAsF <sub>6</sub> (m) <sup>1</sup>	64	320	<32	<32
LiBF <sub>4</sub> (F) <sup>2</sup>	51	160	64	124

\* Saturated solutions, others 1 mol solute/liter of solvent.

<sup>1</sup> Metathetical preparation.

<sup>2</sup> Supplied by Foote Mineral Co.

TABLE A-6

PRISMATIC ELECTRODE CONSTRUCTION BY FILTER-PRESS METHODA. Preparation of Materials

1. Fiber (S & S Paper Pulp): dry overnight at full vacuum.
2. Conductor (Dixon Graphite): dry overnight under vacuum.
3. Vehicle (Fisher Heptane, laboratory grade): use as received.

B. Size Reduction

1. Charge mill jar (Size 00) to 1/3 level with grinding media.
2. Fill to about 1/2 level with vehicle; record volume, cc.
3. Add specified weight of active material and conductor.
4. Place jar on rollers for specified period.

C. Filter-Mat Construction

1. Transfer charge to 800 ml beaker and remove grinding media.
2. Transfer to "Osterizer" blender and add specified weight of fiber. Dilue with additional heptane.
3. Agitate on "low" for 30 seconds and on "high" for 60 seconds.
4. Filter immediately through shark skin paper in sheet mold at 10 in. vacuum.
5. Press pad between blotter paper sheets at 60 lbs./sq. in. of sheet area.

D. Electrode Construction

1. Cut wet fiber pad to size, 1.5 x 1.5 in.
2. Assemble in steel mold with expanded metal connector.
3. Compress at 500 lbs./sq. in. of electrode area.
4. Place electrodes in Mason jar and dry under vacuum overnight or until no heptane odor can be detected.

E. Storage of Electrodes

1. Store electrodes in hermetically sealed Mason jars.
2. Label jars with test number, batch number, operator, and date of preparation.

TABLE A-7

## SPECIFIC CONDUCTANCE MEASUREMENTS

Solvent	Solute	(Room Temperature)		Remarks
		Grams Solute Liter of Solvent	Specific Conductance ( $\Omega^{-1}\text{cm}^{-1}$ )	
PC*	KClO <sub>4</sub>	250	$1.2 \times 10^{-3}$	Slight haze, 97 ppm H <sub>2</sub> O
PC	KPF <sub>6</sub>	250	$8.9 \times 10^{-3}$	
PC	K <sub>2</sub> ZrF <sub>6</sub>	250	$1.7 \times 10^{-6}$	
PC	KPF <sub>6</sub>	184	$7.8 \times 10^{-3}$	
PC	KAsF <sub>6</sub>	228	$8.1 \times 10^{-3}$	Approx. 90% dissolved, 61 ppm H <sub>2</sub> O
PC	KAsF <sub>6</sub>	250	$9.7 \times 10^{-3}$	Approx. 30% dissolved, 97 ppm H <sub>2</sub> O
PC	KBF <sub>4</sub>	126	$0.21 \times 10^{-3}$	
PC	$\times\text{LiBF}_4(\text{m})^1$	94	$6.4 \times 10^{-3}$	Light Tan, 170 ppm H <sub>2</sub> O Tan, 105 ppm H <sub>2</sub> O Clear, 260 ppm H <sub>2</sub> O Clear, 160 ppm H <sub>2</sub> O
PC	$\times\text{LiPF}_6(\text{m})$	152	$6.4 \times 10^{-3}$	
PC	$\times\text{LiAsF}_6(\text{m})$	196	$6.2 \times 10^{-3}$	
PC	$\times\text{NaAsF}_6(\text{m})$	212	$8.2 \times 10^{-3}$	
PC	LiF	250	$3.2 \times 10^{-6}$	
PC	NaF	250	$8.1 \times 10^{-6}$	
PC	KF	250	$3.4 \times 10^{-5}$	
PC	LiBr	250	$8.8 \times 10^{-3}$	
PC	NaBr	250	$3.0 \times 10^{-4}$	
PC	KBr	250	$2.1 \times 10^{-4}$	
PC	Li <sub>2</sub> CrO <sub>4</sub>	250	$1.3 \times 10^{-4}$	
PC	K <sub>2</sub> CrO <sub>4</sub>	250	$5.7 \times 10^{-5}$	
PC	KAlF <sub>6</sub>	250	$2.6 \times 10^{-4}$	
PC	KCRF <sub>6</sub>	250	$3.3 \times 10^{-5}$	
PC	K <sub>2</sub> TiF <sub>6</sub>	250	$6.33 \times 10^{-6}$	

<sup>1</sup> Metathetical.× These salts were prepared by reacting LiClO<sub>4</sub> with the potassium derivative of the desired anion.

TABLE A-7 (Continued)  
 SPECIFIC CONDUCTANCE MEASUREMENTS

(Room Temperature)				
Solvent	Solute	Grams Solute Liter of Solvent	Specific Conductance ( $\Omega^{-1}\text{cm}^{-1}$ )	Remarks
BL*	KClO <sub>4</sub>	250	$3.4 \times 10^{-3}$	
BL	KPF <sub>6</sub>	250	$13.4 \times 10^{-3}$	
BL	K <sub>2</sub> ZrF <sub>6</sub>	250	$1.8 \times 10^{-5}$	
BL	CuF <sub>2</sub> (3.9% H <sub>2</sub> O)	60	$8 \times 10^{-7}$	Colorless solution.
BL	CuF <sub>2</sub> (3.9% H <sub>2</sub> O)	60	$6 \times 10^{-5}$	Dark Tan, 2500 hours agitation
BL	CuF <sub>2</sub> (3.9% H <sub>2</sub> O)	0.2	$8 \times 10^{-7}$	Colorless solution.
BL	CuF <sub>2</sub> (3.9% H <sub>2</sub> O)	0.2	$2 \times 10^{-6}$	Pale yellow, 2500 hrs. agitation
MA*	LiClO <sub>4</sub>	106	$1.4 \times 10^{-3}$	76 ppm H <sub>2</sub> O
MA	NaClO <sub>4</sub>	122	$5.0 \times 10^{-3}$	76 ppm H <sub>2</sub> O
MA	KPF <sub>6</sub>	184	$5.9 \times 10^{-3}$	Saturated sol'n, 110 ppm H <sub>2</sub> O
MA	KAsF <sub>6</sub>	228	$10.9 \times 10^{-3}$	Pale yellow, saturated sol'n, 90 ppm H <sub>2</sub> O
MA	KAsF <sub>6</sub>	250	$10.7 \times 10^{-3}$	Only slightly soluble
MA	KBF <sub>4</sub>	126	$<10^{-7}$	Light tan, 290 ppm H <sub>2</sub> O
MA	xLiAsF <sub>6</sub>	196	$12.1 \times 10^{-3}$	Light tan, 270 ppm H <sub>2</sub> O
MA	xNaAsF <sub>6</sub>	212	$14.9 \times 10^{-3}$	
MA	LiF	250	$1.0 \times 10^{-7}$	
MA	NaF	250	$5.3 \times 10^{-7}$	
MA	KF	250	$4.5 \times 10^{-7}$	
MA	LiBr	250	$5.9 \times 10^{-4}$	
MA	NaBr	250	$2.8 \times 10^{-6}$	

xThese salts were prepared by reacting LiClO<sub>4</sub> with the potassium derivative of the desired anion.

TABLE A-7 (Continued)  
 SPECIFIC CONDUCTANCE MEASUREMENTS  
 (Room Temperature)

Solvent	Solute	Grams Solute Liter of Solvent	Specific Conductance ( $\Omega^{-1}\text{cm}^{-1}$ )	Remarks
MA	KBr	250	$4.4 \times 10^{-7}$	
MA	$\text{Li}_2\text{CrO}_4$	250	$7.7 \times 10^{-7}$	
MA	$\text{K}_2\text{CrO}_4$	250	$1.9 \times 10^{-7}$	
MA	$\text{KAlF}_6$	250	$7.7 \times 10^{-7}$	
MA	$\text{KClO}_4$	250	$4.8 \times 10^{-7}$	
MA	$\text{KCrF}_6$	250	$2.1 \times 10^{-7}$	
MA	$\text{K}_2\text{TiF}_6$	250	$5.4 \times 10^{-7}$	
MA	$\text{K}_2\text{ZrF}_6$	250	$3.4 \times 10^{-7}$	
DMSO*	$\text{KClO}_4$	250	$10.1 \times 10^{-3}$	
DMSO	$\text{KPF}_6$	250	$11.3 \times 10^{-3}$	
DMSO	$\text{K}_2\text{ZrF}_6$	250	$2.9 \times 10^{-5}$	
DMSO	$\text{LiClO}_4$	106	$11.6 \times 10^{-3}$	175 ppm $\text{H}_2\text{O}$
DMSO	$\text{KAsF}_6$	228	$11.6 \times 10^{-3}$	75 ppm $\text{H}_2\text{O}$
AN*	$\text{KClO}_4$	250	$1.7 \times 10^{-3}$	
AN	$\text{KPF}_6$	250	$33.4 \times 10^{-3}$	
AN	$\text{K}_2\text{ZrF}_6$	250	$1.4 \times 10^{-5}$	
NM*	$\text{KPF}_6$	250	$6.5 \times 10^{-3}$	
NM	$\text{KClO}_4$	250	$2.7 \times 10^{-3}$	
NM	$\text{K}_2\text{ZrF}_6$	250	$2.2 \times 10^{-5}$	
NM	$\text{LiClO}_4$	106	$7.4 \times 10^{-3}$	1000 ppm $\text{H}_2\text{O}$
NM	$\text{KAsF}_6$	228	$10.8 \times 10^{-3}$	1366 ppm $\text{H}_2\text{O}$

TABLE A-7 (CONTINUED)  
SPECIFIC CONDUCTANCE MEASUREMENTS

<u>Solvent</u>	<u>Solute</u>	(Room Temperature)		<u>Remarks</u>
		<u>Grams Solute Liter of Solvent</u>	<u>Specific Conductance (<math>\Omega^{-1} \text{cm}^{-1}</math>)</u>	
NDA*	LiClO <sub>4</sub>	106	15.7 x 10 <sup>-3</sup>	185 ppm H <sub>2</sub> O
NDA	KAsF <sub>6</sub>	228	22.3 x 10 <sup>-3</sup>	75 ppm H <sub>2</sub> O
AA*	LiClO <sub>4</sub>	106	10.6 x 10 <sup>-3</sup>	125 ppm H <sub>2</sub> O
AA	KAsF <sub>6</sub>	228	13.6 x 10 <sup>-3</sup>	75 ppm H <sub>2</sub> O

\* PC - Propylene Carbonate  
 BL -  $\gamma$ -Butyrolactone  
 MA - Methyl Acetate  
 DMSO - Dimethyl Sulfoxide  
 AN - Acetonitrile  
 NM - Nitromethane  
 NDA - N, N-dimethylnitrosoamine  
 AA - Acetic Anhydride

TABLE A-8

X-RAY ANALYSIS OF CuF<sub>2</sub>A. Preparation of Sample

About 10g of the material to be analyzed is delivered under argon into a "Hi-Speed" micronizer blender and ground for ca. 20 seconds. The material is then transferred to a polyethylene envelope, and the latter is heat sealed.

Prior to mounting on the diffractometer, the powder is pressed by hand into a 1/16 inch thick aluminum die which has been taped to a microscope slide. A second slide is then taped to the opposite side of the die, and the original slide is removed leaving a smooth plane of compacted material.

B. Analysis

A Phillips Model 12045B/3 X-ray generator is used in conjunction with Phillips No. 12096 Control Panel and No. 52090 Minneapolis-Honeywell Strip Chart Recorder. The sample is rotated from 80° to 10° Bragg angle at the rate of 1 degree/minute under monochromatic CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

C. Calculation1. CuF<sub>2</sub>·2H<sub>2</sub>O

The highest amplitude on the chart between the limits of 18.4 and 18.6 degrees is selected, and percent CuF<sub>2</sub>·2H<sub>2</sub>O is calculated

$$\% \text{ CuF}_2 \cdot 2\text{H}_2\text{O} = \frac{\text{counts/second (unknown)}}{\text{counts/second (pure CuF}_2 \cdot 2\text{H}_2\text{O)}} \times 100$$

## 2. CuO

The highest amplitude between the limits of 38.6 and 38.8 degrees is selected, and percent CuO is calculated

$$\% \text{ CuO} = \frac{\text{counts/second (unknown)}}{\text{counts/second (pure CuO)}} \times 100$$



TABLE A-9

PERFORMANCE OF  $\text{CuF}_2$ -Li CELLS WITH BUTYROLACTONE ELECTROLYTE

Electrolyte: 15g  $\text{LiClO}_4$ /100 ml BL Water Content: 150 ppm  
 Discharge Temperature: 35°C Discharge Load: 200 ohms  
 Electrode Area: 29  $\text{cm}^2$  Separation: 0.03" MPR

Cell No.	Stand Conditions		Theo. $\text{CuF}_2$ Capacity, AH	Hours to 2.5 VF	Capacity to 2.5 VF, AH	Average Discharge Potential Volts	% Cathode Efficiency
	Temp. °C	Time, wks.					
1*	---	-	3.71	70	1.07	3.05	29
2*	---	-	4.18	76	1.17	2.99	28
3*	---	-	3.59	74	1.98	2.92	30
4*	---	-	3.44	75	1.16	3.01	34
9**	---	-	3.90	64	1.00	3.12	26
10**	---	-	4.50	70	1.10	3.13	24
11**	---	-	4.67	62	0.96	3.08	21
12**	---	-	4.60	59	0.93	3.13	20
5*	+35	1	3.92	1	----	----	--
6*	+35	1	4.10	1	----	----	--
13**	+35	1	4.82	1	----	----	--
14**	+35	1	4.58	<1	----	----	--
7*	-15	2	4.26	118	1.80	3.05	42
8*	-15	2	4.12	90	1.36	3.03	33
15**	-15	2	4.62	95	1.45	3.06	31
16**	-15	2	4.71	97	1.45	3.00	31

<sup>1</sup> Open Circuit Voltage < 1 V after stand.

\*  $\text{CuF}_2$ : Dried in argon for 16 hours at 130°C.

\*\*  $\text{CuF}_2$ : Dried in argon for 113 hours at 130°C.

TABLE A-10  
EFFECT OF CATHODE PASTE COMPOSITION ON CELL PERFORMANCE

Electrode Thickness: 0.02 in.		Current: 300 mA		Temperature: -15°C		Discharge Potential		Capacity to 2.0 V <sub>F</sub> , AH	Electrochemical Efficiency, %	Remarks	
		(10 mA/cm <sup>2</sup> )		Average		Initial					
Cell No.	Grams additive/100g of Cu <sub>2</sub>		Cu <sub>2</sub> Capacity AH	Electrolyte Volume cc	Open Circuit Potential	Dry paste Wt., gms.	Cellulose Acetate	Graphite	Capacity to 2.0 V <sub>F</sub> , AH	Electrochemical Efficiency, %	Remarks
	Graphite	Cellulose Acetate									
1-1	20	2	1.27	0.55	3.53	1.27	2	20	0.37	67	
1-2	20	2	1.13	0.49	3.55	1.13	2	20	0.34	69	
1-3	20	2	1.40	0.61	3.52/3.35	1.40	2	20	0.28	40	Apparent internal short.
1-4	20	2	1.30	0.56	3.53	1.30	2	20	0.25	45	MPR Separation.
1-5	20	2	1.42	0.62	3.53	1.42	2	20	0.24	38	MPR Separation.
1-6	20	2	1.44	0.63	3.53	1.44	2	20	0.32	50	MPR Separation.
1-7	20	2	2.20	0.95	3.53	2.20	2	20	0.64	67	
1-8	20	2	2.10	0.91	3.53	2.10	2	20	0.55	60	
1-9	20	2	2.26	0.98	3.51	2.26	2	20	0.33	33	MPR Separation, .040" pos.
1-10	20	2	2.12	0.92	3.51	2.12	2	20	---	--	MPR Separation, .040" pos.
2-1	10	2	1.62	0.76	3.37	1.62	2	10	0.44	58	
2-2	10	2	1.77	0.84	3.49	1.77	2	10	0.57	68	
2-3	10	2	1.54	0.73	3.49	1.54	2	10	0.47	65	
2-4	10	2	1.60	0.76	3.48	1.60	2	10	0.50	66	
2-5	10	2	1.63	0.77	3.54	1.63	2	10	0.51	66	Room temp. sealed.
2-6	10	2	1.57	0.74	3.52	1.57	2	10	0.38	51	Room temp. sealed.
2-7	10	2	1.47	0.69	3.52	1.47	2	10	0.38	55	MPR Separation - room temp.
2-8	10	2	1.53	0.72	3.57	1.53	2	10	0.54	75	MPR Separation - room temp.
3-1	5	2	1.32	0.65	3.51	1.32	2	5	0.43	66	
3-2	5	2	1.47	0.73	3.51	1.47	2	5	0.43	59	
3-3	5	2	1.40	0.69	3.51	1.40	2	5	0.43	62	
3-4	5	2	1.70	0.84	3.51	1.70	2	5	0.28	33	Leak upon activation.
3-5	5	2	1.69	0.84	3.51	1.69	2	5	0.31	37	
3-6	5	2	1.90	0.94	3.51	1.90	2	5	0.58	62	
4-1	2.5	2	1.59	0.81	3.47	1.59	2	2.5	0.49	60	
4-2	2.5	2	1.41	0.72	3.47	1.41	2	2.5	0.39	54	
4-3	2.5	2	1.50	0.76	3.47	1.50	2	2.5	0.50	66	
4-4	2.5	2	1.52	0.77	3.47	1.52	2	2.5	0.45	58	
4-5	2.5	2	1.69	0.86	3.37	1.69	2	2.5	0.15	17	2.35 M Electrolyte.
4-6	2.5	2	1.59	0.81	3.21	1.59	2	2.5	0.20	25	2.35 M Electrolyte.

TABLE A-10 CONTINUED  
EFFECT OF CATHODE PASTE COMPOSITION ON CELL PERFORMANCE

Cell No.	Grams additive/100g of CuF <sub>2</sub>		Dry paste Wt., gms.	CuF <sub>2</sub> Capacity AH	Electrolyte Volume cc	Open Circuit Potential	Discharge Potential		Capacity to 2.0 VF, AH	Electrochemical Efficiency, %	Remarks
	Graphite	Cellulose Acetate					Initial	Average			
5-1	20	1	1.20	0.52	3.0	3.58	2.84	2.70	0.32	61	
5-2	20	1	1.36	0.59	3.0	3.56	2.81	2.64	0.38	64	
5-3	20	1	1.24	0.54	3.0	3.57	2.75	2.64	0.34	63	
5-4	20	1	1.29	0.56	3.0	3.57	2.78	2.69	0.37	64	
6-1	10	1	1.36	0.65	3.0	3.52	2.73	2.70	0.38	58	
6-2	10	1	1.39	0.66	3.0	3.56	2.77	2.66	0.38	58	
6-3	10	1	1.47	0.70	3.0	3.58	2.74	2.68	0.41	59	
6-4	10	1	1.62	0.77	3.0	3.56	2.65	2.63	0.46	60	
7-1	5	1	1.64	0.82	3.0	3.50	2.64	2.68	0.41	50	
7-2	5	1	1.40	0.70	3.0	3.50	2.58	2.66	0.38	54	
7-3	5	1	1.86	0.93	3.0	3.52	2.57	2.67	0.47	51	
7-4	5	1	1.58	0.79	3.0	3.51	2.60	2.68	0.42	53	
8-1	2.5	1	1.80	0.92	3.0	3.48	2.32	2.63	0.50	54	
8-2	2.5	1	1.88	0.96	3.0	3.51	2.29	2.64	0.48	50	
8-3	2.5	1	1.88	0.96	3.0	3.49	2.25	2.57	0.50	52	
8-4	2.5	1	1.88	0.96	3.0	3.49	2.35	2.62	0.50	52	
9-1	20	0.5	1.29	0.57	3.0	3.50	2.94	2.68	0.34	60	
9-2	20	0.5	1.32	0.58	3.0	3.53	2.94	2.70	0.36	62	
9-3	20	0.5	1.23	0.54	3.0	3.54	2.90	2.61	0.32	59	
9-4	20	0.5	1.31	0.58	3.0	3.54	2.82	2.59	0.23	40	Very noisy discharge.
10-1	10	0.5	1.51	0.73	3.0	3.48	2.64	2.68	0.43	59	
10-2	10	0.5	1.61	0.77	3.0	3.48	2.58	2.67	0.45	58	
10-3	10	0.5	1.66	0.80	3.0	3.53	2.61	2.58	0.43	54	
10-4	10	0.5	1.73	0.83	3.0	3.49	2.61	2.64	0.47	57	
11-1	5	0.5	1.65	0.83	3.0	3.42	2.41	2.65	0.50	60	
11-2	5	0.5	2.01	1.01	3.0	3.42	2.49	2.67	0.60	60	
11-3	5	0.5	1.96	0.98	3.0	3.48	2.43	2.63	0.52	53	
11-4	5	0.5	1.70	0.85	3.0	3.48	2.43	2.62	0.49	58	

TABLE A-10 CONTINUED  
 EFFECT OF CATHODE PASTE COMPOSITION ON CELL PERFORMANCE

Cell No.	Grams additive/100g of CuF <sub>2</sub>		Dry paste wt., gms	CuF <sub>2</sub> Capacity AH	Electrolyte Volume cc	Open Circuit Potential	Discharge Potential		Capacity to 2.0 VF, AH	Electrochemical Efficiency, %	Remarks
	Graphite	Cellulose Acetate					Initial	Average			
12-1	2.5	0.5	1.74	0.90	3.0	3.37	1.88	2.62	0.45	50	
12-2	2.5	0.5	1.50	0.78	3.0	3.36	1.88	2.54	0.38	47	
12-3	2.5	0.5	1.84	0.95	3.0	3.42	1.95	2.58	0.45	47	
12-4	2.5	0.5	1.82	0.94	3.0	3.36	1.93	2.55	0.40	43	
13-1	10	1	1.63*	0.76	3.0	3.50	2.79	2.72	0.40	53	
13-2	10	1	1.78*	0.83	3.0	3.50	2.78	2.76	0.52	63	
13-3	10	1	1.53*	0.71	3.0	3.50	2.55	2.69	0.48	68	
13-4	10	1	1.45*	0.67	3.0	3.50	2.61	2.74	0.46	69	3g LiClO <sub>4</sub> /100g CuF <sub>2</sub>
13-5	10	1	1.51*	0.70	3.0	3.50	2.67	2.71	0.49	70	
13-6	10	1	1.85*	0.86	3.0	3.50	2.67	2.69	0.56	65	
13-7	10	1	3.63*	1.69	3.8	3.50	2.13	2.53	0.72	43	.050" cathode.
13-8	10	1	3.65*	1.70	3.8	3.50	1.99	2.54	0.65	39	.050" cathode.
14-1	10	1	1.66*	0.76	3.0	3.45	2.88	2.70	0.38	50	
14-2	10	1	1.93*	0.88	3.0	3.45	2.82	2.52	0.44	50	
14-3	10	1	1.65*	0.75	3.0	3.45	2.87	2.75	0.41	55	
14-4	10	1	1.89*	0.86	3.0	3.45	2.87	2.72	0.47	55	
14-5	10	1	1.78*	0.81	3.0	3.47	3.06	2.73	0.40	49	
14-6	10	1	1.93*	0.88	3.0	3.49	3.08	2.78	0.48	55	6g LiClO <sub>4</sub> /100g CuF <sub>2</sub>
14-7	10	1	1.92*	0.87	3.0	3.56	2.64	2.54	0.51	59	5 mA/cm <sup>2</sup>
14-8	10	1	1.95*	0.89	3.0	3.49	2.58	2.62	0.51	57	15 mA/cm <sup>2</sup>
15-1	10	1	1.88*	0.83	3.0	3.51	2.88	0.69	0.45	54	
15-2	10	1	1.73*	0.77	3.0	3.51	2.90	0.69	0.44	57	
15-3	10	1	1.94*	0.86	3.0	3.51	2.89	2.71	0.50	58	
15-4	10	1	1.79*	0.79	3.0	3.51	2.89	2.72	0.46	58	9g LiClO <sub>4</sub> /100g CuF <sub>2</sub>
15-5	10	1	1.86*	0.83	3.0	3.56	3.14	2.80	0.44	53	5 mA/cm <sup>2</sup>
15-6	10	1	1.91*	0.85	3.0	3.56	3.14	2.73	0.47	55	5 mA/cm <sup>2</sup>
15-7	10	1	1.76*	0.78	3.0	3.56	2.67	2.62	0.50	64	
15-8	10	1	1.87*	0.83	3.0	3.56	2.63	2.57	0.48	58	15 mA/cm <sup>2</sup>
16-1	10	1	1.60*	0.69	3.0	3.50	2.73	2.62	0.38	55	
16-2	10	1	1.84*	0.80	3.0	3.50	2.70	2.62	0.46	57	
16-3	10	1	1.71*	0.74	3.0	3.50	2.72	2.64	0.41	55	
16-4	10	1	1.58*	0.69	3.0	3.50	2.70	2.58	0.37	54	12g LiClO <sub>4</sub> /100g CuF <sub>2</sub>

\* Includes weight of LiClO<sub>4</sub>.

TABLE A-11

LIST OF MATERIALS

<u>Material</u>	<u>Supplier</u>	<u>Catalogue No.</u>	<u>Description</u>
Lithium Ribbon	Foote Mineral Co.	-----	1/2 x 1/16 in.
Lithium Metal Ribbon	Foote Mineral Co.	-----	2 x .015 in.
Lithium Metal Powder	Foote Mineral Co.	-----	98.5% Li
Graphite	Jos. Dixon Crucible Co.	-----	Air-Spun Graphite
Carbon Black	Columbian Carbon Co.	-----	Conductex SC
Paper Pulp	S & S	289	Ash Free
Cellulose Acetate	Eastman Organic Chem.	4644	ASTM Visc. 3
Calcium Oxide	G. & W. H. Corson	-----	Hi Calcium Quick Lime
Microporous Rubber	American Hard Rubber Co.	-----	0.030 in.
Glass Mat	Reeve Angel	934-AH	-----
Silver Grid	Ex-Met Corp.	-----	5Ag14-1/0
Silver Grid	Ex-Met Corp.	-----	5Ag8-1/0

TABLE A-11 (Continued)

LIST OF MATERIALS

<u>Material</u>	<u>Supplier</u>	<u>Cata. No.</u>	<u>Description</u>
$\text{CuF}_2$	Ozark-Mahoning	S-66	99.5% Min.
$\text{CuF}_2$	A. D. Mackay	----	96% Min.
$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	Ozark-Mahoning	S-71	99% Min.
$\text{Ag}_2\text{O}_2$	City Chemical	S-261	Purified
$\text{CoF}_3$	Matheson, Coleman & Bell	CX1835	----
$\text{SbF}_3$	Fischer Scientific	A-854	Tech.
$\text{MnF}_3$	Harshaw Chemical	----	----
S	Matheson, Coleman & Bell	SX1225	Sublimed, N. F.
TICA	FMC	CDB-85	100%
NaDICA	FMC	CDB-60	100%
K DICA	FMC	CDB-59	100%
TCM	Matheson, Coleman & Bell	TX1105	Pract.

TABLE A-11 (Continued)

LIST OF MATERIALSElectrolyte Solvents

<u>Material</u>	<u>Supplier</u>	<u>Cata. No.</u>	<u>Description</u>
γ-Butyrolactone	Matheson, Coleman & Bell	BX2185	----
γ-Butyrolactone	General Aniline & Film Corp.	----	----
Propylene Carbonate	Matheson, Coleman & Bell	PX1705	----
Acetic Anhydride	J. T. Baker	0018	Reagent
Nitromethane	Matheson, Coleman & Bell	NXA615	Spectroquality
N-nitrosodimethylamine	Eastman	7370	----
Dimethylsulfoxide	Fisher Scientific	D-128	Reagent
Methyl Formate	Matheson, Coleman & Bell	MX1040	Spectroquality
Methyl Acetate	Matheson, Coleman & Bell	MX625	Chromatoquality
Nitromethane	Eastman	SI89	Spectroquality

TABLE A-11 (Continued)

LIST OF MATERIALSElectrolyte Solutes

<u>Material</u>	<u>Supplier</u>	<u>Cata. No.</u>	<u>Description</u>
Lithium Perchlorate	G. F. Smith	221	Reagent
Sodium Perchlorate	G. F. Smith	91	Reagent
Potassium Perchlorate	G. F. Smith	80	Reagent
Potassium Hexafluorophosphate	Matheson, Coleman & Bell	PX1425	98-100%
Potassium Hexafluoroarsenate	Alfa Inorg.	AS105	97-99%
Potassium Hexafluoroarsenate	Ozark-Mahoning	S-206	98% Min.
Sodium Hexafluoroarsenate	Ozark-Mahoning	S-566	-----
Lithium Tetrafluoroborate	Foote Mineral Co.	-----	99%
Lithium Chloride	Mallinckrodt	5852	Reagent
Lithium Chloride	J. T. Baker	0498	Anal. Reagent
Lithium Chloride	Mallinckrodt	3147	Anal. Reagent
Lithium Chloride	Matheson, Coleman & Bell	AX684	Reagent



TABLE A-11 (Continued)

LIST OF MATERIALSSupplemental Materials

<u>Material</u>	<u>Supplier</u>	<u>Cata. No.</u>	<u>Description</u>
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Hellige	R-1231C	0.1 N
KFR	Harleco	3786	Stabilized Sol'n
Methanol	Matheson, Coleman & Bell	MX475	Spectroquality
KF Water Std.	Harleco	1849	----
KI	J. T. Baker	3164	Reagent
Acetic Acid	Fischer Scientific	A-38	Reagent
Tetrahydrofuran	Matheson, Coleman & Bell	TX278	Chromatoquality
Ethyl Acetate	J. T. Baker	9280	Reagent
Ethanol	Publicker Industries	----	U.S.P., 200 Proof

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