

CLEARINGHOUSE FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION			
Hardcopy	Microfiche	102	2/2
\$ 4.00	\$ .75	PP	
ARCHIVE COPY			

AD



AD 634491

1  
TECHNICAL REPORT ECOM-01394-3

HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

THIRD QUARTERLY REPORT

By

D. P. BODEN, H. R. BUHNER, V. J. SPERA

JUNE 1966

DDC  
RECEIVED  
JUN 30 1966  
C

.....  
ECOM

UNITED STATES ARMY ELECTRONICS COMMAND • FORT MONMOUTH, N.J.

CONTRACT DA-28-043-AMC-01394(E)  
THE ELECTRIC STORAGE BATTERY COMPANY  
THE CARL F. NORBERG RESEARCH CENTER  
YARDLEY, PENNSYLVANIA

Distribution of this Document is Unlimited

**HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)**

**THIRD QUARTERLY REPORT**

**15 DECEMBER 1965 TO 15 MARCH 1966**

**Report No. 3**

**CONTRACT NO. DA-28-043-AMC-01394(E)**

**Prepared by**

**D. P. BODEN, H. R. BUHNER, V. J. SPERA**

**THE ELECTRIC STORAGE BATTERY COMPANY  
THE CARL F. NORBERG RESEARCH CENTER  
YARDLEY, PENNSYLVANIA**

**For**

**ELECTRONIC COMPONENTS LABORATORY  
U. S. ARMY ELECTRONICS COMMAND, FORT MONMOUTH, N. J.**

**Distribution of this document is unlimited**

## ABSTRACT

The study of high energy density systems in the third quarter included: continued investigation of new electrolyte solvents; corrosion and solubility studies of cathode and anode materials in various electrolytes; a study of the reversibility of glass electrodes in non-aqueous electrolytes; continued efforts to optimize  $\text{CuF}_2$  cathode performance; a study of the effect of electrolyte concentration and discharge current density on cathode performance; lithium anode storage tests; evaluation of various separator materials; construction and testing of  $\text{Li-CuF}_2$  cells in lightweight polyethylene cases.

In the evaluation of new electrolyte solvents, the highest specific conductance was obtained with solutions of  $\text{LiClO}_4$  in 2-Pentanone, ethyl acetate, 2-Chloroethanol, and 2-4-Pentanedione, with values close to that obtained with propylene carbonate. However, none of the solvents tested this quarter was comparable to propylene carbonate with regard to compatibility with lithium.

When compared to  $\text{LiClO}_4$ , solutes such as  $\text{KCNS}$ ,  $\text{AlCl}_3$ , and  $\text{KPF}_6$  were found to yield higher specific conductance, in propylene carbonate, but poor cathode performance was obtained in these electrolytes.

A study of the glass electrode showed that it was reversible to alkali metal ions in purely non-aqueous media, and should therefore be a useful reference electrode in non-aqueous electrochemistry. In addition, since no ions penetrate the glass, it should be stable over a long period of time.

Continued efforts to optimize  $\text{CuF}_2$  cathode performance have shown that, consistent with good handling characteristics, an electrode material containing 87.5%  $\text{CuF}_2$ , 2.5% polyethylene, and 10% graphite, is the best thus far evaluated.

For a  $1\frac{1}{2}$  in. by  $1\frac{5}{8}$  in. structure, it was found that the  $\text{CuF}_2$  cathode weight could be increased from two grams to three and four grams with an improvement of 20 to 24% in energy density.

In the evaluation of the effect of current density on cathode performance, the percent utilization of  $\text{CuF}_2$  was found to decrease from 82% at  $1 \text{ ma/cm}^2$  to 32% at  $5 \text{ ma/cm}^2$ .

A study of the effect of electrolyte concentration ( $\text{LiClO}_4$ /distilled propylene carbonate) on cathode performance revealed maximum efficiency at 1.25 F. There was however, only a slight difference in efficiency in electrolytes ranging from 1.0 to 1.5 F. Below about 0.75 F performance was very poor.

Storage tests of pressed lithium foil anodes revealed that these electrodes could be stored for at least three months in paraffin oil or 1 F  $\text{LiClO}_4$ /distilled propylene carbonate, with no appreciable loss in electrode discharge efficiency.

Separator screening tests have shown that lightly compacted, fibrous separators, such as glass or asbestos filter papers, and asbestos fuel cell papers are the best for use in the Li-CuF<sub>2</sub> cell.

Li-CuF<sub>2</sub> cells have been constructed having a maximum capability of 80 watt hours per pound, at a current density of 2 ma/cm<sup>2</sup>, and based on total cell weight, including case.

The stand characteristics of Li-CuF<sub>2</sub> cells have been improved by the addition of complexing agents to the electrolyte. Copper dendrite formation can be prevented but all of the complexing agents thus far tested severely affect cathode performance, resulting in poor cell discharge performance, even in the absence of storage.

## LIST OF TABLES

- 1 Physicochemical Properties of Various Organic Solvents
- 2 & 3 Response of Glass Electrode to Lithium Ion in Propylene Carbonate
- 4 Response of Glass Electrode to  $C_{Li^+}$  in KCNS Solution in Propylene Carbonate
- 5 Response of Glass Electrode to  $C_{Li^+}$  in  $NH_4Cl$  Solution in DMSO
- 6 Response of Glass Electrode to  $C_{Li^+}$  in the Presence of  $Mg^{++}$
- 7 Response of Glass Electrode to  $C_{Li^+}$  in  $(C_2H_5)_4NClO_4$  Solution
- 8 Separator Materials - Electrolyte Absorption and Resistivity
- 9 Effect of Separator Material on  $CuF_2$  Cathode Performance
- 10 Weight Analyses of Multi-Electrode Li- $CuF_2$  Cells
- 11 Effect of Complexing Agents on Li- $CuF_2$  Cells
- 12 Effect of Complexing Agents on Performance of Li- $CuF_2$  Cells after Activated Storage
- 13 Effect of Concentration of Diethylene Triamine on Performance after 7 Days Activated Stand
- 14 Effect of Concentration of Ethylene Diamine on Performance after 7 Days Activated Stand

## LIST OF FIGURES

### Figure

- 1 & 2 Specific Conductance of  $\text{LiClO}_4$  in Organic Solvents
- 3 & 4 Equivalent Conductance of  $\text{LiClO}_4$  in Organic Solvents
- 5 Rate of Corrosion of Lithium in Various Electrolytes
- 6 Performance of Cupric Fluoride Electrodes in Various Electrolytes
- 7 Specific Conductance of Various Solutes in Propylene Carbonate
- 8 Effect of Solute on Cathode Performance
- 9 Glass Electrode Test Cell
- 10 Response of Beckman General Purpose Electrode to  $\text{C}_{\text{Li}^+}$
- 11 Response of Beckman General Purpose Electrode to  $\text{C}_{\text{Li}^+}$  in Propylene Carbonate
- 12 Response of Glass Electrode to  $\text{C}_{\text{Li}^+}$  in KCNS Solution
- 13 Response of Glass Electrode to  $\text{C}_{\text{Li}^+}$  in  $\text{NH}_4\text{Cl}$  Solution
- 14 Response of Glass Electrode to  $\text{C}_{\text{Li}^+}$  in  $\text{Mg}(\text{ClO}_4)_2$  Solution
- 15 Response of Glass Electrode to  $\text{C}_{\text{Li}^+}$  in  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  Solution
- 16 Effect of Percent Polyethylene on Cathode Performance
- 17 Percent Polyethylene vs Watt-Hours per Pound of Cathode Mix
- 18 Effect of Percent Graphite on Cathode Performance
- 19 Percent Graphite vs Watt-Hours per Pound of Cathode Mix
- 20 Effect of  $\text{CuF}_2$  Cathode Weight on Performance
- 21-23 Discharge characteristics of Li- $\text{CuF}_2$  Cells with Cathode Weight as Parameter

LIST OF FIGURES (cont'd)

Figure

- 24 & 25 Effect of Discharge Current Density on Electrode Performance
- 26 - 28 Effect of Electrolyte Concentration on Cathode Performance
- 29 Effect of Storage in Paraffin Oil on Performance of Pressed Lithium Ribbon Anodes
- 30 Effect of Storage in Electrolyte on Performance of Pressed Lithium Ribbon Anodes
- 31 Separator Resistance Test Cell
- 32 - 36 Effect of Separator on Cathode Performance
- 37 Vacuum Molded Polyethylene Jar and Cover
- 38 Li-CuF<sub>2</sub> Cell - 3.5 Ampere Hours
- 39 - 41 Discharge Characteristics of Li-CuF<sub>2</sub> Cells in Lightweight Polyethylene Cases

## TABLE OF CONTENTS

Abstract .....	i
List of Tables .....	iii
List of Figures .....	iv
Introduction .....	1
Experimental .....	1
1. Electrolyte Studies .....	1
1.1 Investigation of Organic Solvents .....	2
1.1.1 Choice of Solvents .....	2
1.1.2 Determination of Conductance .....	2
1.1.3 Corrosion and Compatibility Studies .....	3
1.1.4 Effect of Electrolyte on Cathode Performance .....	4
1.2 Investigation of Electrolyte Solutes .....	4
1.2.1 Conductance of Solutes in Propylene Carbonate .....	5
1.2.2 Discharge of Li-CuF <sub>2</sub> Cells .....	5
2. Reference Electrode Studies .....	6
2.1 Electrodes of the Second Kind .....	6
2.2 The Glass Electrode .....	6
2.2.1 Measurement of Alkali Metal Ion Response .....	7
2.2.2 Response of the Glass Electrode to C <sub>Li<sup>+</sup></sub> in the Presence of Other Ions .....	10
3. Cathode Studies .....	14
3.1 Effect of the Amount of Binder on Performance .....	14
3.2 Effect of the Amount of Graphite on Performance .....	15

TABLE OF CONTENTS (cont'd)

3.3	Effect of Cathode Weight on Performance .....	16
3.4	Effect of Current Density on Cathode Performance ....	17
3.5	Effect of Electrolyte Concentration on Cathode Performance .	18
4.	Anode Studies .....	19
4.1	Storage Tests .....	19
4.2	Effect of Discharge Current Density on Anode Performance ..	20
5.	Separator Studies .....	20
5.1	Absorption and Retention .....	21
5.2	Determination of Separator Resistance .....	21
5.3	Effect of Separators on Cathode Performance .....	21
6.	Lithium-Cupric Fluoride Cells .....	22
6.1	Design and Fabrication of Lightweight Polyethylene Cell Cases .....	22
6.2	Construction of Multi-Electrode Cells .....	23
6.3	Effect of Activated Storage on Performance .....	28
6.3.1	Effect of Complexing Agents on Performance .....	31
6.3.2	Effect of Complexone Concentration on Performance .....	31
	Materials and Suppliers .....	32
	References .....	34

## INTRODUCTION

This report describes the work performed between December 15, 1965 and March 15, 1966 on Contract No. DA-28-043-AMC-01394(E) "High Energy Systems" (Organic Electrolyte). The goal of this work is to carry our research and development leading to the construction of a battery with an energy density greater than 200 watt hours/lb.

It will be recalled that the work conducted during the first and second quarter had indicated that the lithium-cupric fluoride couple was worthy of further study. Thus a program of work was undertaken to develop suitable fabrication techniques for the anode and cathode and to optimize those techniques to produce the best possible performance. It was found that good cupric fluoride electrodes could be made by hot pressing a mixture of cupric fluoride, graphite and polyethylene onto a suitable current collecting screen. The preparative parameters were adjusted to achieve optimum performance and this resulted in a cathode capable of discharge at  $2 \text{ ma/cm}^2$  with 80% coulombic efficiency. Lithium anodes, having quite good characteristics were made by pressing the metal foil directly onto a retaining grid. These electrodes were capable of discharge at  $10 \text{ ma/cm}^2$  with 80% coulombic efficiency.

An electrolyte of  $1\text{F LiClO}_4$  in propylene carbonate was used in the majority of experiments but its high viscosity and low electrolytic conductance placed quite severe limitations on its use at high current densities. A continuing search was made to discover solvents and electrolytes of superior properties but none in fact were found which combined high conductance with chemical stability towards the electrode materials.

Prototype three plate cells (two anodes and one cathode) were assembled from electrodes prepared as described above and these were capable of delivering 600 watt hours/lb based on total electrode weight at  $1.8 \text{ ma/cm}^2$ .

It was decided in this quarter to pursue further the fabrication and improvement of the small prototype cells and to construct multiplate units if the performance warranted it. A program was initiated to study the properties of separator materials to determine their suitability for cell construction. Further studies were made on electrolyte solvents and solutes and studies were continued on the problem of developing a suitable reversible reference electrode.

## EXPERIMENTAL

### 1) ELECTROLYTE STUDIES

The work conducted in the first 6 months had produced no electrolyte solvent having better all round properties than propylene carbonate. Although several solvents had been found which gave solutions of higher conductivity than the

presently used 1F LiClO<sub>4</sub> in propylene carbonate, none were found which combined the properties of high conductivity, low viscosity and inertness towards the anode and cathode materials. Propylene carbonate solutions have allowed good electrode performance at low rates (2 ma/cm<sup>2</sup>) but the electrode performance drops off rapidly as the current density is increased. This is thought to be associated with the poor mass transfer properties of the electrolyte as evidenced by its rather low conductance and high viscosity. For these reasons, a continuing search was made for solvents with the necessary properties to meet the above requirements.

## 1.1 Investigation of Organic Solvents

### 1.1.1 Choice of Solvents

The solvents to be studied were chosen on the basis of their dielectric constants and viscosities which are the most influential parameters on the conductance of a solution. The solvents chosen together with some of their physico-chemical properties are shown in Table 1. Since physico-chemical data is not available for all the solvents there are a number of gaps in the table; however it is possible, on the basis of the data collected, to predict which of the solvents will form the most conducting solutions. The order of conductance for a given solute dissolved in different solvents should be in the order of  $D/\eta$  for the solvent. Thus one would expect ethanolamine and 2-pentanone to form the most highly conducting solutions.

### 1.1.2 Determination of Conductance

The solvents used were the purest commercially available and were not purified before use. Only LiClO<sub>4</sub> was used as a solute to obtain a direct comparison with previous results (1 & 2). The LiClO<sub>4</sub> was dried at 120°C under reduced pressure for 16 hours and all solutions were prepared in a dry argon atmosphere to prevent contamination by water from the atmosphere.

It was found that meta and ortho nitrotoluene and ethyl nitrate were poor solvents and their use was discontinued.

The conductance of the solutions was determined as described in previous reports (1 & 2). Results of measurements of specific conductance are shown in Figures 1 and 2. The highest values of specific conductance were obtained with 2-pentanone, ethyl acetate, 2-chloroethanol, and 2-4-pentanedione. The conductance maxima for these solutions ranged from  $6 \times 10^{-3} \text{ ohm}^{-1}$  to  $9 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ , which is fairly close to the value found for propylene carbonate. The maximum conductance was found to occur in solutions of widely varying concentration depending on the solvent chosen: 0.75F in n-ethyl morpholine to 2.25F for ethyl acetate. About one half of the solvents evaluated had conductance maxima at concentrations of 1.0 to 1.25F.

Values of equivalent conductance were calculated from conductance data and the results are shown in Figures 3 and 4. Generally, equivalent conductance can be seen to decrease with increasing concentration as is usually observed. For ethyl acetate and n-ethyl morpholine however, the equivalent conductance is found, first, to increase with increasing concentration and after reaching a maximum, to decrease again. This is consistent with the existence of triple ion formation as discussed in the Second Quarterly Report.

### 1.1.3 Corrosion and Compatibility Studies

#### 1.1.3.1 Corrosion of Li in Organic Electrolytes

The corrosion of lithium in the various electrolytes described in section 1.1.2 was determined as previously described [1] by use of the special gassing pipettes. The rate of attack on the lithium by the electrolytes was determined by measuring the amount of gas evolved and by visual inspection of the sample to observe film formation, color changes, etc. The results of this study are shown in Figure 5. The lowest rate of attack, as determined by the rate of gassing, was found in 2-pentanone, cyclohexanone and n-ethyl morpholine. Extremely rapid corrosion rates were observed for lactic acid, 2-chloroethanol and monoethanolamine; two to three orders of magnitude greater corrosion rates than for the least corrosive solvents.

A flocculent white precipitate was found to develop in the electrolyte very near the test piece in 2-pentanone. In cyclohexanone and sulfolane a black film formed on the lithium. In 2-4-pentanedione a thick, adherent, white film was formed on the lithium, and at the end of the test the entire volume of electrolyte was an opaque, white, viscous mass. Although no gas evolution was observed in the 2-pentanone solution, it cannot be concluded that the material has no corrosive action on lithium. The flocculent white precipitate observed in the solution is certainly indicative of attack, but of such a nature as to produce no gassing.

It appears that none of the solvents evaluated this quarter are comparable to propylene carbonate with regard to compatibility with lithium.

#### 1.1.3.2 Solubility of $\text{CuF}_2$ in Organic Electrolytes

Studies were initiated to determine the solubility of  $\text{CuF}_2$  in the electrolytes evaluated this quarter. All operations, including preparation of solutions and addition of  $\text{CuF}_2$ , were conducted in a dry argon atmosphere. The flasks, containing electrolyte and  $\text{CuF}_2$ , were shaken periodically for one month. The solutions have been submitted to the analytical section for analyses of total copper by polarography.

The results of  $\text{CuF}_2$  solubility measurements will be presented in the Fourth Quarterly Report.

As an indication of the solubility of  $\text{CuF}_2$ , simply on the basis of the color of the solution, it may be noted that the solutions of  $\text{CuF}_2$  in 2-pentanone and cyclohexanone were very deeply colored and almost opaque; green in 2-pentanone and dark red in cyclohexanone. It is presumed that a high  $\text{CuF}_2$  solubility will be found in these solutions. The solubility of  $\text{CuF}_2$  in the other solvents may be expected to be lower than in 2-pentanone and cyclohexanone, since the solutions were much more lightly colored; generally, light green or blue.

#### 1.1.4 Effect of Electrolytes on Cathode Performance

A number of cathodes were prepared from a mixture of 85%  $\text{CuF}_2$  (-170 mesh), 10% micronized graphite (Southwestern 1651) and 5% polyethylene powder (-100 mesh). The materials were blended by tumbling on a Fisher-Kendall mixer for 16 hours after which two gram portions were pressed onto expanded copper screens (5 Cu 14 2/0) at 90°C for 3 minutes at 4000 lbs/cm<sup>2</sup>. All electrode preparation and testing was carried out under a dry argon atmosphere to prevent hydration of the  $\text{CuF}_2$ . The electrodes were one square inch in geometrical area and were discharged at 25.8 ma (2 ma/cm<sup>2</sup>) in a glass cell equipped with platinum counter electrodes; the cell is shown in Figure 13 of the Second Quarterly Report. The results of the discharges are shown in Figure 6. The electrodes discharged in 1.25F  $\text{LiClO}_4$  in 2.4 pentanedione appeared to give 120% of their coulombic capacity which is clearly impossible. It thus appears that the electrolyte was being reduced and contributing to the overall capacity. The cathodes in this electrolyte started to evolve gas and flake apart after about 4 hours of discharge. At the end of discharge, the electrodes were red on the surface but were still black on the inside showing that reduction was incomplete. The poor performance of the electrodes discharged in 1M  $\text{LiClO}_4$  in cyclohexanone was caused primarily by excessive flaking of the active material from the cathode. This experiment will be repeated in compact cells where flaking is prevented. The electrodes discharged in 1.25F  $\text{LiClO}_4$  in 2-pentanone gave the most encouraging performance. A calculated efficiency of 104% was obtained at a cut of voltage of -3.0 volts with respect to a silver/silver chloride reference electrode. It is thought that this high figure is due to the uncertainty in calculating the theoretical capacity of the electrode since there was no visual evidence of electrolyte reduction. At the end of discharge, the electrode was red and spongy right through, indicating complete reduction.

Of the electrolytes tested the 2-pentanone solution appeared to be of some promise and will be further investigated in the future. Conclusions on the 2.4 pentanedione solution will be reserved until data are available under conditions where the cathode does not shed.

#### 1.2 Investigation of Electrolyte Solutes

Almost all of the work carried out to date has involved the use of only one electrolyte solute, lithium perchlorate. Although this has in general been

satisfactory, one problem associated with its use is the formation of the highly insoluble lithium fluoride in the cathode during discharge. It was thought that solutes having different cations would modify the cathode reaction since soluble or more porous fluorides might be formed on discharge. In this context it was decided to examine  $\text{AlCl}_3$ ,  $\text{KPF}_6$ ,  $\text{KCNS}$  and  $\text{NH}_4\text{CNS}$  as electrolyte solutes.

### 1.2.1 Conductance of Solutes in Propylene Carbonate

The solutions were prepared and the conductance was determined as described previously. The values obtained from the various solutes dissolved in propylene carbonate are shown in Figure 7. A curve of  $\text{LiClO}_4$  solution is shown for reference. It can be seen that  $\text{KCNS}$ ,  $\text{AlCl}_3$  and  $\text{KPF}_6$  give solutions of higher conductivity than  $\text{LiClO}_4$ . Solutions having the concentration that gave the maximum conductance were used as electrolytes in cell discharges.

### 1.2.2 Discharge of Li/CuF<sub>2</sub> Cells

Cupric fluoride electrodes were prepared as described in Section 1.1.4 and were compacted at a pressure of 4000 lbs/cm<sup>2</sup>. The lithium anodes were prepared by the standard pressed foil technique. Each cell comprised two lithium electrodes and one cupric fluoride electrode separated by two thicknesses of glass fibre filter paper. They were activated by filling with the electrolyte to be studied and discharged immediately at 2 ma/cm<sup>2</sup>. The electrode potentials were measured with respect to a silver/silver chloride reference electrode in the same electrolyte previously calibrated against a  $\text{Li}/\text{Li}^+$  reference electrode in 1F  $\text{LiClO}_4$  in propylene carbonate. The results for the cupric fluoride electrodes are shown in Figure 8.

It can be seen that the performance was very much reduced in the presence of the other solutes. The cathodes discharged in 1.15F  $\text{AlCl}_3$  showed very little visual evidence of reduction, there being no copper color either on the surface or in the interior of the electrodes. The cathodes appeared to be quite soluble in the  $\text{KCNS}$  solution since the electrolyte became a dense red color shortly after filling the cell. At the end of the discharge the electrolyte was dark brown in color. It was observed that the  $\text{NH}_4\text{CNS}$  solution reacted vigorously with the lithium anodes resulting in considerable gas evolution. Thus, this cell was scrapped and a single cathode was discharged in the glass cell described previously. This is the result shown in Figure 8. Immediately on placing the cathode in the cell the cupric fluoride started to dissolve and the electrolyte became colored deep red. During discharge, the electrode was observed to be gassing vigorously indicating electrolyte decomposition. At the end of discharge, the surface of the electrode was copper colored but the interior appeared unreduced.

## 2) REFERENCE ELECTRODE STUDIES

In the first quarter of this contract, an investigation was made of the  $\text{Li}/\text{Li}^+$  reference electrode. It was found that the couple was reversible but that practical difficulties mitigated against its use in working cells. The electrolyte in a lithium/cupric fluoride cell always contains a finite amount of copper ion and this was progressively deposited on the lithium reference electrode during use. After a while fluctuations in the reference potential developed and the electrode had to be discarded. The measurements made to date have been taken with respect to a silver/silver chloride electrode in the same electrolyte as the working electrode. Although this system is not expected to be reversible, it does provide a fairly steady non-thermodynamic standard to report the results against. One disadvantage of this system, apart from its non-thermodynamicity, is that the reference electrodes have to be frequently recalibrated and their potentials can be as much as 20 mv apart.

It was thus thought worthwhile to pursue the search for a reversible reference electrode which would be stable over long periods of time in the electrolytes that we commonly use.

### 2.1 Electrodes of the Second Kind

This type of electrode comprises a metal in contact with a sparingly soluble salt of the metal in a solution containing a soluble salt having an anion common to the sparingly soluble salt. Since we have most commonly used lithium perchlorate as our electrolyte solute, it was decided to investigate the possibility of developing a metal/metal perchlorate/ $\text{ClO}_4^-$  reference electrode. A number of heavy metal perchlorates were purchased and tested to determine their solubility in propylene carbonate. It was found that the perchlorates of bismuth, mercury, lead, iron<sup>III</sup> and silver were all appreciably soluble in propylene carbonate, nitromethane, and acetonitrile and were thus useless for reference electrodes of this type. It thus appears that a metal/metal perchlorate electrode cannot be used in the organic solutions which we commonly use.

### 2.2 The Glass Electrode

It has been known for some time that the glass electrode is sensitive to alkali metal ions (3). The pH response of the majority of glass electrodes is imperfect at the high end of the pH scale, the error being greatest in strong solutions of the alkali and alkali earth metal ions. The departures from ideal response decrease as the radius of the ions in the solution increases probably because large ions cannot penetrate the silicon-oxygen network of the glass. This phenomenon has been discussed by Dole and Nicolsky who assumed that the glass behaved as an ion exchange resin.

It seems reasonable to suppose that if a glass electrode is responsive to alkali metal ions in aqueous solutions where hydrogen ions are present, it would be

even more responsive to alkali metal ions in non-aqueous solutions which contain no hydrogen ions. Cation responsive glass electrodes have been made available recently and have been quite extensively studied. Eisenman, Rudin and Casby (4) found that glasses containing 18 mole percent of alumina had a high specificity for sodium ion in aqueous solutions. Leonard (5) showed that glasses in the lithium aluminum silicate series behaved reversibly towards sodium over a wide range of concentrations. Rechnitz and Brauner (6) and Rechnitz and Zamochnick (7) studied the formation constants of alkali metal chelates by use of a cation sensitive glass electrode.

A number of studies have been made of the glass electrode in non-aqueous and partly aqueous solutions. The glass electrode has been used successfully in benzene-isopropyl solvents after saturation of the surface with water (8). The electrode gradually loses its response in non-aqueous media but this can be restored by soaking in water. Rechnitz and Zamochnick (9) showed that glass electrodes are reversible to  $K^+$ ,  $Na^+$  and  $Rb^+$  in partially aqueous ethanol, acetone, ethylene glycol and dimethyl formamide.

The autoprotolysis constant of acetonitrile was studied by Coetzee and Padmanabhan (10) who showed that the response of the glass electrode was reversible to  $H^+$  in acetonitrile. Useful results have also been obtained in dimethyl formamide (11).

The foregoing work would suggest that the glass electrode should be reversible to alkali metal ions in purely non-aqueous media. If this is so, then the glass electrode should be a useful reference electrode in non-aqueous electrochemistry. In addition, since no ions penetrate the glass, it should be stable over long periods of time.

### 2.2.1 Measurement of Alkali Metal Ion Response

In this contract only lithium is being studied as an anode metal, therefore, we decided to investigate the reversibility of the glass electrode towards lithium ion in propylene carbonate solutions.

The glass electrodes used in this study were as follows.

- (i) Beckman General Purpose No. 40498.
- (ii) Beckman General Purpose No. 40498 modified by draining the glass bulb of the aqueous solution and refilling with 1F  $LiClO_4$  in propylene carbonate.
- (iii) Beckman Cationic Glass Electrode No. 39137.

The electrodes were aged by immersing in twice distilled propylene carbonate for one week and were then kept in 1F  $LiClO_4$  in propylene carbonate for several

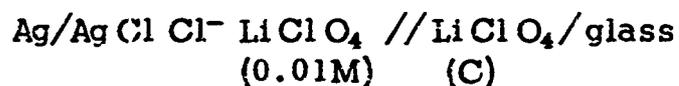
days before use. Propylene carbonate was supplied by Jefferson Chemical Company and was purified by twice distilling from Ca O under a pressure of 1 mm Hg. The salts used were the purest commercially available and were vacuum dried at 100°C for 16 hours before use. The potentials were measured against a silver/silver chloride reference electrode using a Beckman Model G pH meter in the cell shown in Figure 9.

In the first experiment the cell was assembled with 0.01F LiClO<sub>4</sub> in propylene carbonate which had been saturated with AgCl in the reference compartment and 0.01F LiClO<sub>4</sub> in the glass electrode compartment. The cell was allowed to stand for 16 hours or until the potential became steady. This usually took several hours after which the potential was extremely constant.

Additions of 1F LiClO<sub>4</sub> in propylene carbonate were made to the glass electrode compartment from a burette and the potential was recorded until a steady value was obtained. This usually took 5 minutes but sometimes as long as fifteen minutes were required.

Only the general purpose electrode was used in this experiment to determine whether any response was obtained from solutions of lithium ions in the absence of water. The results are shown in Table 2 and a log plot is shown in Figure 10.

The cell can be represented as:



If the electrode potential of the left hand side is constant then:

$$E_{\text{cell}} = E_g^\circ - E_{\text{ref}} + \frac{RT}{F} \ln a_{\text{Li}_2^+} + E_j$$

Where  $E_{\text{cell}}$  is the cell potential,  $E_{\text{ref}}$  is the potential of the reference electrode,  $a_{\text{Li}_2^+}$  is the activity of the lithium ions in the glass electrode compartment, and  $E_j$  is the junction potential.

If the electrolyte is assumed to be fully dissociated and if the activity is replaced by concentration then:

$$E_{\text{cell}} = E_g^\circ - E_{\text{ref}} + \frac{RT}{F} \ln C_{\text{Li}_2^+} + E_j$$

or

$$E_{\text{cell}} = E_g^\circ - E_{\text{ref}} + E_j + 0.05915 \log C_{\text{Li}_2^+} \text{ at } 25^\circ\text{C}$$

Thus a slope of 0.059 volts would be expected for the log plot. As can be seen from Figure 10 a slope of 0.090 volts is obtained. The difference between the experimental and theoretical slopes must be due to the liquid junction potential. The liquid junction potential in a cell is usually calculated by the Henderson-Planck equation:

$$E_j = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1 + V_1) - (U_2 + V_2)} \ln \left[ \frac{U_1 + V_1}{U_2 + V_2} \right]$$

Where  $U = \sum c_+ \lambda_+^{\circ}$  ,  $V = \sum c_- \lambda_-^{\circ}$

$$U = \sum c_+ \lambda_+^{\circ} z_+ , \quad V = \sum c_- \lambda_-^{\circ} z_-$$

The subscripts 1 and 2 refer to the end solutions.

To apply this equation the limiting ionic conductances must be known and these have not been determined for  $\text{LiClO}_4$  in propylene carbonate. The limiting equivalent conductance of the salt has been determined however, and if the transference number of the ions were known, the ion conductances could be determined from:

$$\lambda_+^{\circ} = \Lambda^{\circ} t_+$$

$$\lambda_-^{\circ} = \Lambda^{\circ} t_-$$

Since the Henderson-Planck equation is not exact in itself there is little need for an extremely accurate transference number. An approximate value can be obtained from polarographic measurements. For example in the absence of supporting electrolyte the cathodic limiting current at a dropping mercury electrode is given by:

$$i_e = i_d + i_m$$

Where  $i_d$  is the diffusion current and  $i_m$  the migration current. If  $i_m$  is defined as  $i_1 t_+$  then:

$$i_e = i_d + i_1 t_+$$

or

$$i_e(1 - t_+) = i_d$$

Thus, if the current is measured in the absence of supporting electrolyte ( $i_e$ ) and in the presence of supporting electrolyte ( $i_d$ ) the transport number of the ion can be determined. This was done for 0.002F  $\text{LiClO}_4$  in propylene carbonate using tetraethyl ammonium perchlorate (TEAP) as the supporting electrolyte with the following results.

Concentration of Li <sup>+</sup> (mole/ltr)	Concentration of TEAP (mole/ltr)	Limiting Current (μA)
0.002	0	3.98
0.002	0.002	2.92
0.002	0.005	2.66
0.002	0.010	2.54
0.002	0.050	2.37
0.002	0.075	2.56
0.002	0.100	2.54

The diffusion current was taken to be 2.55 μA whereby the transference number comes out to be 0.359. The limiting ionic conductances are thus:

$$\lambda_{\text{Li}^+}^{\circ} = 26.39 \times 0.359 = 9.474$$

$$\lambda_{\text{ClO}_4^-}^{\circ} = 26.39 \times 0.641 = 16.915$$

These values were substituted into the Henderson-Planck equation which allowed the liquid junction potential to be calculated. The revised results are shown in Table 3, and the log plot in Figure 11. A slope of 0.070 volts is obtained, which is fairly good agreement with the theoretical slope, considering the uncertainty in the liquid junction potential. It thus appears that the glass electrode is reversible towards lithium ions in propylene carbonate. It was then decided to investigate the response of the glass electrode to lithium ion in the presence of other ions.

### 2.2.2 Response of the Glass Electrode to C<sub>Li<sup>+</sup></sub> in the Presence of Other Ions

In order to avoid the uncertainty of calculating the liquid junction potential, it was decided to set up the cell so that the ionic strength of the solution was the same on both sides of the junction. In this case only the conductance influences the junction potential which is probably quite small. The response of the glass electrodes was determined in the presence of Mg<sup>++</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> N<sup>+</sup> ion as follows.

Solutions of ionic strength 0.75 were prepared of the salts of the above ions and placed in the cell. Lithium perchlorate solution of 0.75F was added from a burette so that the total ionic strength remained constant. The concentration of the lithium ion was calculated from the total volume of solution and the amount of lithium perchlorate added.

#### 2.2.2.1 Response of Glass Electrodes to Lithium ion in the Presence of K<sup>+</sup>

Since potassium perchlorate is insoluble in propylene carbonate, KCNS was used in this experiment. The results are shown in Table 4 and a log plot is shown in

Figure 12. It can be seen that over a large part of the concentration range the potential is independent of the lithium ion concentration. At about 0.125F in lithium ion a response starts to be developed although it is doubtful whether a linear plot is obtained.

#### 2.2.2.2 Response of Glass Electrode to Lithium Ion in the Presence of $\text{NH}_4^+$

A solution of  $\text{NH}_4\text{Cl}$  in dimethyl sulphoxide was used as the source of  $\text{NH}_4^+$  ions while a solution of 0.750F  $\text{LiClO}_4$  in dimethyl sulphoxide was used to add the  $\text{Li}^+$  ion. The results are shown in Table 5 and a log plot is shown in Figure 13. The general purpose and modified general purpose electrodes begin to show a response to the changing lithium ion concentration at 0.30F. This is considerably higher than the concentration at which response is first observed in the potassium solution. The cation specific electrode develops response to the lithium ion concentration at 0.125F and approaches a slope of 0.058 volts at the highest concentrations. Thus the cation specific electrode is reversible to  $\text{Li}^+$  in  $\text{NH}_4^+$  solutions at concentrations higher than 0.175F.

#### 2.2.2.3 Response of Glass Electrodes to Lithium Ion in the Presence of $\text{Mg}^{++}$

The cell was filled with 0.25F  $\text{Mg}(\text{ClO}_4)_2$  solution in propylene carbonate and lithium ion was added from a burette filled with 0.75F  $\text{LiClO}_4$  solution in the same solvent. The results are shown in Table 6, and a log plot is shown in Figure 14. The general purpose and modified electrodes achieve a linear response at a concentration of lithium ion around 0.05F, whereas the cation specific electrode develops linearity at 0.023F showing increased specificity. The slopes are 0.055, 0.034 and 0.069 for the general purpose, modified and cation specific electrodes respectively. Reversibility is thus attained over a wide range of concentration for the general purpose and cation specific electrodes.

#### 2.2.2.4 Response of Glass Electrodes to Lithium Ion in the Presence of $(\text{C}_2\text{H}_5)_4\text{N}^+$

The cell was filled with 0.75F  $(\text{C}_2\text{H}_5)_4\text{N} \cdot \text{ClO}_4$  solution in propylene carbonate and lithium ion was added from a burette filled with 0.75F  $\text{LiClO}_4$ . The results are shown in Table 7, and a log plot is shown in Figure 15. A linear dependence was observed over the concentration range studied for all three electrodes. The reason for the break in the curve of the modified electrode is not known. Possibly this electrode was scratched or cracked during the experiment although no sign of damage could be seen. Slopes of 0.055, 0.056 and 0.056 volts were obtained for the modified, general purpose and cation specific electrodes. Thus all the electrodes were reversible in the  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  solution.

#### 2.2.3 Discussion of Results

A number of interesting conclusions can be drawn from the results. Firstly, the

glass electrodes do behave in a reversible manner towards the lithium ion concentration. In the presence of small ions ( $K^+$ ,  $NH_4^+$ ) the reversibility is observed only after a fairly high concentration of lithium ion has been reached. In solutions of intermediate sized ions ( $Mg^{++}$ ) reversibility is observed at quite low concentrations and in solutions of large ions ( $(C_2H_5)_4 N^+$ ) Nernstian behaviour is seen down to the lowest concentration studied. The concentration at which reversible behaviour begins thus depends upon the size of the other ions present in the solution. There does appear to be some advantage in using a cation specific electrode since this assumes reversible behaviour at a lower concentration than the others.

If we regard the glass electrode as an ion exchange membrane, this behaviour can be explained. If we can write the exchange reaction as:



Where I refers to any univalent cation and the subscripts s and g refer to ions in the solution and in the glass. According to Gregor (12) the ion exchange equilibrium is given by:

$$RT \ln \left[ \frac{a_{I_g^+}}{a_{Li_g^+}} \right] \left[ \frac{a_{Li_s^+}}{a_{I_s^+}} \right] = p \left[ V_{Li^+} - V_{I^+} \right]_g \quad (1)$$

Where p is the swelling pressure of the resin and V is the specific volume of the resin.

The ionic electrical potential is given by:

$$\bar{\mu}_i = \mu_i + z_i F \psi \quad (2)$$

Thus the potential at the glass/solution interface is given by:

$$E = (\psi_g - \psi_s) = \frac{\bar{\mu}_{I_g^+} - \mu_{I_g^+} - \bar{\mu}_{I_s^+} + \mu_{I_s^+}}{F} = \frac{\bar{\mu}_{Li_g^+} - \mu_{Li_g^+} - \bar{\mu}_{Li_s^+} + \mu_{Li_s^+}}{F} \quad (3)$$

At ion exchange equilibrium:

$$\bar{\mu}_{I_g^+} = \bar{\mu}_{I_s^+} \quad (4)$$

$$\bar{\mu}_{Li_g^+} = \bar{\mu}_{Li_s^+} \quad (5)$$

$$\text{Therefore } E = (\psi_g - \psi_s) = \frac{\mu_{I_s^+} - \mu_{I_g^+}}{F} = \frac{\mu_{Li_s^+} - \mu_{Li_g^+}}{F} \quad (6)$$

Since  $\mu_i = \mu_i^\circ + RT \ln a_i$  (7)

$$E = \frac{\mu_{\text{Li}_s}^\circ - \mu_{\text{Li}_g}^\circ}{F} + \frac{RT}{F} \ln \frac{a_{\text{Li}_s}^+}{a_{\text{Li}_g}^+} \quad (8)$$

or  $E = \frac{\mu_{\text{Li}_s}^\circ - \mu_{\text{Li}_g}^\circ}{F} + \frac{RT}{F} \ln \frac{C_{\text{Li}_s}^+ \cdot f_{\text{Li}_s}^+}{C_{\text{Li}_g}^+ \cdot f_{\text{Li}_g}^+}$  (9)

Substituting  $a_i = c_i f_i$  into the expression for the ion exchange equilibrium gives:

$$RT \ln \frac{C_{\text{I}_g}^+ \cdot f_{\text{I}_g}^+ \cdot C_{\text{Li}_s}^+ \cdot f_{\text{Li}_s}^+}{C_{\text{Li}_g}^+ \cdot f_{\text{Li}_g}^+ \cdot C_{\text{I}_s}^+ \cdot f_{\text{I}_s}^+} = p(V_{\text{Li}^+} - V_{\text{I}^+})_g \quad (10)$$

or  $\frac{C_{\text{I}_g}^+ \cdot f_{\text{I}_g}^+ \cdot C_{\text{Li}_s}^+ \cdot f_{\text{Li}_s}^+}{C_{\text{Li}_g}^+ \cdot f_{\text{Li}_g}^+ \cdot C_{\text{I}_s}^+ \cdot f_{\text{I}_s}^+} = \exp \left[ \frac{p}{RT} (V_{\text{Li}^+} - V_{\text{I}^+})_g \right]$  (11)

Since electroneutrality exists in the glass phase, we can put (13)

$$C_{\text{I}_g}^+ + C_{\text{Li}_g}^+ = C_0 \quad (12)$$

Therefore  $\frac{(C_0 - C_{\text{Li}_g}^+) f_{\text{I}_g}^+ \cdot C_{\text{Li}_s}^+ \cdot f_{\text{Li}_s}^+}{C_{\text{Li}_g}^+ \cdot f_{\text{Li}_g}^+ \cdot C_{\text{I}_s}^+ \cdot f_{\text{I}_s}^+} = \exp \left[ \frac{p}{RT} (V_{\text{Li}^+} - V_{\text{I}^+})_g \right]$  (13)

Rearranging equation (13) gives:

$$\frac{C_{\text{Li}_s}^+ f_{\text{Li}_s}^+}{C_{\text{Li}_g}^+ f_{\text{Li}_g}^+} = \frac{\exp \left[ \frac{p}{RT} (V_{\text{Li}^+} - V_{\text{I}^+})_g \right] C_{\text{I}_s}^+ f_{\text{I}_s}^+ + f_{\text{I}_g}^+ \cdot C_{\text{Li}_s}^+ \cdot f_{\text{Li}_s}^+}{C_0 f_{\text{I}_g}^+} \quad (14)$$

Substituting (14) into equation (9), one obtains:

$$E = \frac{\mu_{\text{Li}_s}^\circ - \mu_{\text{Li}_g}^\circ}{F} + \frac{RT}{F} \ln \left[ C_{\text{I}_s}^+ f_{\text{I}_s}^+ \exp \left[ \frac{p}{RT} (V_{\text{Li}^+} - V_{\text{I}^+})_g \right] + f_{\text{I}_g}^+ + C_{\text{Li}_s}^+ f_{\text{Li}_s}^+ \right] - \frac{RT}{F} \ln C_0 f_{\text{I}_g}^+ \quad (15)$$

If the activity coefficients are taken as unity:

$$E = \frac{\mu_{\text{Li}_s^+}^\circ - \mu_{\text{Li}_g^+}^\circ}{F} - \frac{RT}{F} \ln C_0 + \frac{RT}{F} \ln \left[ C_{\text{I}_s^+} \exp \left[ \frac{p}{RT} (V_{\text{Li}^+} - V_{\text{I}^+})_g \right] + C_{\text{Li}_s^+} \right] \quad (16)$$

$$\text{or } E = E^\circ + \frac{RT}{F} \ln \left[ C_{\text{I}_s^+} \exp \left[ \frac{p}{RT} (V_{\text{Li}^+} - V_{\text{I}^+})_g \right] + C_{\text{Li}_s^+} \right] \quad (17)$$

This equation predicts the behaviour of the glass electrode in solutions containing ions which can compete for places on the glass. If the solution contains no cations other than  $\text{Li}^+$  then the first term in parenthesis disappears and the expression becomes:

$$E = E^\circ + \frac{RT}{F} \ln C_{\text{Li}_s^+} \quad (18)$$

If the solution contains ions of approximately the same size as the lithium ion, then the exponential term becomes unity and:

$$E = E^\circ + \frac{RT}{F} \ln \left[ C_{\text{I}_s^+} + C_{\text{Li}_s^+} \right] \quad (19)$$

This explains the behaviour of the electrodes in the presence of  $\text{K}^+$  and  $\text{NH}_4^+$  which are approximately the same size as the lithium ion. Nernstian response to the concentration of lithium ion will not be obtained until this is large compared to the  $\text{I}^+$  concentration.

When the competing ion is much larger than lithium, the exponential term becomes very small and:

$$E = E^\circ + \frac{RT}{F} \ln C_{\text{Li}_s^+} \quad (20)$$

This is the behaviour observed in  $(\text{C}_2\text{H}_5)_4\text{N} \cdot \text{ClO}_4$  solution. For ions of intermediate size the equation predicts a curve with a limiting slope of 0.059 volts at  $25^\circ\text{C}$  for high concentrations of  $\text{Li}^+$  and this is indeed the behaviour observed.

We can thus conclude that the glass electrode is reversible to lithium ions and can be used as a reference electrode in our system where only lithium ions are present.

### 3) CATHODE STUDIES

#### 3.1 Effect of the Amount of Binder on Performance

In order to reduce the amount of unproductive weight in the electrode and thus increase the energy density, an investigation was undertaken to determine the

minimum amount of polyethylene binder necessary for maximum performance without sacrificing physical strength. A batch of cupric fluoride electrodes were prepared from a mix of 90%  $\text{CuF}_2$  (-170 mesh) and 10% graphite (Southwestern 1651) to which varying amounts of polyethylene powder was added. The blends were then tumbled in a Fisher-Kendall mixer for 16 hrs and pressed onto expanded copper grids (5 Cu 14 2/0) at  $90^\circ\text{C}$  for 3 minutes at  $500 \text{ lbs/cm}^2$ . The cathodes were assembled into three-plate cells in conjunction with two pressed foil lithium anodes. The separator was two thicknesses of 15 mil glass fiber filter paper. The cells were filled with  $1\text{F LiClO}_4$  in propylene carbonate and discharged immediately at  $2 \text{ ma/cm}^2$ . All operations with the exception of pressing were carried out in a dry argon atmosphere.

Cathode potentials were measured with respect to a silver/silver chloride electrode in the same electrolyte having a potential of 3.62 volts with respect to lithium. All the tests were replicated and average values are shown in Figure 16. A graph of the energy density versus the amount of binder is shown in Figure 17. The energy density figures as based on the total mix weights only, and does not include the grid. It can be seen that the electrodes with the least amount of binder gave the best performance. This is partly due to the reduction in the relative weight of inert to active material and partly due to increased cathode efficiency. Although the electrodes containing no binder gave the highest performance, these were too fragile for practical use, and had to be handled with extreme delicacy. The electrodes containing 2.5% binder, however, retained the good performance and were strong enough to be handled without breaking. At the end of discharge, it was observed that the electrodes were all copper colored and had compacted considerably during discharge.

### 3.2 Effect of Amount of Graphite on Performance

The amount of graphite presently incorporated into the cathode mix accounts for a large part of the unproductive weight of the cathode. Since the product of the cathode reaction is copper metal, it was thought that the amount of graphite in the cathode mix could be reduced without impairing the performance to any marked degree. The electrodes were prepared as described above from a mixture of 97.5% cupric fluoride (-170 mesh) and 2.5% polyethylene powder (-100 mesh) to which varying amounts of graphite were added in the range zero to ten percent. The electrodes were assembled into cells, activated and discharged as described before. Figure 18 shows the average results of replicated sets containing various amounts of graphite. A graph of amount of graphite versus the energy density is shown in Figure 19. Here again the energy density is based on the total mix weight and does not include the grid. It is clear that increasing the amount of graphite increases both the coulombic efficiency and the energy density. This is most marked where the graphite concentration is low. The energy density curve approaches a maximum value of approximately 525 watt hours per lb at a graphite content of 10 percent. There thus appears to be no advantage in reducing the graphite content of the mix below 10 percent.

The electrodes containing no graphite gave very poor performance, presumably due to the poor conductivity of the mix. Poor conductivity is also evident in the electrodes containing 2.5 percent graphite as shown by the voltage dip at the beginning of discharge. This eventually disappears as the amount of copper in the electrode increases. After discharge, all the electrodes with the exception of that containing no graphite were copper colored and were considerably harder than when placed in the cells.

### 3.3 Effect of Cathode Weight on Performance

A study was made to determine the effect of variations in cathode active material weight on performance. The object of this work was to increase the cathode energy density by increasing the ratio of active to inactive electrode component weights.

Electrodes were prepared from a blend containing:

- i) 85%  $\text{CuF}_2$  (-170 mesh)
- ii) 10% Southwestern 1651 graphite (dried at  $120^\circ\text{C}$ )
- iii) 5% polyethylene powder (-100 mesh)

The powders were mixed by tumbling in a Fisher-Kendall mixer for 16 hours.

Electrodes were made by hot-pressing the blend into a  $1\frac{1}{2}$  in. by  $1\frac{5}{8}$  in. grid of 5 Cu 14 2/0 expanded copper. Pressing carried out at  $500\text{ lbs/cm}^2$  for 3 minutes at  $90^\circ\text{C}$ . Duplicate electrodes were made with respectively 2, 3, and 4 grams of powder blend. All operations, except hot-pressing, were done in a dry argon atmosphere.

Tests were conducted in cells of compact design containing three electrodes; 2 lithium anodes and 1  $\text{CuF}_2$  cathode, the cathode being positioned between the anodes. The insulation used was two thicknesses of 15 mil glass fiber filter paper designated as No. 934 AH (Hurlbut Paper Co.). The element was inserted into a polypropylene jar, together with sufficient plastic shims to insure a minimum of clearance between the surfaces of the various components. This design has been used successfully in the evaluation of structurally fragile cathodes.

The cells were placed in a vacuum desiccator in order to evacuate the cells before filling with approximately 10 ml of 1F  $\text{LiClO}_4$  in propylene carbonate. This was done to insure complete wetting of the cathode and separator and to remove occluded argon. A separatory funnel was attached to the cover of the desiccator, with the spout extending into the vessel to a point over the cell opening. With the stop cork closed on the funnel, the desiccator was evacuated for several minutes. The stop cork was then opened slowly and electrolyte was drawn into the cells.

The cells were discharged at  $2 \text{ ma/cm}^2$  ( $60 \text{ mc/cell}$ ) using a constant current d.c. power supply. Cathode potentials were measured against a Ag/Ag Cl reference electrode using a high impedance electrometer. The percentage of the theoretical  $\text{CuF}_2$  capacity utilized on discharge was taken as a criterion of performance.

The results of this experiment are shown in Figure 20. The highest utilization, about 78% average, was obtained with 3 gram cathodes, followed by 2 gram cathodes with an average of 74.8%, and finally 4 gram cathodes with an average of 79% utilization. The maximum variation in utilization was only about 10% for the three weights evaluated.

The discharge characteristics of the 3 and 4 gram cathodes were somewhat better than that of the 2 gram electrodes, showing a flat profile throughout most of the discharge and falling off sharply at the end.

The discharge characteristics of the  $\text{LiCuF}_2$  cells described above are shown in Figures 21, 22 and 23. Energy density calculations were made from this data to determine the effect of cathode weight on the energy density of a complete cell.

In determining energy densities, the following factors were considered:

The total weight of the cathode was used including the grid or screen weight. For the anode, the weight of lithium consumed on discharge only was used. The weight of the other cell components were not included. The energy densities found were as follows:

2 gram cathodes	-	257	watt	hours/lb	average
3 gram cathodes	-	320	"	"	"
4 gram cathodes	-	308	"	"	"

An increase in energy density of 24% and 20% was obtained for three and four gram cathodes respectively as compared to two gram electrodes. Two factors appear to have effected this improvement in energy density: i) the discharge characteristics were better, i.e., higher average discharge voltages were obtained with the heavier cathodes and ii) the ratio of active to inactive electrode component weights was higher with the heavier cathode.

### 3.4 Effect of Current Density on Cathode Performance

The effect of discharge current density on performance was determined for cathodes made as described in section 3.3 of this report. The electrodes were made with 2 grams of  $\text{CuF}_2$  blend and were discharged at current densities of 1 to  $5 \text{ ma/cm}^2$  in  $1 \text{ ma/cm}^2$  increments, in cells of the type described in section 3.3. Replicates of two electrodes were tested at each current density. The electrolyte used was  $1\text{F LiClO}_4$  in distilled propylene carbonate.

Electrode potentials were measured against a Ag/Ag Cl reference electrode using a high impedance electrometer.

In this study the discharge characteristics of the lithium anodes were also measured to compare performance with that obtained in cells with no separator system. The results of this part of the test will be discussed in section 4.2.

The results of this experiment are shown in Figures 24 and 25. In general, increasing current density resulted in decreasing cathode efficiency, in the range studied. Percent utilization of  $\text{CuF}_2$  decreased from an average of 82% at  $1 \text{ ma/cm}^2$ , to an average of 32% at  $5 \text{ ma/cm}^2$ , or about 60% decrease in utilization.

The rapid loss in  $\text{CuF}_2$  cathode efficiency with increasing current density appears to be due to concentration polarization effects. The mass transport of ionic species to the reaction sites appears to be reduced by various factors:

- i) The viscosity of the electrolyte used is high so that ionic mobility is inherently low.
- ii) The product of discharge at the cathode,  $\text{LiF}$ , is insoluble in the electrolyte and therefore deposits in the pores of electrode, further limiting access of electrolyte to the reaction sites.
- iii) The separator material reduces the convective transport of electrolyte so that movement of the ionic species required to sustain the reaction is controlled essentially by diffusion.

The lower series of curves in the figures described above, showing lithium anode performance, will be discussed in section 4.2.

### 3.5 Effect of Electrolyte Concentration on Cathode Performance

The effect of electrolyte concentration on cathode performance was determined using solutions of  $\text{LiClO}_4$  in distilled propylene carbonate over the range 0.25 to 1.5F.

Cathodes were made as described in section 3.3 of this report and had a  $\text{CuF}_2$  blend weight of two grams giving them a nominal capacity of 0.865 A.H. The electrodes were tested in cells of the type described in section 3.1. The electrolytes were made using  $\text{LiClO}_4$  dried at  $120^\circ\text{C}$  under reduced pressure for 16 hours. All operations were conducted in a dry argon atmosphere. The cells were discharged at  $2 \text{ ma/cm}^2$ , and cathode potentials were measured against a Ag/Ag Cl reference electrode using a high impedance electrometer. Figures 26 and 27 show the results of this study.

The figures show the performance of replicates of two electrodes at each level of concentration. The average percentage utilization of  $\text{CuF}_2$  with respect to

concentration is shown in Figure 28. The percent utilization of  $\text{CuF}_2$  increases sharply from about 15% at 0.25 F to 65% at 0.75 F, then increases less rapidly, reaching a peak efficiency of 77% at 1.25 F and finally decreases again to 72% at 1.5 F.

There was only a small difference in performance, about 5%, between 1.0 and 1.5 F solutions. Although maximum cathode performance was obtained with 1.25 F electrolyte, most of the tests in this quarter, concerning the effect of electrode construction and operating variables, continued to be with 1.0 F electrolyte in order to compare results with these previously obtained.

#### 4) ANODE STUDIES

##### 4.1 Storage Tests

Anode studies were continued in the third quarter in order to determine the effect on performance of storage in paraffin oil and electrolyte.

Lithium anodes were made as previously described (2) by pressing lithium ribbon, 15 mils thick, on a 3 Cu 7 3/0 expanded copper screen. The electrodes, immediately after fabrication were immersed in the respective storage media, paraffin oil and 1 F  $\text{LiClO}_4$  in distilled propylene carbonate for various intervals. Storage was in glass jars with gasketed screw top lids which were tightly sealed and taped to exclude air and moisture.

At various intervals, the jars were opened in a dry argon atmosphere, the electrodes to be tested were removed from the media, wiped with facial tissues to remove excess fluid and immediately immersed in the test electrolyte. Discharge of the anodes was carried out in polypropylene cell jars between sheet copper cathodes as already described (1 and 2). Discharge was at  $2 \text{ ma/cm}^2$  in 1 F  $\text{LiClO}_4$  in distilled propylene carbonate. Anode potentials were measured against Ag/Ag Cl reference electrodes using a high impedance voltmeter.

The results of this study are shown in Figure 29. No loss in percent utilization of lithium was suffered as a result of storage in paraffin oil for as long as 5 months. The polarization of an electrode stored for 5 months, however, was considerably higher than that obtained at 2 months. It should be noted that the surface of the anode, after 5 months storage in paraffin oil, was considerably blackened, and this coating might possibly be resistive enough to cause an increase in polarization.

In Figure 30 the results of storage in 1 F  $\text{LiClO}_4$  in distilled propylene carbonate show practically no change in electrode performance, with respect to potential or percent lithium utilized, after a period of 3 months storage. The surfaces of anodes stored in electrolyte were somewhat brighter and cleaner than

was observed for anodes stored in paraffin oil for approximately the same interval. However, this may have been the result of a somewhat better cover seal in the case of the electrolyte storage, and therefore no definite conclusion can be made at this time as to the advantages of either method of storage. However, it appears that lithium anodes may be stored for at least 3 months, in either paraffin oil or 1 F LiClO<sub>4</sub> in distilled propylene carbonate, without any appreciable detrimental effect.

#### 4.2 Effect of Discharge Current Density on Anode Performance

Observations have been made of the effect of current density on anode performance for electrodes assembled into cells of compact design as described in section 3.3 of this report.

The electrodes were discharged at current densities of 1-5 ma/cm<sup>2</sup> in 1 ma/cm<sup>2</sup> increments. The results are shown in Figures 24 and 25 which also show the effect of current density on cathode performance. The data have been presented in this manner rather than show anode performance separately, since there appears to be an interaction between cathode and anode performance, and it was intended to show this behaviour. In a few instances, and mostly at higher current densities, 3 to 5 ma/cm<sup>2</sup>, the anode polarization was somewhat higher than at 1-2 ma/cm<sup>2</sup>, and appeared to increase rapidly as the cathode polarization increased near the termination of discharge. This kind of behaviour was not observed for anodes discharged in half cells against copper cathodes as previously described (2). In half cells, the anodes could be discharged over a range of 1 to 10 ma/cm<sup>2</sup> without appreciably affecting either electrode polarization or percent utilization of lithium. It appears that the unusual anode polarization observed in testing of compact cells might be due to concentration polarization effects. The separator used in the compact cells probably reduces the convective transport of electrolyte so that mass transport is essentially diffusion controlled. This process appears to be too slow, especially at the higher current densities, to prevent accumulation of reaction products and consequent concentration polarization.

#### 5) SEPARATOR STUDIES

Four standard screening tests were given in the previous report (2) as criteria to be used in determining the suitability of a material as a separator. These were:

- i) Stability in the electrolyte
- ii) Absorption of electrolyte
- iii) Retention of absorbed electrolyte
- iv) Electrical resistance of wetted separator

The materials evaluated in the third quarter were found to be essentially inert in propylene carbonate. The electrolyte absorption and retention and electrical

resistance of these materials was therefore determined.

### 5.1 Absorption and Retention

Electrolyte absorption and retention were determined as previously described (2). The results are shown in Table 8. In general the lightly compacted, fibrous separator materials, such as the glass fiber and asbestos materials, were found to have a high percent absorption of electrolyte, whereas the tightly compacted, fibrous materials and microporous materials had a low absorption.

### 5.2 Determination of Separator Resistance

Construction of the separator resistance test cell described in the previous report was completed in the third quarter. A photograph of this cell is shown in Figure 31. It has proved to be very satisfactory for measurement of separator resistance in organic electrolytes. The procedure used in measuring resistance with this cell was described previously (2). The results of measurements of specific resistance of various separators are shown in Table 8. All measurements were made in 1 F  $\text{LiClO}_4$  in distilled propylene carbonate.

In analyzing the results in Table 8, asbestos and glass fiber filter papers were taken as basis for comparison, since these materials have performed satisfactorily in  $\text{Li/CuF}_2$  cells. The resistance values for these materials are among the lowest obtained in this study. The absorption of electrolyte was found to be high and this may be an undesirable characteristic in a high energy system. Other materials with low resistance and high absorption are the asbestos fuel cell papers and fiber glass mat. These separators would be expected to perform comparably to the glass fiber and asbestos filter paper separators. In general, the separators with high resistivity also show a low electrolyte absorption.

### Conclusion

Low separator resistance has been found to be associated generally with high electrolyte absorption. These characteristics are found in lightly compacted fibrous materials such as asbestos fuel cell and glass fiber papers. The high electrolyte absorption is an undesirable characteristic in a high energy density system.

Materials with low electrolyte absorption generally show high resistivity. Separators with these characteristics were of the microporous and membrane or ion exchange types. It appears that these materials would not be suitable for use in organic electrolyte systems.

### 5.3 Effect of Separators on Cathode Performance

The separators discussed above were incorporated into three plate cells to

determine their effect on the electrode performance. Cupric fluoride electrodes were prepared from a mix containing 87.5%  $\text{CuF}_2$  (-170 mesh), 10% micronized graphite (Southwestern 1651) and 2.5% polyethylene powder (-100 mesh). The ingredients were mixed by tumbling for 16 hours and two gram portions were pressed for 3 minutes at  $90^\circ\text{C}$  into expanded copper screens at  $500 \text{ lbs/cm}^2$ . The lithium anodes were prepared by the standard pressed foil technique. The cells were assembled as described previously with the electrodes separated by the material under examination. One formal  $\text{LiClO}_4$  in distilled propylene carbonate was added and the cell was then evacuated to remove occluded argon. Discharge was effected at  $2 \text{ ma/cm}^2$  and cut off when the cathode potential was 0.00 volts with respect to a  $\text{Li/Li}^+$  reference electrode. Relevant details of the cell performance are shown in Table 9 together with cell resistance values measured with a Wayne-Kerr Impedance bridge Model B221. Figures 32, 33, 34, 35 and 36 show performance curves for cells containing the separators given in Table 9.

The poor performance of the cells containing the Lexan and CdS ion exchange separators is probably due to their high electrical resistance and extremely low permeability to the electrolyte. It is probable that severe concentration polarization occurs at the electrode surface causing the rapid fall off in time.

The diatomaceous earth resin bonded separator employs a copolymer of PVC/PVAc as the binder. This appears to be soluble in the electrolyte since at the end of discharge the electrodes were seen to be covered with a gummy sludge. This breakdown of the separator possibly allowed short circuiting in addition to blocking of the pores of the cathode with the gum. The reason for the poor performance of the cells containing fuel cell paper is not readily apparent but again may be due to concentration effects because of this separator's extremely strong electrolyte retention.

The porous mat type separators generally allowed better performance than the other types, the best result being obtained with the asbestos filter paper. The differences in the performance of the mat type materials is probably due to the relative ease with which mass transport of ions can occur through them.

## 6) LITHIUM-CUPRIC FLUORIDE CELLS

In the third quarter the performance of  $\text{CuF}_2$  cathodes and lithium anodes was thought to have been sufficiently optimized to justify construction and testing of prototype multi-electrode cells. At the same time it was decided to package these cells in lightweight containers, to determine how closely the overall cell design would approach the desired 200 watt hrs/lb.

### 6.1 Design and Fabrication of Lightweight Polyethylene Cell Cases

Polyethylene was used as the material of construction since it is very resistant to attack by organic electrolytes and is easily molded or formed. The jar design

as finally evolved was based on considerations of lightweight, simplicity of fabrication and a method of obtaining an airtight seal.

The fabrication technique used was as follows:

A 12 in. square sheet of 30 to 40 mil polyethylene was mounted on a wood frame and the assembly placed in an oven set at 300°F for 4 to 5 minutes. This was done to soften the plastic so that it could be formed into the desired shape. The assembly was removed from the oven and the polyethylene sheet pressed tightly over a plaster of paris mold having the desired jar configuration. A vacuum was applied to the cavity causing the softened plastic to be drawn into and assume the configuration of the cavity. Cold water was then applied to the plastic, by means of a sponge, causing the plastic to harden and thereby allowing extraction of the jar without deformation. The excess plastic was then trimmed from the molded jar leaving a flange about  $\frac{1}{2}$  in. wide completely around the perimeter of the case. The inside dimensions of this jar were  $1\frac{3}{4}$  in. by  $1\frac{3}{4}$  in. by  $\frac{7}{16}$  in. The cover for this jar was simply a sheet of polyethylene cut to fit the contour of the jar. A typical jar and cover is shown in Figure 37.

In assembly of the cell, the components were stacked inside the jar, the cover sheet positioned and the assembly placed in an aluminum pressing fixture for the sealing operation. The pressing fixture was simply a heavy aluminum block containing a square opening large enough to accommodate the main body of the jar, and thereby allowing the flange to rest on the aluminum block. A solid plate of aluminum was then positioned over the assembly and the cover sealed to the jar at the flange area under heat and pressure. The heavy aluminum block was preheated to 200°F, and the aluminum pressing plate to 300°F, before assembly of the cell into the pressing fixture for the sealing operation. After application of light pressure for about 20 seconds the pressing plate was removed and cold water was applied to the seal area. The finished cell could then be removed from the pressing fixture without damage to the jar. A complete, sealed cell is shown in Figure 38. The electrode contact wires can be seen to be sealed into the plastic in the flange area. The cell is filled with electrolyte by a hypodermic syringe through the tubular section extending from the cell.

## 6.2 Construction of Multi-Electrode Cells

Lithium-cupric fluoride cells were constructed with 5, 7 and 9 electrodes per cell. Variations in construction were generally concerned with attempts to improve energy density, by reducing component weights and increasing the weight ratio of active to inactive components.

In assembly of cells, the electrodes were stacked alternately with the separator material within the jar cavity. The separator, with dimensions  $1\frac{3}{4}$  in. by  $3\frac{7}{8}$  in., was folded in half along its length and a cathode was positioned in the fold.

The electrode contact wires were bent to accommodate the contours of the jar during assembly, and where the wires extended out of the case through the flanged section, they were positioned sufficiently spaced apart to provide for a good plastic to wire bond during the sealing operation. After completing the assembly of the element, the cover was sealed to the case as described in section 6.1. A weight analyses of the cells described in the following section is shown in Table 10.

#### 6.2.1 Fabrication and Testing of Cells C-1-5 and C-2-5

These cells were replicates, made with 5 electrodes per cell; three anodes and two cathodes. Construction was as follows:

##### i) Anodes

The anodes were made using the technique previously described (2), except that a sheet of 15 mil lithium ribbon was pressed into each side of a 3 Cu 7 3/0 copper screen, as compared to the usual one thickness of ribbon per electrode.

##### ii) Cathodes

The cathodes were made with four grams of  $\text{CuF}_2$  blend as described in section 3.3. The cathode screen was 5 Cu 14 2/0 expanded copper.

##### iii) Separator

The separator material used in both cells was a double thickness of 15 mil glass fiber filter paper (Hurlbut No. 934 AH).

##### iv) Cell Case

Cell cases were vacuum molded using 40 mil polyethylene sheet.

##### 6.2.1.1 Testing of Cell C-1-5

This cell was filled under vacuum using the technique described in section 3.3. The electrolyte was 1 F  $\text{LiClO}_4$  in distilled propylene carbonate. This cell was discharged immediately after fabrication at 120 ma ( $2 \text{ ma/cm}^2$ ) using a constant current d.c. power supply. Cell voltage was measured using a high impedance voltmeter.

The performance of cell C-1-5 is shown in Figure 39. An energy density of 81 watt hours/lb was calculated from the discharge data.

##### 6.2.1.2 Testing of Cell C-2-5

Cell C-2-5, the replicate of cell C-1-5 was placed on dry storage for one month. It had originally been intended to test this cell, after the storage

period in exactly the same way as cell C-1-5. The vacuum filling technique, however, was not used. Instead the cell was filled in a dry argon atmosphere using a hypodermic syringe. The electrolyte was 1 F LiClO<sub>4</sub> in distilled propylene carbonate.

The cell was discharged at 120 ma (2ma/cm<sup>2</sup>) using the same apparatus described for C-1-5.

The performance obtained with cell C-2-5 is shown in Figure 40. The energy density calculated for this cell, from the discharge data, was only about 47 watt hrs/lb or about half that of cell C-1-5.

It is difficult to conclude as to the cause of the large difference in performance between cells C-1-5 and C-2-5. The dry storage for one month may have adversely affected performance. Possibly the permeability of the polyethylene case to air and moisture is higher than expected. Also, it may be possible that entrapped gas prevented proper filling and wetting of cell C-2-5, since the vacuum filling technique was not used in this instance. It appears that further work may be required, with respect to both, dry storage capabilities and new electrolyte filling techniques.

#### 6.2.2 Fabrication and Testing of Cell C-1-7

This cell was made with seven electrodes; four anodes and three cathodes. Construction was as follows:

##### i) Anodes

Single thickness anodes, i. e., anodes made with only one 15 mil thick sheet of lithium pressed into a grid were used as outside electrodes in the cell stack. Double thickness anodes (section 6.2.1) were used in the middle of the stack. The anodes were made with 3 Cu 7 3/0 expanded copper screens, as in all previous work, except that a contact wire of smaller diameter was used, thereby effecting a 30% reduction in screen weight.

##### ii) Cathodes

Three cathodes were used, each with four grams of CuF<sub>2</sub> blend, and made as described in section 3.3. The cathode screens were identical in construction to those used in the anodes. This effected more than a 50% reduction in screen weight for cathodes as compared to the usual 5 Cu 14 2/0 copper. It should be noted that adhesion of the cathode material to this finer screen was not satisfactory, and extreme care had to be taken in handling the electrodes.

##### iii) Separators

The separator chosen for use was Schleicher and Schuell No. 589 white ribbon filter paper. This material was used because of its low electrolyte absorption.

The specific resistance, however, was high, almost seven times that of the glass fiber filter paper.

#### iv) Cell Case

The cell case was vacuum molded using 40 mil polyethylene sheet.

#### 6.2.2.1 Testing of Cell C-1-7

This cell was filled with 1 F  $\text{LiClO}_4$  in distilled propylene carbonate using the vacuum filling technique. The cell was discharged using the same apparatus described for cells C-1-5 and C-2-5. An attempt was made to test the cell at  $2 \text{ ma/cm}^2$  but this current density could not be sustained. It was found that the cell would sustain  $1 \text{ ma/cm}^2$  ( $90 \text{ ma/cell}$ ) and the testing was continued at this level. The results of this test are shown in Figure 40. The energy density obtained from this discharge was 116 watt hrs/lb. Discontinuities in the discharge curve, shown by asterisks, were caused when the cell case was compressed lightly. This resulted in an improvement in cell potential which persisted generally for only a short time. This improvement might be due to either or both of the following factors:

i) Increased convective mass transport of electrolyte resulting in reduced concentration polarization.

ii) Release of entrapped gas which was observed when the cell was compressed. Trapped gas, especially between the working surfaces of the electrodes may have caused an increase in current density, and consequently an increase in polarization, especially at the cathodes.

It appears that the major factor in the failure of this cell to yield higher energy density was the separator material used. Because of its high resistivity, the cell suffered high IR losses as was shown by the inability to sustain a current density of  $2 \text{ ma/cm}^2$ . Also, the high resistance may have had an effect on concentration polarization.

#### 6.2.3 Fabrication and Testing of Cell C-1-9

This cell was made with nine electrodes; five anodes and four cathodes. Construction was as follows:

#### i) Anodes

Two of the single thickness anodes were used as outside electrodes in the cell stack, and three of the double thickness type were used in the middle of the stack. The electrode screens were of the usual type; 3 Cu 7 3/0 copper.

## ii) Cathodes

Four cathodes, each with four grams of  $\text{CuF}_2$  blend, were made as described in section 3.3. The standard cathod screen, i. e., the 5 Cu 14 2/0 expanded copper was used rather than the fine 3 Cu 7 3/0 material used in cell C-1-7.

## iii) Separator

One thickness of 8 mil Whatman No. 54 filter paper was used as insulation. This material was chosen on the basis of low electrolyte absorption.

## iv) Cell Case

The cell case was vacuum molded using 30 mil polyethylene sheet. The use of 30 mil, as compared with the usual 40 mil material, was an attempt to reduce case weight.

### 6.2.3.1 Testing of Cell C-1-9

This cell was filled with 1 F  $\text{LiClO}_4$  in distilled propylene carbonate using the vacuum filling technique. The cell was discharged at 240 ma ( $2 \text{ ma/cm}^2$ ) using the apparatus previously described.

The performance of cell C-1-9 is shown in Figure 41. An energy density of only 75 watt hours/lb was calculated from the discharge data. This cell had about twice the theoretical  $\text{CuF}_2$  capacity of cell C-1-5 and yet yielded about the same energy density. The major factor in the failure of this cell to yield a higher energy density appears to have been the separator material used, since the other cell components were essentially the same as those used in the previous cells.

### Conclusion

Evaluation of multi-electrode  $\text{Li CuF}_2$  cells has thus far shown a maximum capability of about 80 watt hrs/lb when discharged at a current density of  $2 \text{ ma/cm}^2$ . Attempts to improve performance by a reduction in the percent inactive cell components and an increase in the percent active components were not successful.

The major factor in the failure of cells to produce a greater energy density appears to be the separator materials used. Separator materials with high specific resistance adversely affected performance by increasing IR losses, and possibly by introducing high concentration polarization effects.

The best separator material thus far evaluated in cell construction appears to be the glass fiber filter paper, although there is the disadvantage of high electrolyte absorption for this material. The search for a material with similar

or lower specific resistance but with low electrolyte absorption characteristics, appears to be in order.

### 6.3 Effect of Activated Storage on Performance

It had been previously observed that the lithium/cupric fluoride cells had very poor ability to survive a prolonged activated stand. It was observed that copper was galvanically deposited on the lithium electrodes and this resulted in the formation of copper dendrites and nodules which were able to penetrate the separator and short circuit the cell. Cells containing two layers of asbestos paper as the separator were capable of activated storage for only two days before deterioration commenced. Since the copper fluoride is slightly soluble in the electrolyte this will always be a problem with the present system, unless some method can be found either to prevent the copper ions diffusing across the cell, or to prevent them depositing on the lithium electrode. The first of these possibilities is being studied as a part of the separator investigation wherein agents are added to the separator to prevent copper ions from diffusing through. The second alternative of preventing copper deposition on the lithium may be achievable by complexing the copper ions so that they can be reduced only at extremely negative potentials. It was decided therefore to determine the effect of the addition of complexing agents to the electrolyte.

#### 6.3.1 Effect of Complexing Agents on Performance

A search of the literature was made to find a selection of complexing agents which give complexes of high stability constants with cupric ion. Since complex stability constants have not been evaluated in non-aqueous solutions, the aqueous values were used as the criterion of choice. The following complexing agents were chosen for investigation:

Compound	Log. Stability Constant with $\text{Cu}^{++}$ (aqueous)
$\text{Na}_4$ E. D. T. A	18.8
8-hydroxy quinoline	12.2
8-hydroxy quinoline · 5 sulphonic acid	11.9
1.2 diaminopropane	10.65
Ethylene diamine	10.7
Diethylene triamine	16.0

The complexes were used as a 1% solution in the electrolyte with the exception of  $\text{Na}_4$  E. D. T. A which was found to be insoluble. A 1% solution of  $\text{Na}_4$  E. D. T. A (in water) was prepared and this was used to impregnate the separator, which was then vacuum dried at 60°C for 16 hours. The cells were identically constructed from two pressed foil lithium anodes and two hot pressed cupric fluoride

cathodes. The cathodes were prepared from a mixture of 85%  $\text{CuF}_2$  (-170 mesh) 10% micronized graphite (SW 1651) and 5% polyethylene powder (-100 mesh) pressed for 3 minutes at  $90^\circ\text{C}$  under a pressure of  $500 \text{ lbs/cm}^2$ . Two thicknesses of glass fiber paper (Hurlbut No. 934 AH) were wrapped around the cathode as the separator. The cells were primed with the electrolyte containing the complexing agent and allowed to stand in an argon atmosphere for various periods of time. One cell was assembled and discharged immediately at  $2 \text{ ma/cm}^2$  to determine the effect of the complexing agent in the absence of any storage period. The results for the cells discharged immediately after assembly are shown in Table 11.

An average cell without complexing agents in the electrolyte would operate for approximately 9 hours. It can thus be seen that all of the cells were affected adversely by the complexing agents with the exception of that containing  $\text{Na}_4 \text{ E.D.T.A.}$  Generally the cupric fluoride electrode was most affected, but in the cell containing ethylene diamine, the performance of both electrodes was reduced. Post mortem examination of the cells was conducted and the separators and lithium electrode were examined microscopically to reveal if any copper dendrites had been formed. In no case was metallic copper observed in the separator or on the anode.

Identical cells to those described above were then placed on storage in argon filled desiccators at room temperature and left for 7 days. They were then discharged as above at  $2 \text{ ma/cm}^2$ . The results are shown in Table 12. It can be seen that the performance was severely reduced by the activated stand with the exception of the cells containing diethylene triamine and ethylene diamine, which behaved about the same as the unstored counterparts. The cells were examined after discharge with the following observations.

i) Cell with Electrolyte Containing 1% 8-OH-Quinoline

Lithium Electrodes: The electrodes were spotted with black and copper colored patches. Examination under a stereoscopic microscope indicated that the black patches were finely divided copper, while the red spots were copper dendrites.

Cupric Fluoride Electrodes: These were soft and of a dull red color indicating reduction to copper.

Separator: The separator was covered with black and red spots which were very numerous on the lithium side and less numerous on the cupric fluoride side.

ii) Cell with Separator Containing 1%  $\text{Na}_4 \text{ E.D.T.A.}$

Lithium Electrodes: These had dark patches and also copper colored spots on the side adjacent to the cupric fluoride electrode.

Cupric Fluoride Electrode: The electrode was hard and had red colored patches

on the surface. The extent of electrode reduction seemed far greater than could be accounted for by the amount of electricity consumed.

Separator: The separator was covered with black patches and red spots on the lithium side and a few red spots on the cupric fluoride side. Microscopic investigation revealed that the copper nodules had penetrated through the separator.

iii) Cell with Electrolyte Containing 1% Diethylene Triamine

Lithium Electrodes: These were clean and shiny on both sides.

Cupric Fluoride Electrodes: The electrodes appeared to be only partially reduced to copper.

Separator: Slightly discolored on the lithium side but no evidence of copper dendrites.

iv) Cell with Electrolyte Containing 1% Ethylene Diamine

Lithium Electrodes: These were clean and free from dark spots.

Cupric Fluoride Electrodes: The electrodes were soft and black indicating little reduction to copper.

Separator: The separator was slightly discolored on the lithium side but there was no evidence of copper dendrites.

v) Cell with Electrolyte Containing 1% 1:2 Propanediamine

Lithium Electrodes: The electrodes were covered with patches of copper on the sides facing the  $\text{CuF}_2$  electrodes.

Cupric Fluoride Electrodes: These were soft and had dull red patches indicating extensive reduction.

Separator: The separator was stained with orange/red patches on the lithium side and spots of copper were seen to be growing through to the cathode.

From these observations it appears that 8-OH-quinoline,  $\text{Na}_4$  E. D. T. A and 1:2 propanediamine were ineffectual in controlling the deposition of copper on the anode. Diethylene triamine and ethylene diamine both prevented the deposition of copper but their use resulted in a drop in the cathode performance. For this reason it was decided to investigate the effect of the concentration of the two effective complexones on the cell performance.

### 6.3.2 Effect of Complexone Concentration on Performance

A number of lithium/cupric fluoride cells were assembled identically to those described in section 6.3.1. Two cells each were activated with 1 F  $\text{LiClO}_4$  in propylene carbonate containing 1%, 0.5%, 0.1% of the complexing agent. The cells were then stored as before for 7 days and then discharged at  $2 \text{ ma/cm}^2$ . The results are shown in Tables 13 and 14. Post mortem examination of the cells showed that those primed with electrolyte containing 1% of the complexing agent were free from dendrite formation and the electrodes and separators were in good condition. It must be concluded in this case that the reason for the premature failure was the influence of the ethylene diamine and diethylene triamine on the cathode. The cells in which 0.5% of the complexing agent was added to the electrolyte showed slight evidence of dendrite formation, there being a few nodules of copper growing through the separator. The improved performance of these cells is attributed to the dual effect of the prevention of copper deposition and the lesser effect of the complex on the cathode performance.

The cells where 0.1% of the complexing agent was used were very poor because of the increased incidence of dendrite growth. Post mortem examination revealed extensive short circuiting as evidenced by the severe reduction of the cathode.

The results to date show that dendrite formation can be prevented by the use of suitable complexing agents. However, all the complexes tested to date, severely affected the cathode performance resulting in poor discharge capability even in the absence of storage.

LIST OF MATERIALS AND SUPPLIERS

Ethyl Acetate	Fisher Certified	Fisher Scientific Co.		
Ethanolamine	Purified	"	"	"
2-Chloroethanol	Highest Purity	"	"	"
Maleic Anhydride	Fisher Certified	"	"	"
2-4-Pentanedione	Fisher Reagent	"	"	"
2-Pentanone	Practical	"	"	"
Cyclohexanone	Highest Purity	"	"	"
0-Nitrotoluene	"	"	"	"
M-Nitrotoluene	"	"	"	"
Ethyl Nitrate	"	"	"	"
Malononitrile	Practical	"	"	"
Lactonitrile	"	"	"	"
N-Ethyl Morpholine	"	"	"	"
Ammonium Thiocyanate	Reagent	"	"	"
Potassium Perchlorate	Fisher Certified	"	"	"
Magnesium Perchlorate	Fisher Reagent	"	"	"
Na <sub>4</sub> E. D. T. A.	Technical	"	"	"
8-Hydroxyquinoline	Fisher Certified	"	"	"
8-Hydroxyquinoline-5 quinoline Sulfonic Acid	Highest Purity	"	"	"
Ethylene Diamine	Fisher Certified	"	"	"
Diethylenetriamine	Technical	"	"	"

LIST OF MATERIALS AND SUPPLIERS (cont'd)

Crotononitrile	Practical	City Chemical Corp.
1-2-Diaminopropane		" " "
Sulfolane		K & K Laboratories
Bismuth Perchlorate		" "
Mercuric Perchlorate		" "
Lead Perchlorate		" "
Ferric Perchlorate		" "
Silver Perchlorate		" "
Potassium Thiocyanate	Reagent	Mallinckrodt
Potassium Hexafluorophosphate		Ozark-Mahoning Co.

## REFERENCES

1. Boden D. P., Buhner H. R., Spera V. J. - First Quarterly Report  
Contract No. DA-28-043-AMC-01394(E)
2. Boden D. P., Buhner H. R., Spera V. J. - Second Quarterly Report  
Contract No. DA-28-043-AMC-01394(E)
3. R. G. Bates, Determination of pH, Theory and Practice  
John Wiley and Sons Inc., N. Y. 1964
4. G. Eisenman, D. O. Rudin, J. U. Casby Science Vol 126, Oct. 1957
5. J. E. Leonard, Glass Electrodes for the Direct Measurement of  
Sodium Ion Activity in Aqueous Solutions, Beckman Reprint R-6148
6. G. A. Rechnitz and J. Brauner, Talanta 11, 617-620, 1964
7. G. A. Rechnitz and S. B. Zamochnick, Talanta 11, 1061-1065, 1964
8. L. Lykken, ASTM Special Technical Publication 73, 71-79, 1947
9. G. A. Rechnitz and S. B. Zamochnick, The Response of Cation  
Sensitive Glass Electrodes to Alkali Metal Ions in Partially Aqueated  
Media Beckman Reprint R-6224
10. J. F. Coetsee and G. R. Padmanabhan J. Phs. Chem 66, 1708, (1962)
11. M. Tézé and R. Schaal Bull. Soc. Chim. France 1372 (1962)
12. H. P. Gregor, J. Am. Chem. Soc. 70, 1293, (1948)
13. B. P. Nicol'sky, Zh. Fiz Khim 27, 724, (1953)

TABLE 1

Non-Aqueous Solvents

Solvent	Dielectric constant	Viscosity (cp)	D/η	Density g/cc	M. Pt °C	B. Pt °C
Ethyl acetate	6.4	0.409	15.65	0.900	-83.6	77.15
Ethanolamine	37.72	1.022	36.91	19.36	10.5	172.2
Glycolonitrile	69.00	--	--	--	-72.0	183.0
2-chloroethanol	25.8	--	--	--	-67.5	128.0
Maleic anhydride	50.0	--	--	--	56.0	198.0
2,4 pentanedione	25.7	--	--	0.9721	-23.0	139.0
2 pentanone	22.0	0.47	46.808	0.8124	-77.8	102.0
Cyclohexanone	18.0	2.80	6.43	0.9978	-16.4	155.65
o-nitrotoluene	27.4	2.37	11.56	1.1629	- 2.9	220.40
m-nitrotoluene	23.0	2.33	9.87	1.1571	15.0	232.60
Ethyl nitrate	19.7	--	--	1.105	-102.0	87.00
Malononitrile	47.2	--	--	--	-70.0	108.00
Lactonitrile	38.0	2.19	17.35	0.9877	-40.0	183.00
Crotonic nitrile	36.0	--	--	0.8318	-84	119.00
Sulfolane	44	--	--	--	28.37	285.00
N-ethyl morpholine	--	0.9166	--	--	--	138.00

**TABLE 2****Response of Glass Electrodes to Lithium Ion in Propylene Carbonate**Cell: Glass Electrode/C Li Cl O<sub>4</sub> - PC//0.01 F Li Cl O<sub>4</sub> - PC/Ag Cl, Ag

Concentration of Li Cl O <sub>4</sub> (Formal)	log <sub>10</sub> C <sub>Li<sup>+</sup></sub>	Cell Potential (Volts) Beckman General Purpose Electrode
0.01	-2.0000	0.264
0.042	-1.3768	0.336
0.0719	-1.1433	0.359
0.100	-1.0000	0.370
0.1263	-0.8986	0.378
0.1513	-0.8202	0.385
0.1755	-0.7558	0.392
0.2203	-0.6570	0.400
0.2578	-0.5887	0.406
0.3405	-0.4679	0.419
0.406	-0.3915	0.426
0.514	-0.2890	0.437

**TABLE 3****Response of Glass Electrode to Lithium Ion in Propylene Carbonate**Cell: Glass Electrode/ $\text{C LiClO}_4 - \text{PC} // 0.01 \text{ F LiClO}_4 - \text{PC} / \text{Ag Cl, Ag}$ 

<b>Concentration of <math>\text{LiClO}_4</math> (Formal)</b>	<b><math>\log_{10} C_{\text{Li}^+}</math></b>	<b>Potential (Volts)</b>	<b>Liquid junction Potential (Volts)</b>	<b>True Potential (Volts)</b>
0.01	-2.0000	0.264	0.00	0.264
0.042	-1.3768	0.336	0.0092	0.327
0.0719	-1.1433	0.359	0.0135	0.346
0.100	-1.0000	0.370	0.0166	0.353
0.1263	-0.8986	0.378	0.0185	0.360
0.1513	-0.8202	0.385	0.0199	0.365
0.1755	-0.7558	0.392	0.0210	0.371
0.2203	-0.6570	0.400	0.0225	0.377
0.2578	-0.5887	0.406	0.0235	0.382
0.3405	-0.4679	0.419	0.0251	0.394
0.406	-0.3915	0.426	0.0265	0.400
0.514	-0.2890	0.437	0.0287	0.408

TABLE 4

Response of Glass Electrode to  $C_{Li^+}$  in KCNS Solution in Propylene Carbonate

Cell: Glass Electrode/C Li Cl O<sub>4</sub> - PC//0.01 F Li Cl O<sub>4</sub> - PC/Ag Cl, Ag

Concentration of KCNS = 0.75 F

Concentration of Li Cl O <sub>4</sub> (mole/ltr)	$\log_{10} C_{Li^+}$	Potential (Volts)		
		General Purpose	Modified G. P	Cation Specific
0.00745	-2.1278	0.449	0.287	0.597
0.0228	-1.6421	0.449	0.288	0.600
0.0358	-1.4461	0.449	0.289	0.596
0.0491	-1.3089	0.448	0.290	0.590
0.0684	-1.1649	0.448	0.291	0.593
0.0980	-1.0089	0.447	0.291	0.588
0.1251	-0.9028	0.446	0.298	0.590
0.1734	-0.7610	0.448	0.301	0.591
0.2145	-0.6686	0.451	0.309	0.603
0.2505	-0.6021	0.456	0.321	0.607
0.3075	-0.5107	0.469	0.343	0.632
0.3670	-0.4353	0.483	0.365	0.668

**TABLE 5****Response of Glass Electrodes to  $C_{Li^+}$  in  $NH_4Cl$  Solution in DMSO**Cell: Glass Electrode/ $LiClO_4$  - PC//0.01 F  $LiClO_4$  - PC/AgCl, AgConcentration of  $NH_4Cl = 0.750 F$ 

Concentration of $LiClO_4$ (mole/ltr)	$lg_{10} C_{Li^+}$	Potential (Volts)		
		General Purpose	Modified G. P	Cation Specific
0.00745	-2.1278	0.408	0.322	0.489
0.0228	-1.6421	0.410	0.323	0.490
0.0358	-1.44	0.409	0.326	0.492
0.0491	-1.3089	0.411	0.328	0.492
0.0684	-1.1649	0.411	0.328	0.492
0.0980	-1.0088	0.410	0.321	0.497
0.1251	-0.9028	0.410	0.324	0.499
0.1734	-0.7610	0.410	0.329	0.501
0.2145	-0.6686	0.410	0.330	0.506
0.2505	-0.6021	0.412	0.330	0.510
0.3075	-0.5107	0.411	0.331	0.515
0.3670	-0.4335	0.413	0.330	0.519
0.4170	-0.3799	0.416	0.333	0.521

**TABLE 6**

**Response of Glass Electrodes to  $C_{Li^+}$  in the Presence of  $Mg^{++}$**

Cell. Glass Electrode/C Li Cl O<sub>4</sub> - PC // 0.01 F Li Cl O<sub>4</sub> - PC / Ag Cl, Ag

Concentration of Mg (Cl O<sub>4</sub>)<sub>2</sub> = 0.25 F

Concentration of Li Cl O <sub>4</sub> (mole/ltr)	log <sub>10</sub> C <sub>Li<sup>+</sup></sub>	Potential (Volts)		
		General Purpose	Modified G. P	Cation Specific
0.00745	-2.1278	-0.393	-0.394	-0.232
0.0228	-1.6421	-0.380	-0.387	-0.219
0.0358	-1.4461	-0.374	-0.381	-0.208
0.0491	-1.3089	-0.371	-0.378	-0.195
0.0684	-1.1649	-0.364	-0.379	-0.187
0.0980	-1.0088	-0.359	-0.371	-0.175
0.1251	-0.9028	-0.350	-0.368	-0.160
0.1734	-0.7610	-0.343	-0.363	-0.151
0.2145	-0.6686	-0.335	-0.359	-0.142
0.2505	-0.6021	-0.330	-0.358	-0.140
0.3075	-0.5107	-0.330	-0.356	-0.130
0.3670	-0.4353	-0.324	-0.352	-0.124

**TABLE 7****Response of Glass Electrodes to  $C_{Li}^+$  in  $(C_2H_5)_4NClO_4$  Solution**Cell: Glass Electrode/C LiClO<sub>4</sub> - PC//0.01 F LiClO<sub>4</sub> - PC/Ag Cl, AgConcentration of  $(C_2H_5)_4NClO_4 = 0.75F$ 

Concentration of LiClO <sub>4</sub> (mole/ltr)	log <sub>10</sub> C <sub>Li</sub>	Potential (Volts)		
		General Purpose	Modified G. P	Cation Specific
0.0074	-2.1278	0.134	0.029	0.372
0.0228	-1.6421	0.158	0.050	0.398
0.0358	-1.4461	0.170	0.059	0.413
0.0491	-1.3089	0.176	0.069	0.420
0.0604	-1.1649	0.182	0.071	0.422
0.0980	-1.0088	0.192	0.248	0.430
0.1251	-0.9028	0.201	0.250	0.433
0.1734	-0.7610	0.211	0.251	0.440
0.2145	-0.6686	0.220	0.252	0.445
0.2505	-0.6021	0.222	0.256	0.451
0.3075	-0.5107	0.230	0.257	0.457

TABLE 8Separator MaterialsElectrolyte Absorption and Resistivity in 1 F LiClO<sub>4</sub> in  
Distilled Propylene Carbonate

Separator Material	Thickness (inches)		Electrolyte Absorption (percent)	Electrolyte Retention (percent)	Specific Resistance (OHM-cm)
	Dry	Wet			
Pellon - # 34 - 235	0.015	0.015	620	93	207.8
Glass Fiber Filter Paper - Hurlbut # 934 AH	0.015	0.015	710	98	109.9
Johns - Manville High Strength Fibroid Asbestos	0.015	0.015	80	97	556.8
Johns - Manville Asbestos Fuel Cell Paper (0.03 in.)	0.032	0.120	600	99	71.7
Fiber Glass Mat (Hydramatic Packing)	0.030	0.032	1130	97	99.8
CdS # 1021 Ion Exchange Membrane (ESB Company)	0.008	0.013	29	69	Beyond Range of Bridge (> 5500 ohm-cm)
Schleicher & Schuell Filter Paper - # 589 White Ribbon	0.008	0.008	162	88	709.8
Asbestos Filter Paper	0.015	0.019	945	93.5	90.2
Johns - Manville Asbestos Fuel Cell Paper (0.015 in.)	0.015	0.035	448	96	88.2
Diatomaceous Earth Separator - Microporous (ESB Company)	0.012	0.012	137	95	469.9

TABLE 8 Continued

Separator Material	Thickness (inches)		Electrolyte Absorption (percent)	Electrolyte Retention (percent)	Specific Resistance (OHM-cm)
	Dry	Wet			
Lexan Film (General Electric Co.)	0.001	0.002	199	43.3	(>35,000 ohm-cm) Beyond Range of Bridge
Kim-Wipes # 900-S (Kimberly-Clark)	0.005	0.006	735	50	281
Porothene Microporous Polyethylene 70% Porous-Expanded 5:1 (ESB Company)	0.002	0.002	368	27	1611
Non-Woven Mat 100% Polypropylene # H-612 (Kendall Mills)	0.050	0.100	1920	96.5	434
White Scotties Facial Tissue (Scott Paper Co.)	0.0025	0.003	555	54	309
Pellon # FT 2140 100% Polypropylene	0.010	0.010	345	75.5	415
Porothene Microporous Polyethylene 70% Porous-Expanded 5:1 (ESB Company)	0.005	0.005	835	68.5	634
Woven Teflon # T-214-18 (Huguet Fabrics)	0.020	0.020	30	64	633
Whatman # 40 Filter Paper	0.010	0.010	193	86	553
Schleicher & Schuell # 589 Black Ribbon Filter Paper	0.008	0.008	176	80	681
Schleicher & Schuell # 589-1H Filter Paper	0.008	0.008	217	84	324

TABLE 9

Separator	Thick- ness	No. of layers used	Percent efficiency of $\text{CuF}_2$	Observations of $\text{CuF}_2$ cathode at end of discharge	Cell Resis- tance
Asbestos Filter Paper	15 mil	2	84	Dense red on surface and red in black matrix underneath	--
Polypropylene mat 100% Polypropyl No. 34-235 (Pellon Corp.)	15 mil	2	64	Same as above	--
Diatomaceous earth (PVC-PVAc binder) Microporous (ESB Co.)	12 mil	2	17	Dense red on surface and black matrix inside	--
Analytical Filter Paper No. 589 (Schleicher and Schuell Co.)	8 mil	2	49	Red on surface and red in black matrix underneath	4.7 ohms
Glass mat Styrene Bound (Hydramatic Packing)	30 mil	1	68	Dense red on surface and red in black matrix underneath	1.3 ohms
CdS Ion Exchanger No. 1021 (ESB Co.)	12 mil	1	7	Spots of dense red on surface and black matrix underneath	7.2 ohms
Lexan Film (General Electric Co.)	1 mil	1	16	Red on surface and a little red in black matrix inside	4.7 ohms
Asbestos Fuel Cell Paper (Johns-Manville)	15 mil	1	16	Dense red on surface and a little red in blk mat. underneath	8.6 ohms
Polypropylene SM 91 (Webril)	5 mil	1	37	Same as above	--
Glass Fiber Filter Paper No. 934-AH (Hurlbut Paper Co.)	15 mil	2	69	Dense red on surface and very dense red in black matrix under- neath	7.4 ohms

TABLE 9 (cont'd)

Separator	Thick- ness	No. of layers used	Percent efficiency of $\text{CuF}_2$	Observations of $\text{CuF}_2$ cathode at end of discharge	Cell Resis- tance
High strength Fibroid Asbestos (Johns-Manville)	17 mil	1	60	Dense red on surface and red dispersed in black matrix underneath	13.6 ohms
Porous Polyethylene, Porethene, 70% porous, Expanded 5:1, (ESB Co.)	2 mil	1	63	Same as above	3.0 ohms
Kimwipes # 900-S (Kimberly-Clark)	5 mil	3	63	Same as above	4.4 ohms
Polypropylene, non-woven mat, 100% Polypropylene, No. H-612, (Kendall Mills)	50 mil	1	70	Same as above	10.1 ohms
Porous Polyethylene, Porethene, 70% porous, Expanded 5:1, (ESB Co.)	5 mil	1	63	Same as above	2.6 ohms
Polypropylene Mat, (Pellon) No. FT 2140, 100% Polypropylene	10 mil	1	64	Same as above	3.8 ohms

TABLE 10

Weight Analysis of Multi-Electrode Cells

	Cell Number			
	C-1-5	C-2-5	C-1-7	C-1-9
Dry Weight of Cell (grams)	22.72	22.05	27.11	29.95
Dry Weight of Element (grams)	13.16	11.65	17.68	23.58
Weight of Cell Case (grams)	9.56	10.4	9.43	6.37
Wet Weight of Cell (grams)	39.87	37.25	38.6	42.39
Weight of Electrolyte (grams)	17.15	15.2	11.49	12.9
Percent Element Weight of Total Cell Weight (wet)	33	31.3	45.8	55.5
Percent Case Weight of Total Cell Weight (wet)	23.8	28	24.5	15
Percent Electrolyte Weight of Total Cell Weight (wet)	43	40.8	29.8	30.5
Theoretical Capacity (Ampere Hours) Based on $\text{CuF}_2$ Capacity	3.55	3.05	5.23	7.0

**Table II**

**Effect of Complexing Agents on Lithium/Cupric Fluoride Cells**

2/cm<sup>2</sup>  
20°C

0.90 a.h. at 2ma/cm<sup>2</sup> discharge

Quinoline CuF <sub>2</sub> Volts	Na <sub>2</sub> EDTA		Diethylene Triamine		Ethylene diamine		1,2 Propanediamine	
	Cell Volts	Li Volts	Cell Volts	Li Volts	Cell Volts	Li Volts	Cell Volts	Li Volts
-0.15	3.45	-3.60	3.42	-3.50	3.40	-3.62	3.55	-3.65
-0.28	3.20	-3.50	2.97	-3.48	2.40	-3.45	3.20	-3.50
-0.56	3.05	-3.50	2.60	-3.40	2.30	-3.45	3.30	-3.55
-1.00	2.85	-3.40	2.35	-3.40	2.00	-3.25	3.30	-3.55
-0.295	2.80	-3.40	2.15	-3.40	1.73	-3.10	3.25	-3.55
-1.04	2.80	-3.40	1.89	-3.40	1.45	-2.95	3.20	-3.55
-1.11	2.80	-3.475	1.69	-3.40	0.85	-2.70	2.95	-3.60
-1.25	2.80	-3.485	1.19	-3.40	0.55	-2.40	2.34	-3.55
-1.45	2.80	-3.61	0.73	-3.40	0.00	-2.10	0.00	-3.45
-1.95	2.70	-3.56	0.0	-3.40				
-3.00	2.65	-3.55						
	2.65	-3.61						
	2.55	-3.60						
	2.30	-3.66						
	1.70	-3.38						
	0.0	-3.00						



TABLE 13

Effect of Concentration of Diethylene Triamine on Performance After  
7 Days Activated Stand

Discharge at 2 ma/cm<sup>2</sup>

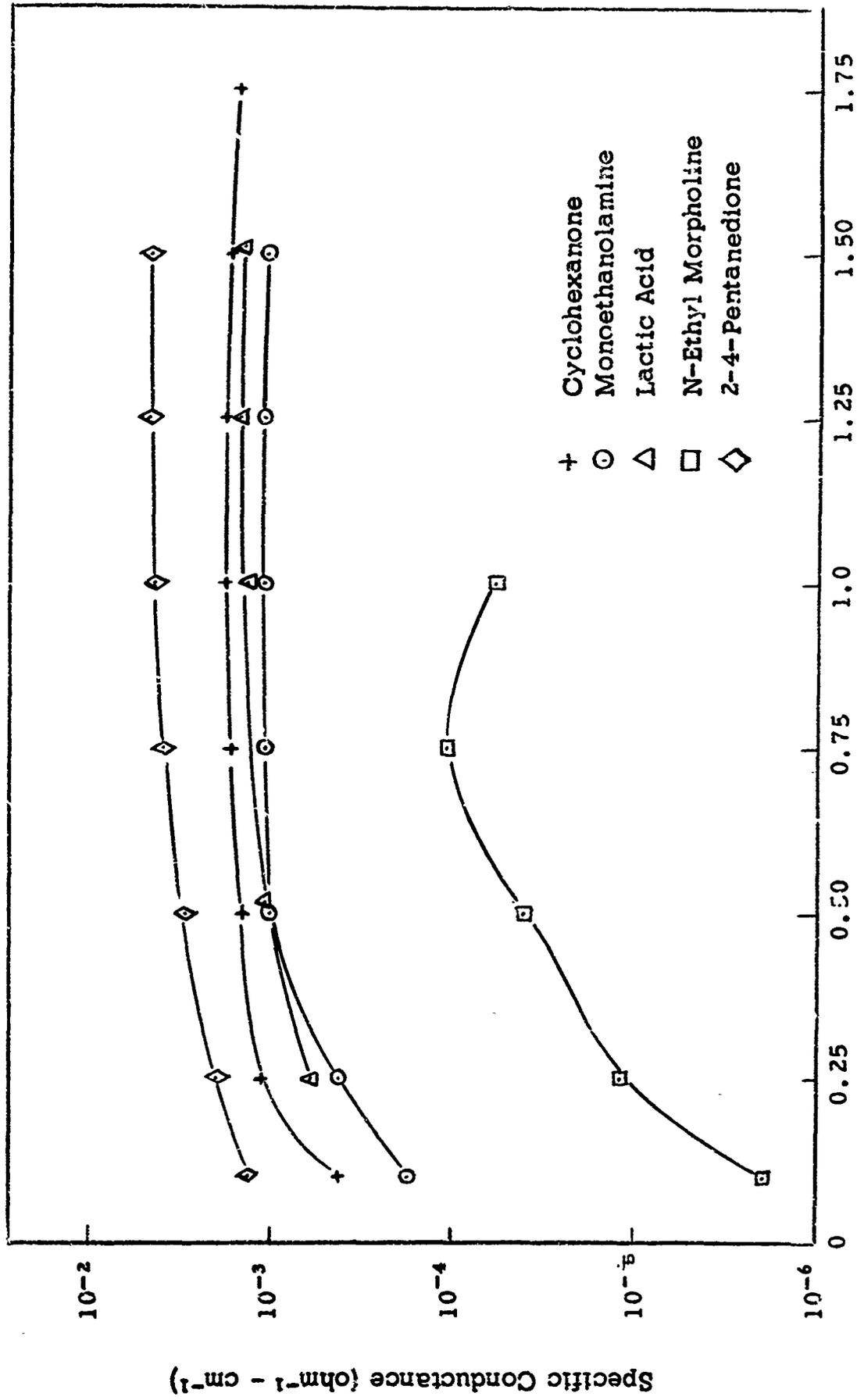
Temperature = 25°C

Nominal Capacity = 0.85 a.h. ≈ 8 1/2 hours at 2 ma/cm<sup>2</sup> discharge

Time	1% Diethylene Triamine			0.5% Diethylene Triamine			0.1% Diethylene Triamine		
	Cell Volts	CuF <sub>2</sub> Volts	Li Volts	Cell Volts	CuF <sub>2</sub> Volts	Li Volts	Cell Volts	CuF <sub>2</sub> Volts	Li Volts
O.C	2.96	-0.54	-3.50	2.95	-0.625	-3.60	2.81	-0.75	-3.60
5m	2.00	-1.35	-3.45	1.55	-1.95	-3.50	1.075	-1.91	-3.21
15m	2.00	-1.35	-3.425	1.425	-2.075	-3.50	0.950	-1.975	-3.00
30m	2.00	-1.41	-3.41	1.68	-1.82	-3.50	0.125	-2.76	-2.88
1 hr	1.96	-1.36	-3.39	1.85	-1.75	-3.60			
1 1/2 hr	1.75	-1.64	-3.39	1.90	-1.70	-3.60			
2 "	1.66	-1.69	-3.39	2.05	-1.55	-3.60			
2 1/2 "	1.51	-1.88	-3.39	1.98	-1.62	-3.60			
3 "	1.04	-2.36	-3.40	1.75	-1.85	-3.60			
3 1/2 "	0.32	-3.09	-3.41	1.55	-2.05	-3.60			
4 "				1.36	-2.24	-3.60			
4 1/2 "				1.20	-2.40	-3.60			
5 "				0.99	-2.61	-3.60			
5 1/2 "				0.79	-2.81	-3.60			
6 "				0.30	-3.30	-3.60			



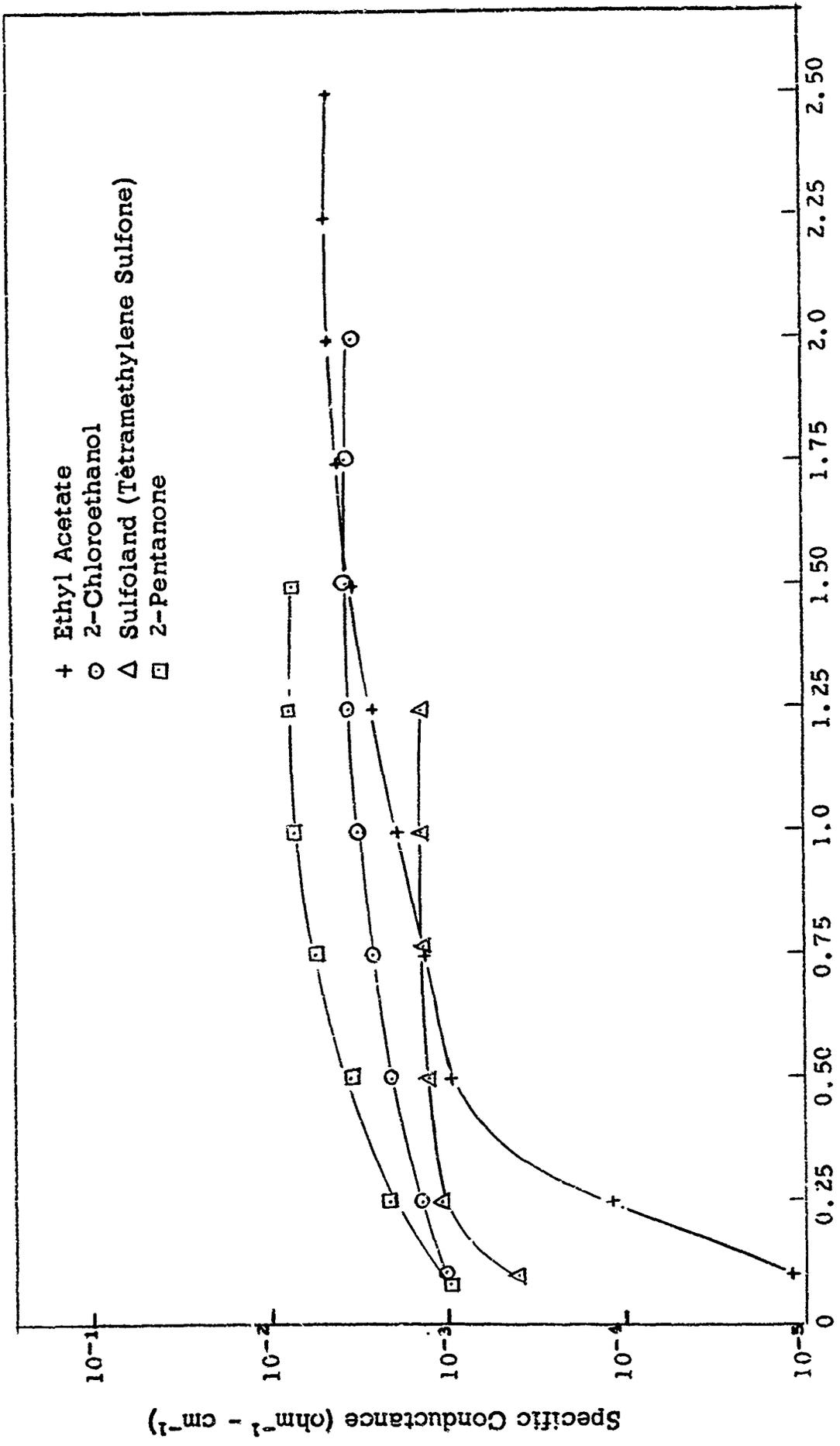
Specific Conductance of  $\text{LiClO}_4$  in Organic Solvents



Concentration (Formal)

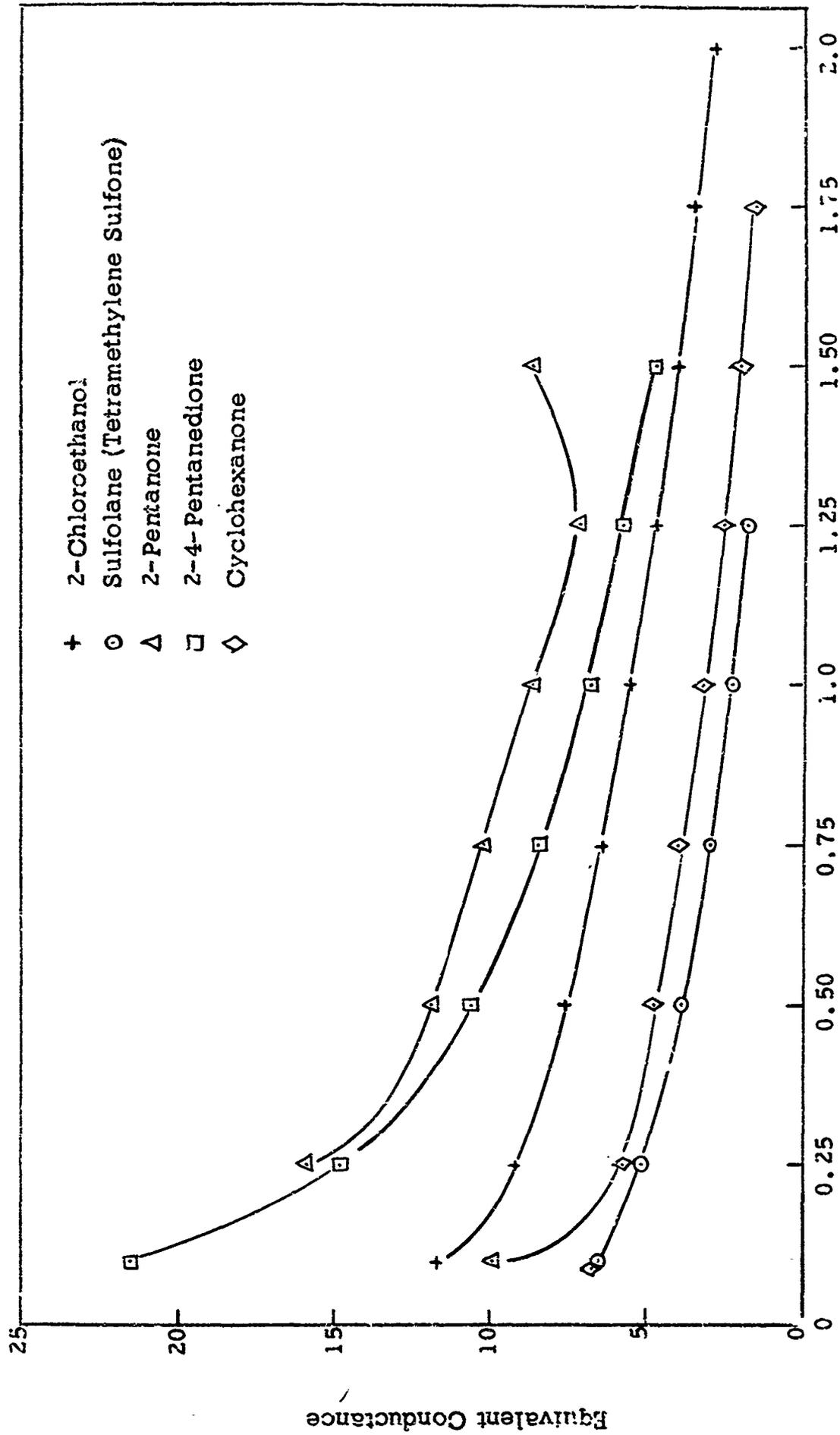
Figure 1

Specific Conductance of  $\text{LiClO}_4$  in Organic Solvents



Concentration (Formal)  
Figure 2

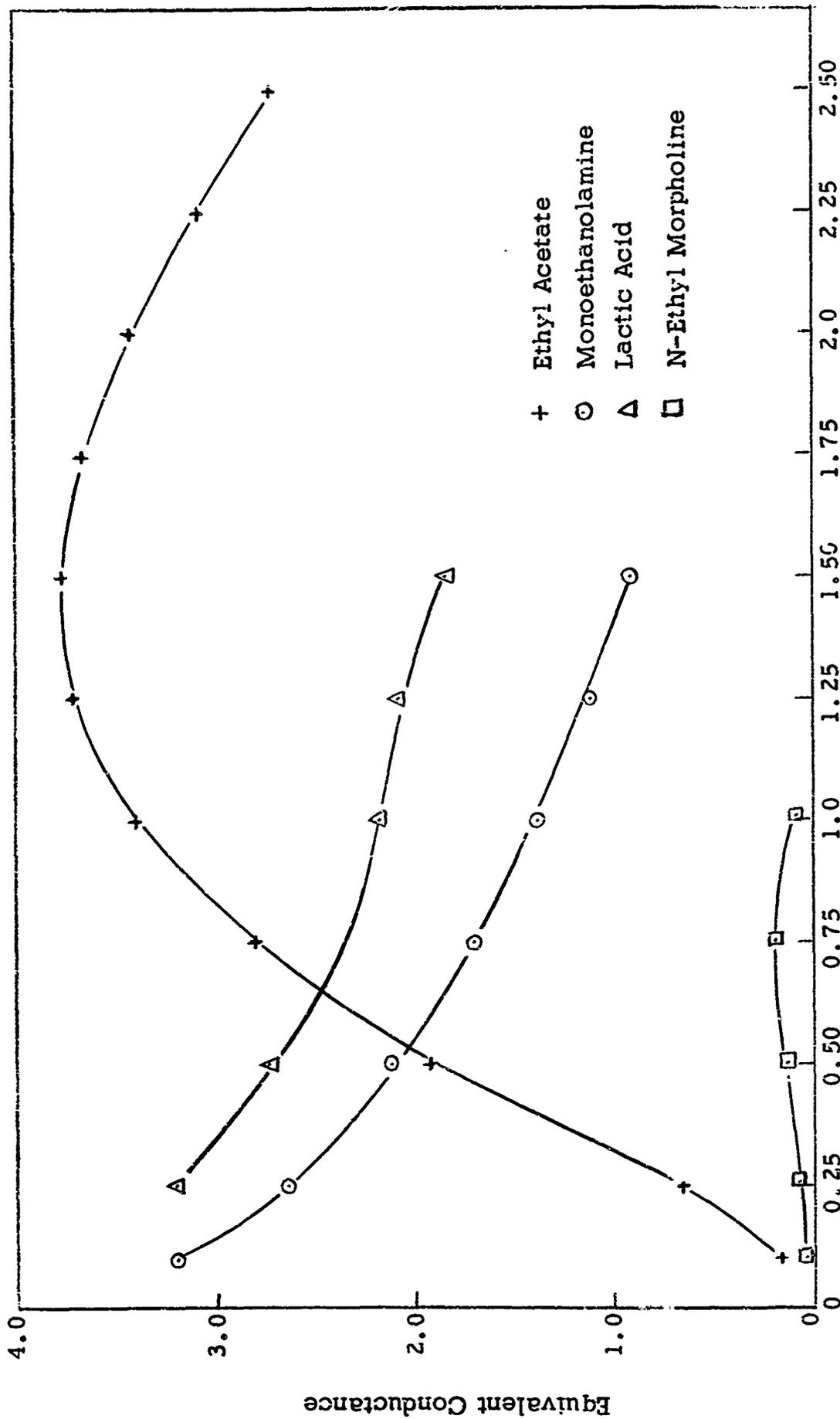
# Equivalent Conductance of $\text{LiClO}_4$ in Organic Solvents



Concentration (Formal)

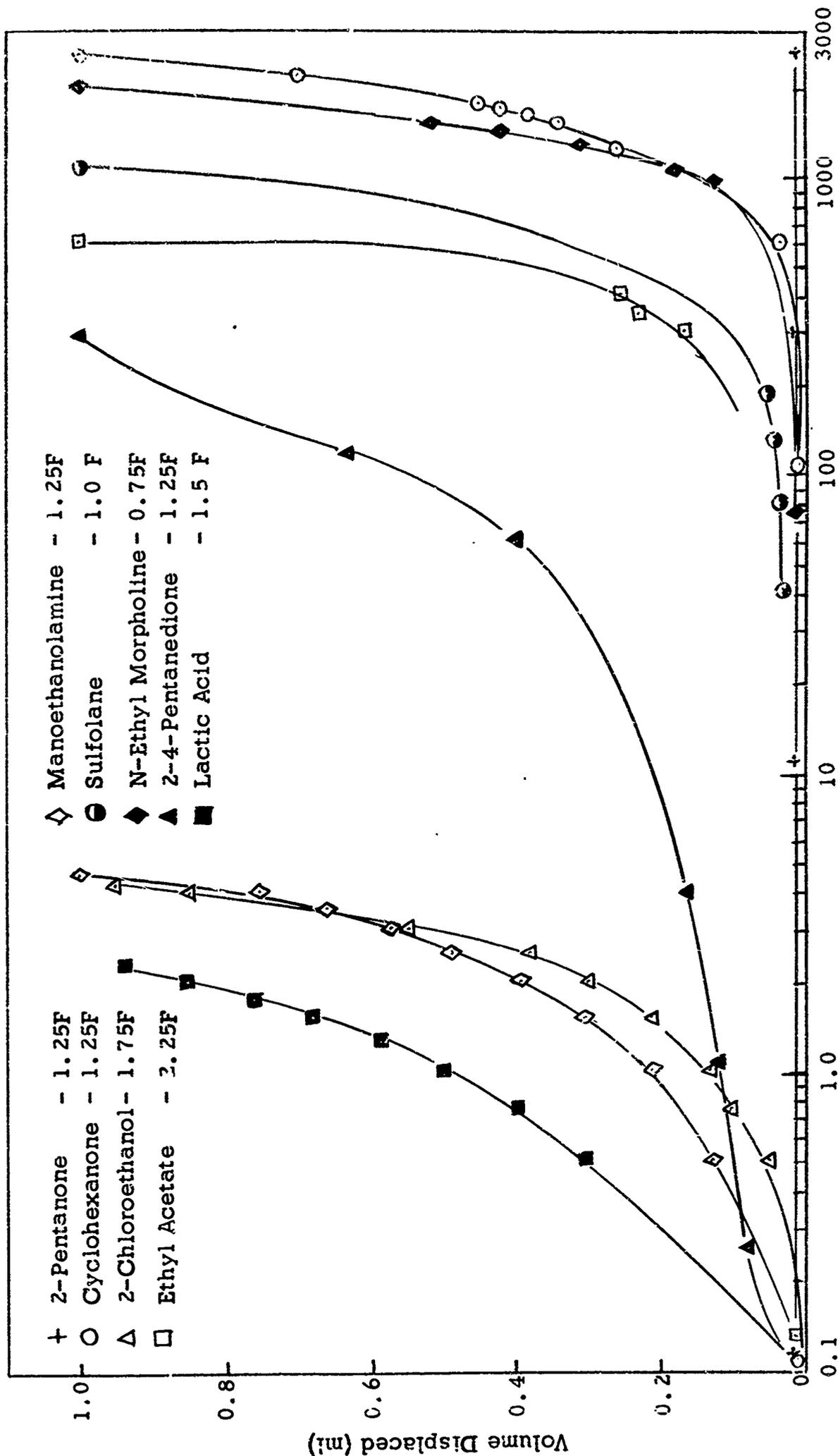
Figure 3

# Equivalent Conductance of $\text{LiClO}_4$ in Organic Solvents



Concentration (Formal)  
Figure 4

Rate of Corrosion of Lithium in Electrolytes  
Solutions of  $\text{LiClO}_4$  in Organic Solvents



Time (minutes)

Figure 5

Performance of Cupric Fluoride Electrodes in Various Electrolytes

- 1.25M LiClO<sub>4</sub> in 2,4 Pentanedione
- × 1 M LiClO<sub>4</sub> in Cyclohexanone
- ρ 1.25M LiClO<sub>4</sub> in 2-Pentanone

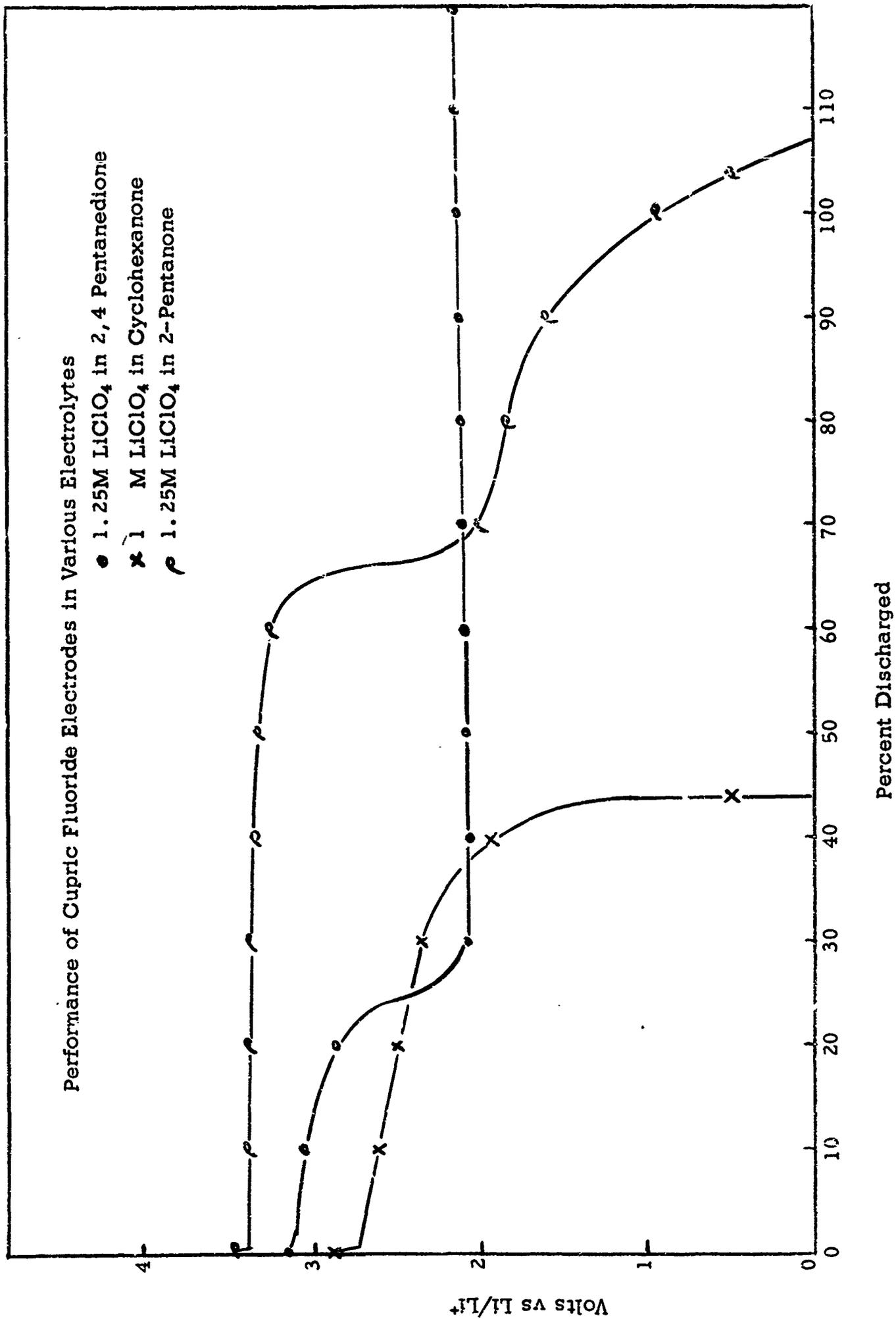
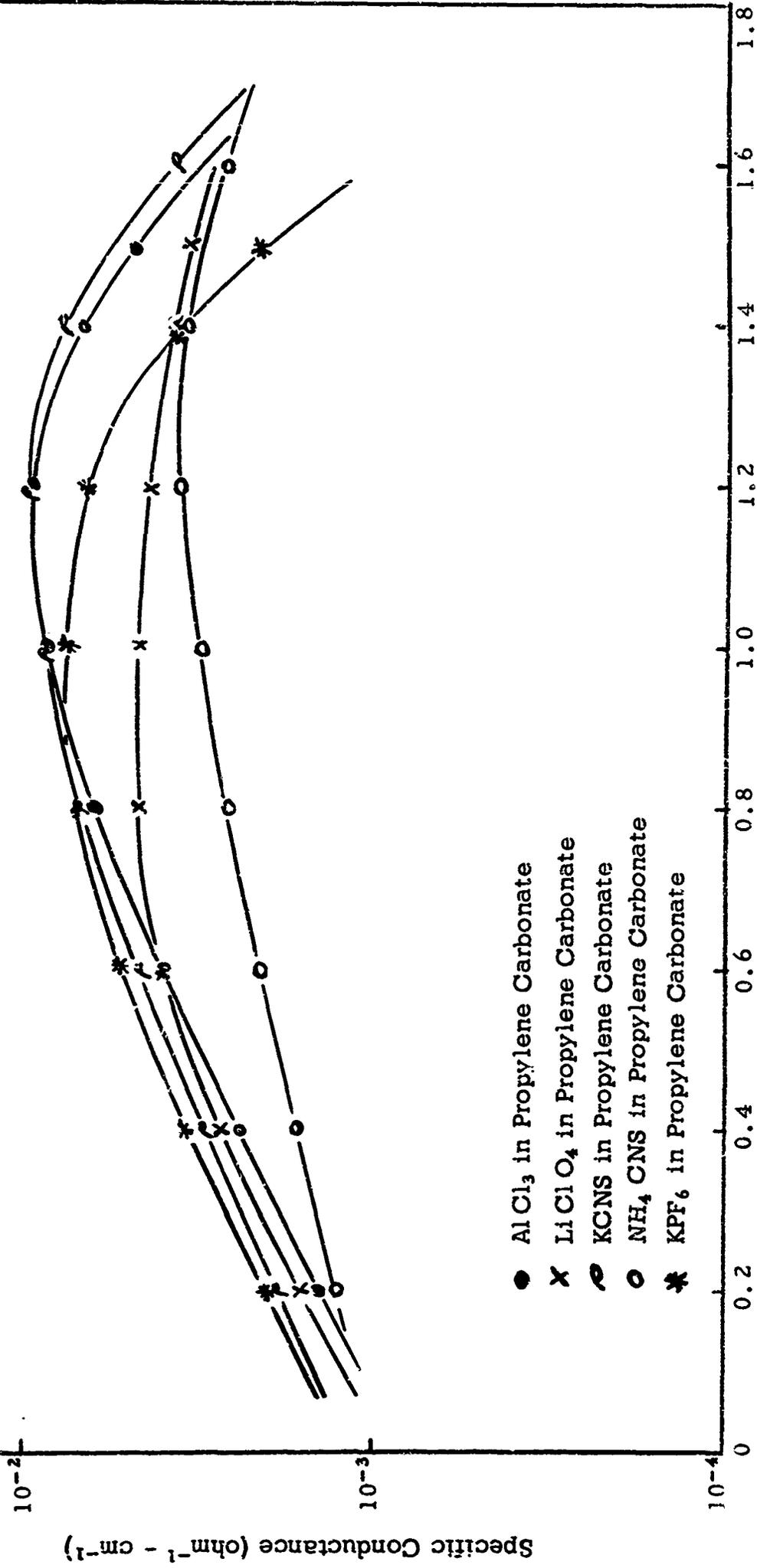


Figure 6

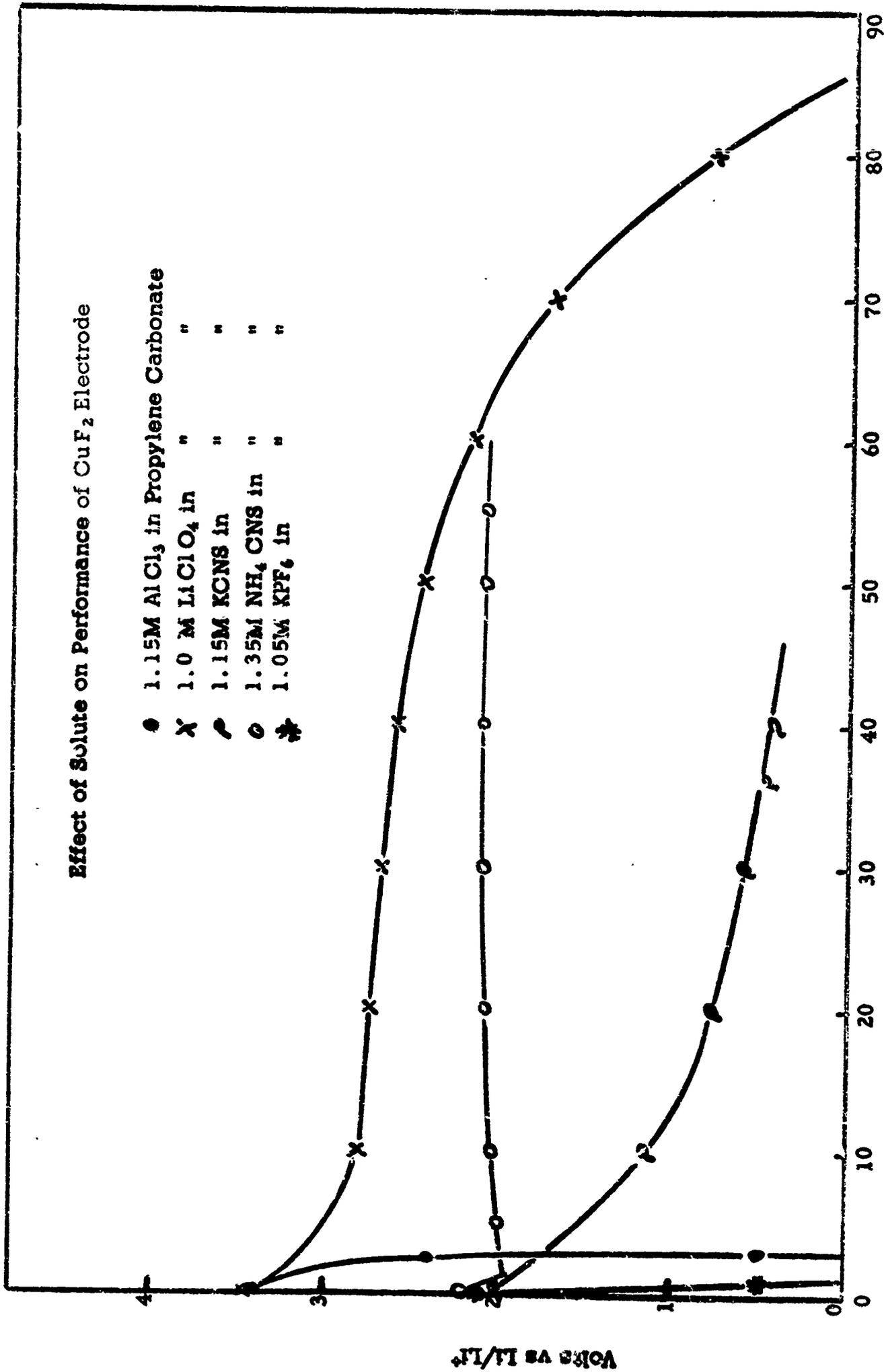
Specific Conductance of Non-Aqueous Electrolytes



Concentration (Formal)  
Figure 7

**Effect of Solute on Performance of  $\text{Cu F}_2$  Electrode**

- 1.15M  $\text{AlCl}_3$  in Propylene Carbonate
- X 1.0 M  $\text{LiClO}_4$  in " "
- ◐ 1.15M  $\text{KCNS}$  in " "
- 1.35M  $\text{NH}_4 \text{ CNS}$  in " "
- ✱ 1.05M  $\text{KPF}_6$  in " "



**Percent Discharged**

**Figure 8**

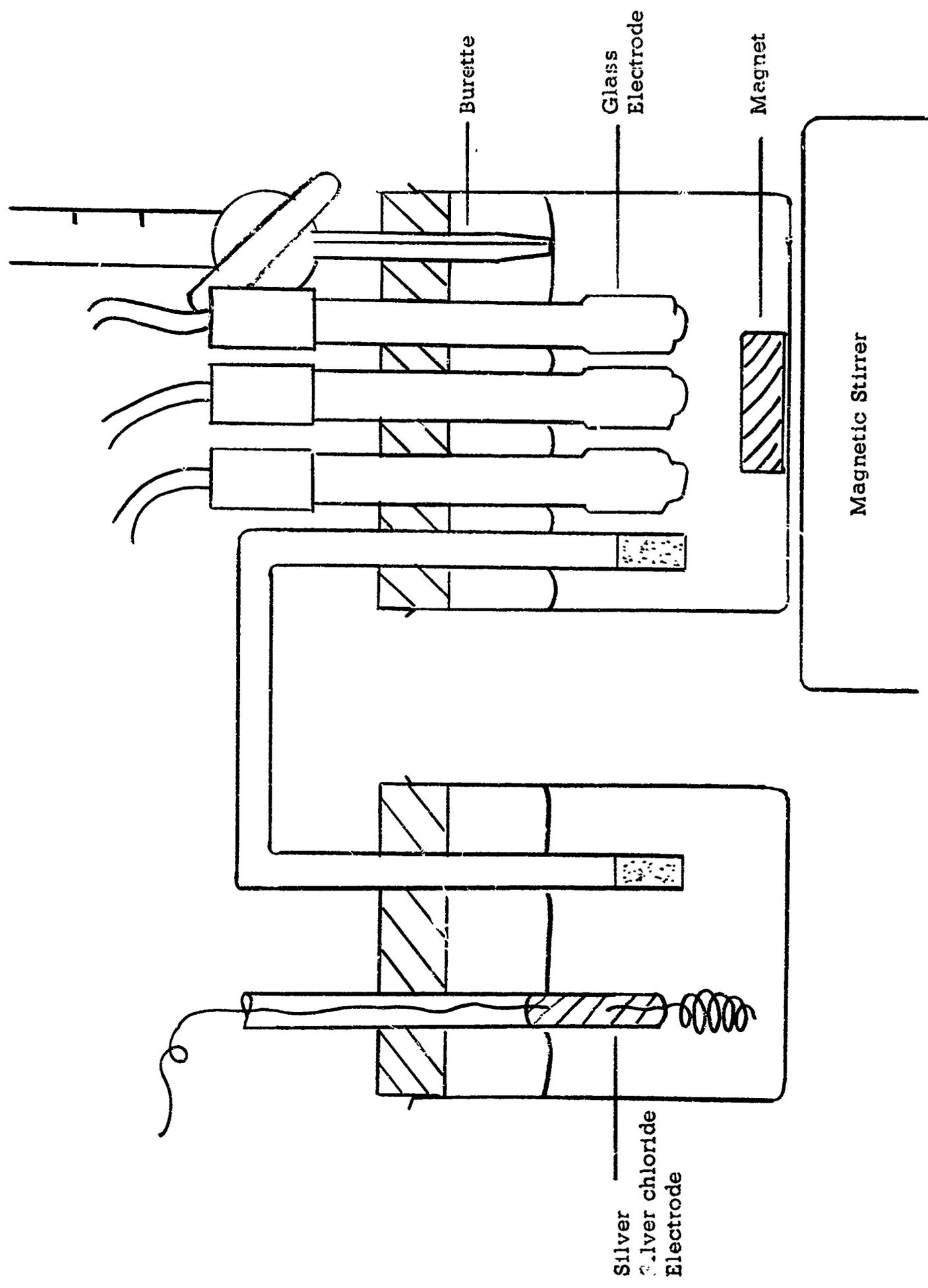
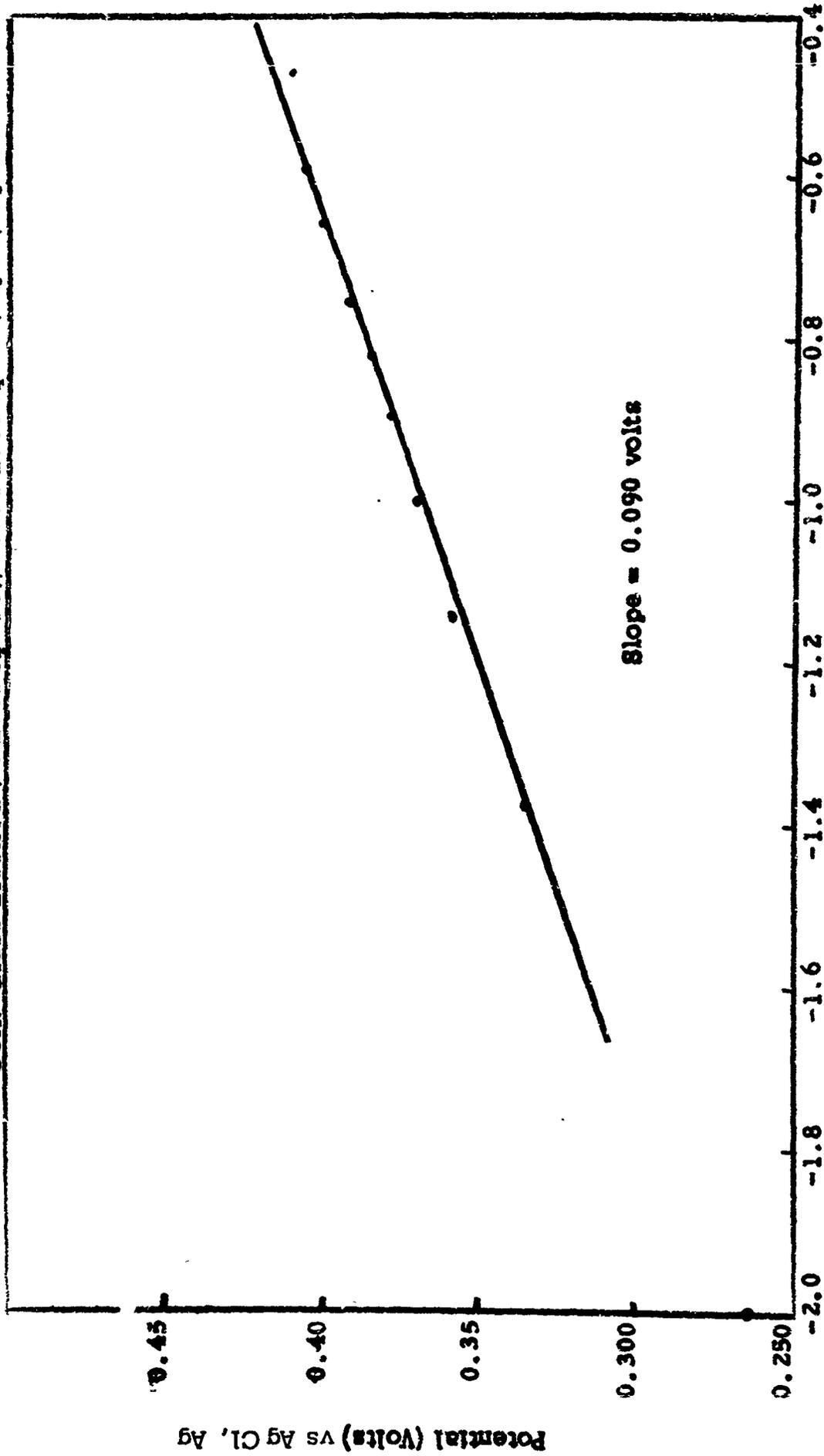


Figure 9

**Response of Beckman General Purpose Electrode to  $C_{Li^+}$   
Without Correction for the Liquid Junction Potential**

Cell: Glass Electrode/ $ClLiClO_4 - PC // 0.01 F LiClO_4 - PC / Ag Cl, Ag$



$\log C_{Li^+}$

Figure 10

**Response of General Purpose Electrode to  $C_{Li^+}$  in Propylene Carbonate**  
With Correction for the Liquid Junction Potential

Cell: Glass Electrode/ $CaLiClO_4$  - PC//0.01 F  $LiClO_4$  - PC/AgCl, Ag

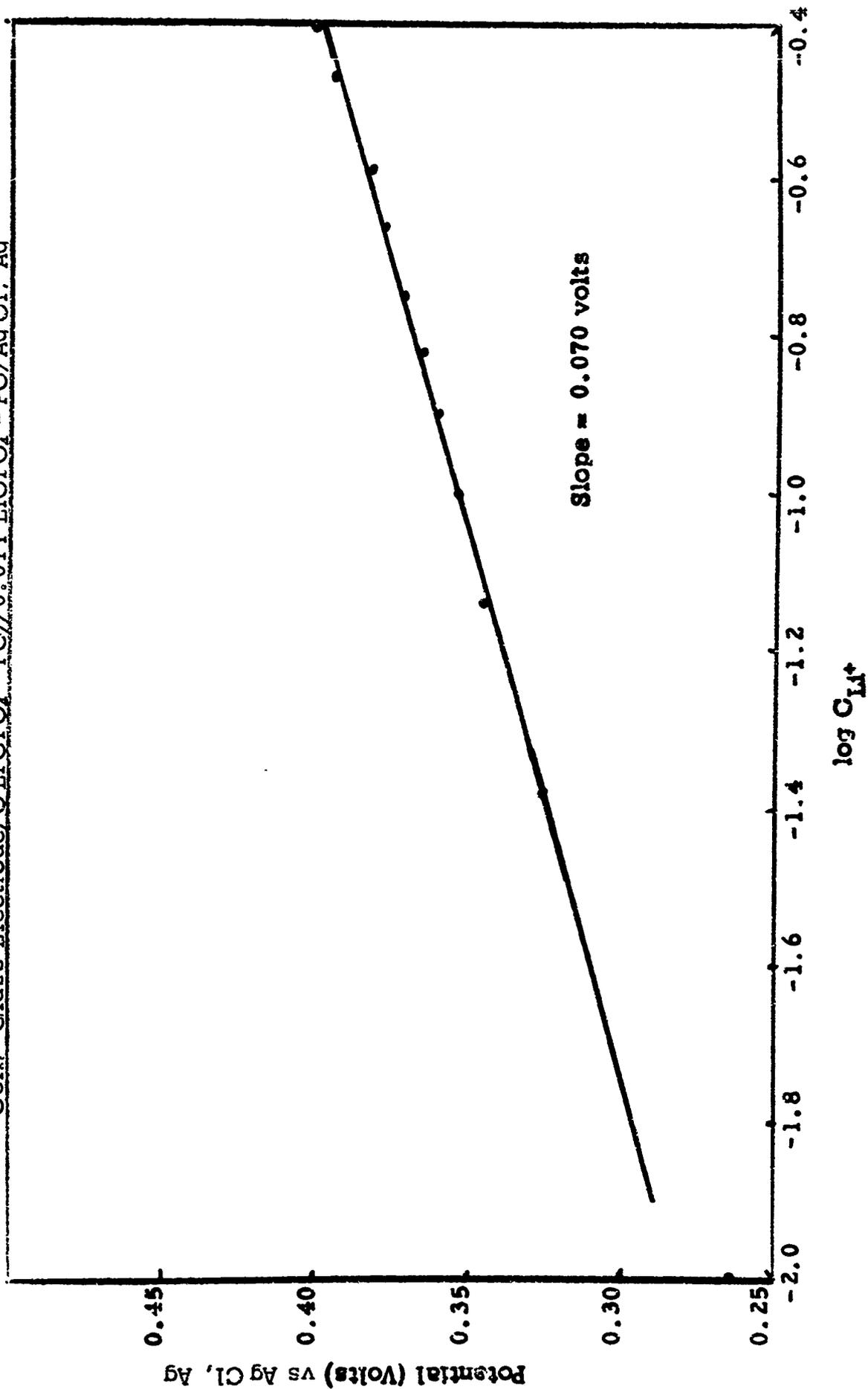


Figure 11

Response of Glass Electrodes to  $C_{Li^+}$  in KCNS Solution

Cell: Glass Electrode/ $LiClO_4 - PC // 0.01 F LiClO_4 - PC / AgCl, Ag$

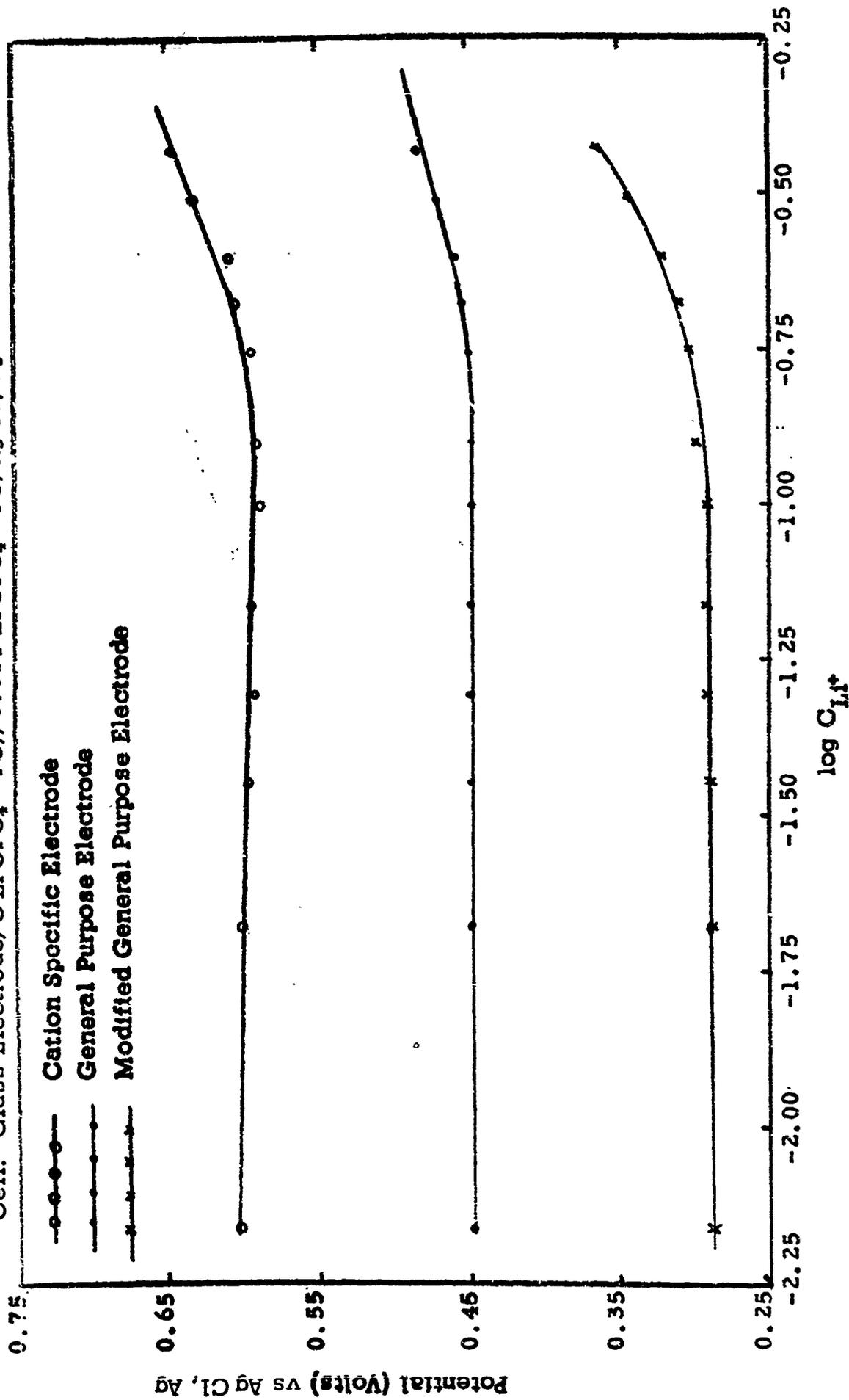
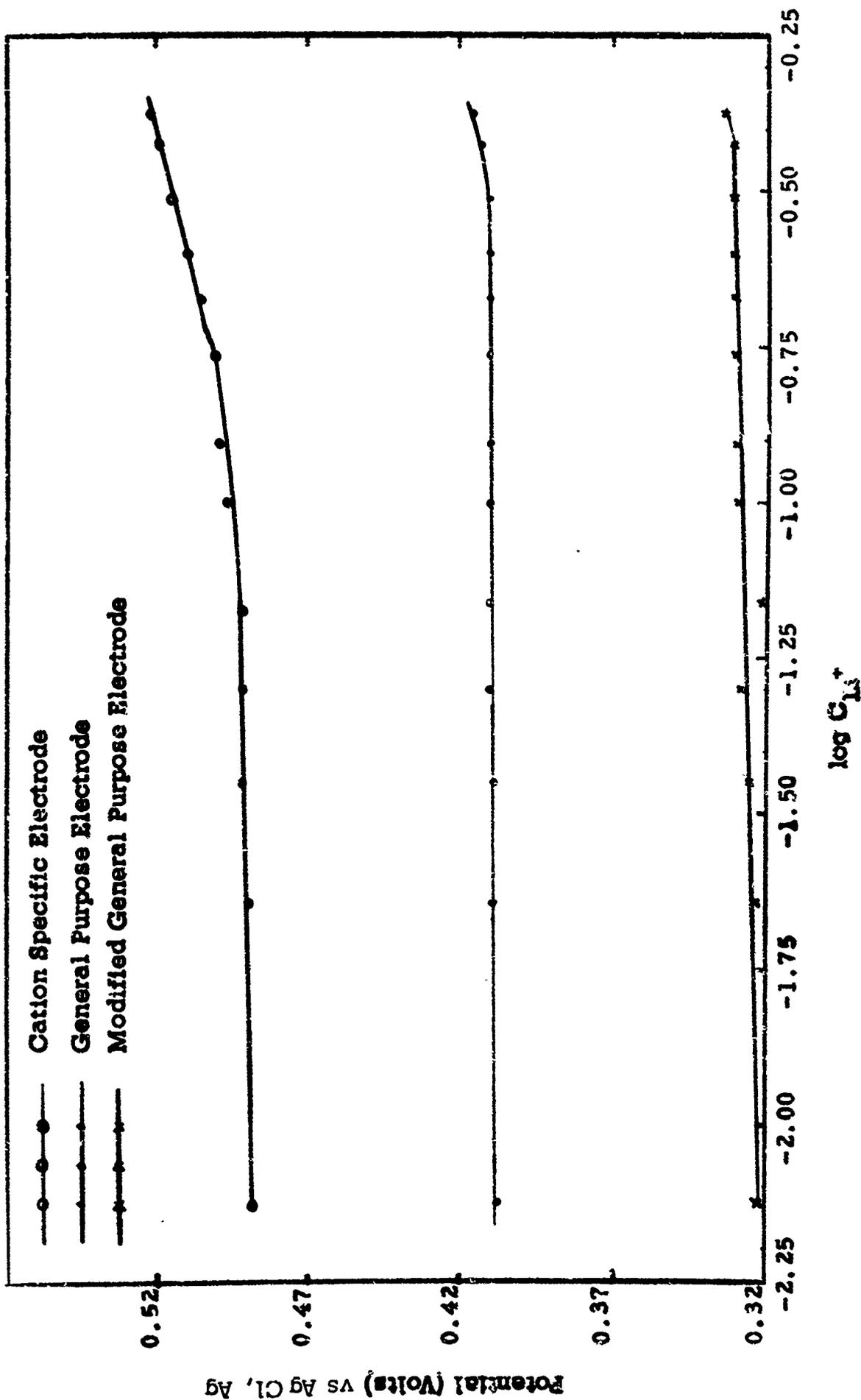


Figure 12

**Response of Glass Electrodes to  $C_{Li^+}$  in  $NH_4Cl$  Solution**  
 Cell: Glass Electrode/ $LiClO_4 - PC // 0.01 F LiClO_4 - PC / Ag Cl, Ag$

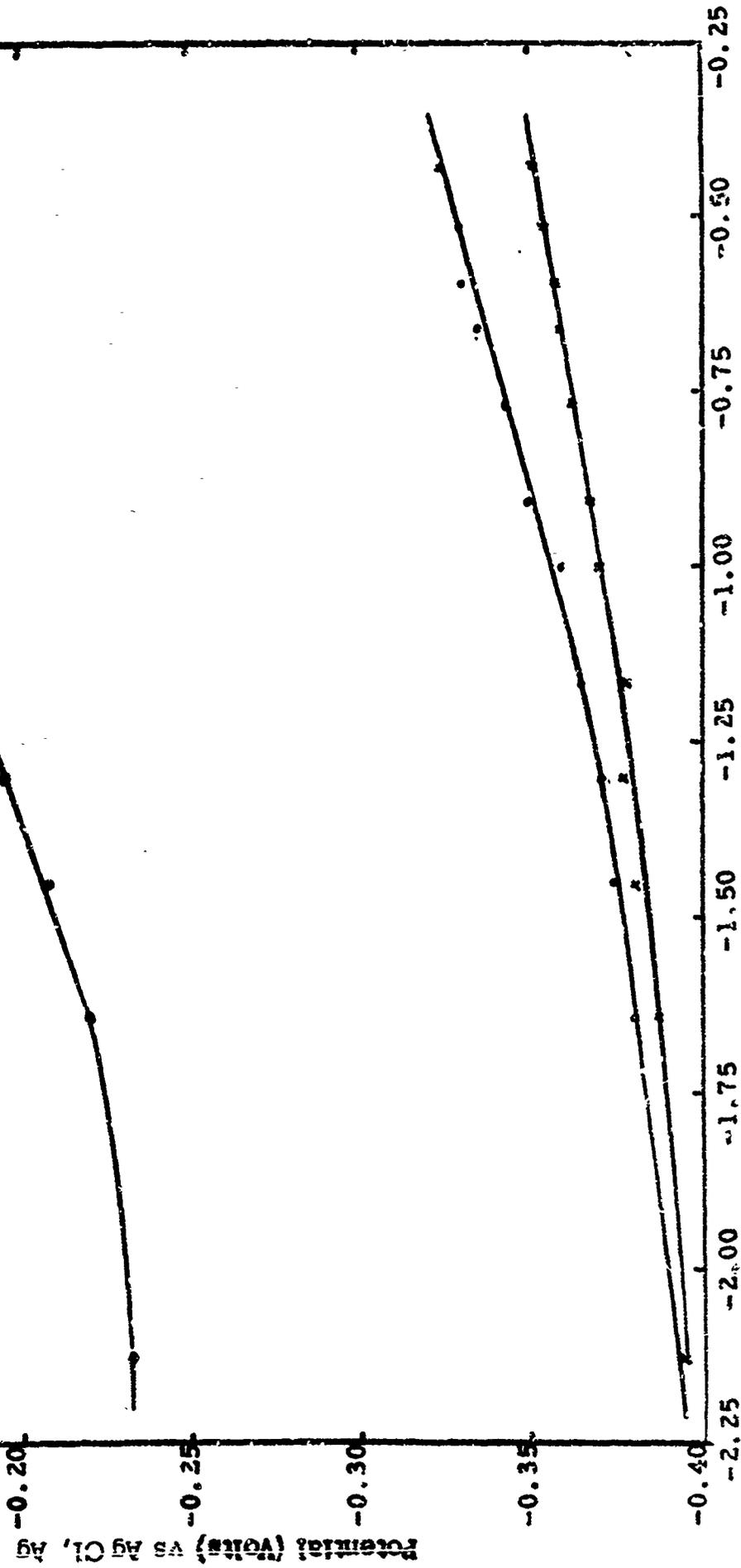


**Figure 13**

Response of Glass Electrodes to  $C_{Li^+}$  in  $Mg(ClO_4)_2$  Solution

Cell: Glass Electrode/ $ClLiClO_4 - PC // 0.01 F LiClO_4 - PC / Ag Cl, Ag$

- Cation Specific Electrode
- ▲—▲ General Purpose Electrode
- Modified G.P. Electrode

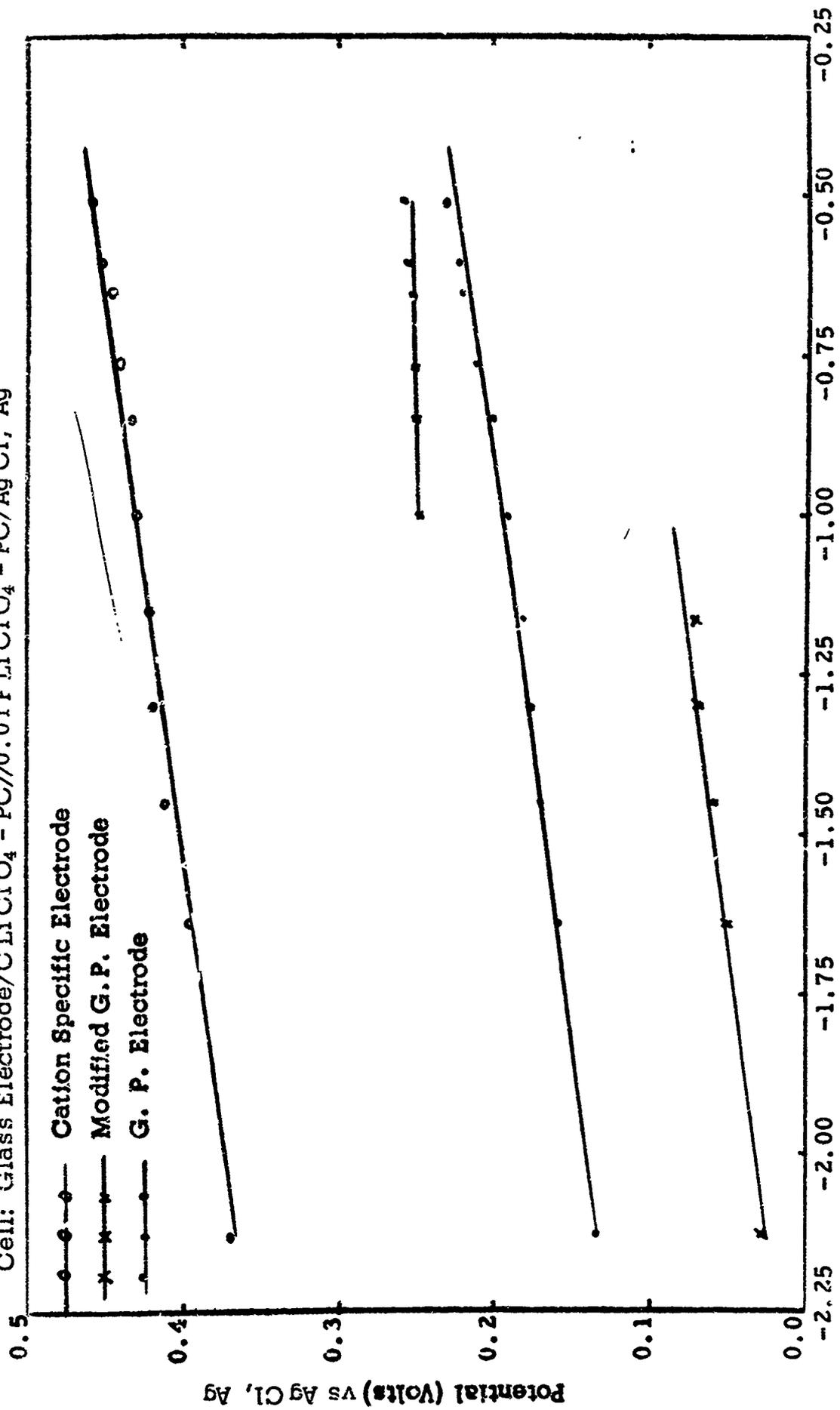


$\log_{10} C_{Li^+}$

Figure 14

Response of Glass Electrodes to  $C_{Li^+}$  in  $(C_2H_5)_4NClO_4$  Solution

Cell: Glass Electrode/ $LiClO_4$  - PC/ $0.01F LiClO_4$  - PC/ $AgCl, Ag$

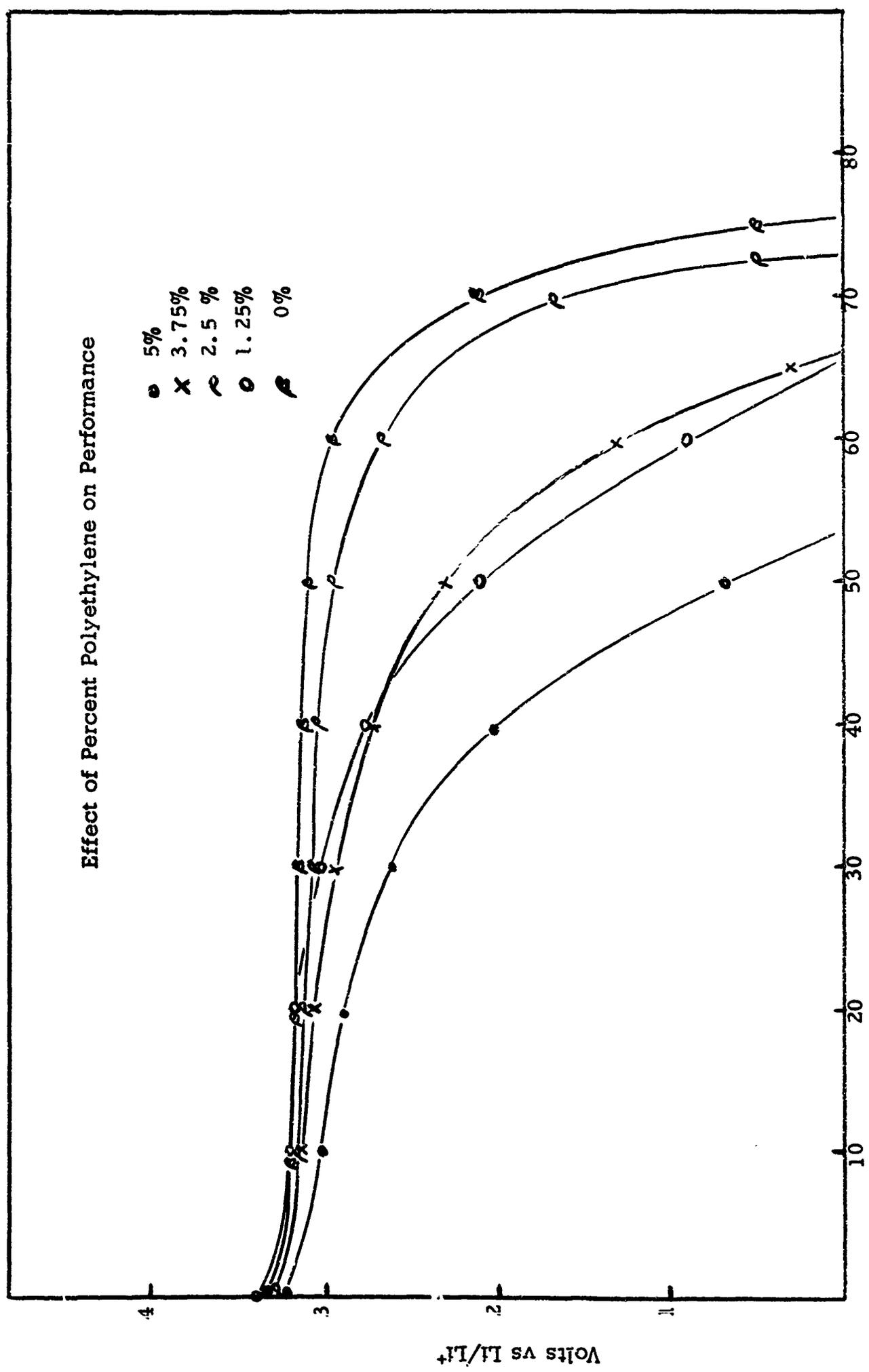


$\log C_{Li^+}$

Figure 15

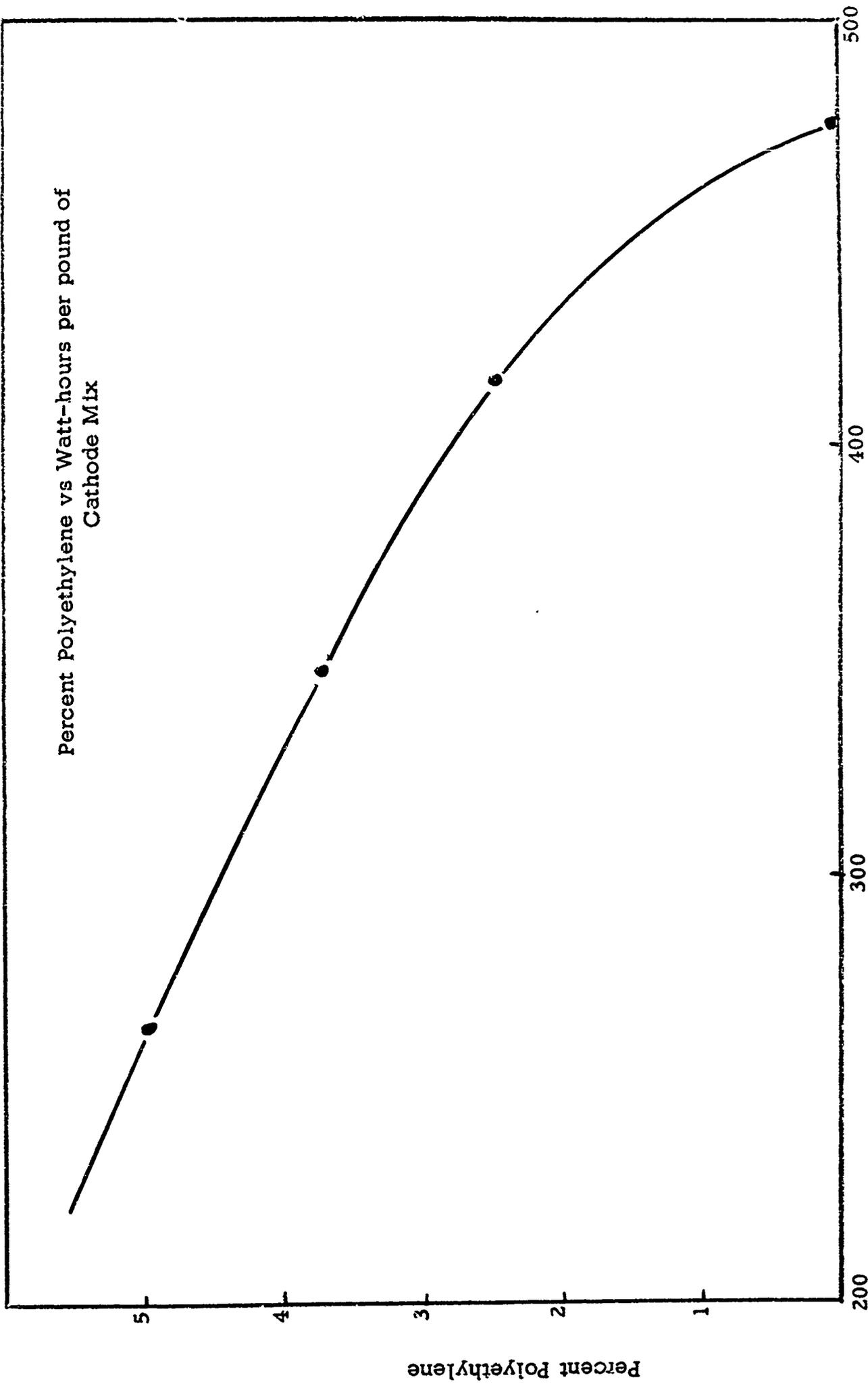
Effect of Percent Polyethylene on Performance

- 5%
- × 3.75%
- ⊖ 2.5%
- 1.25%
- ⊕ 0%



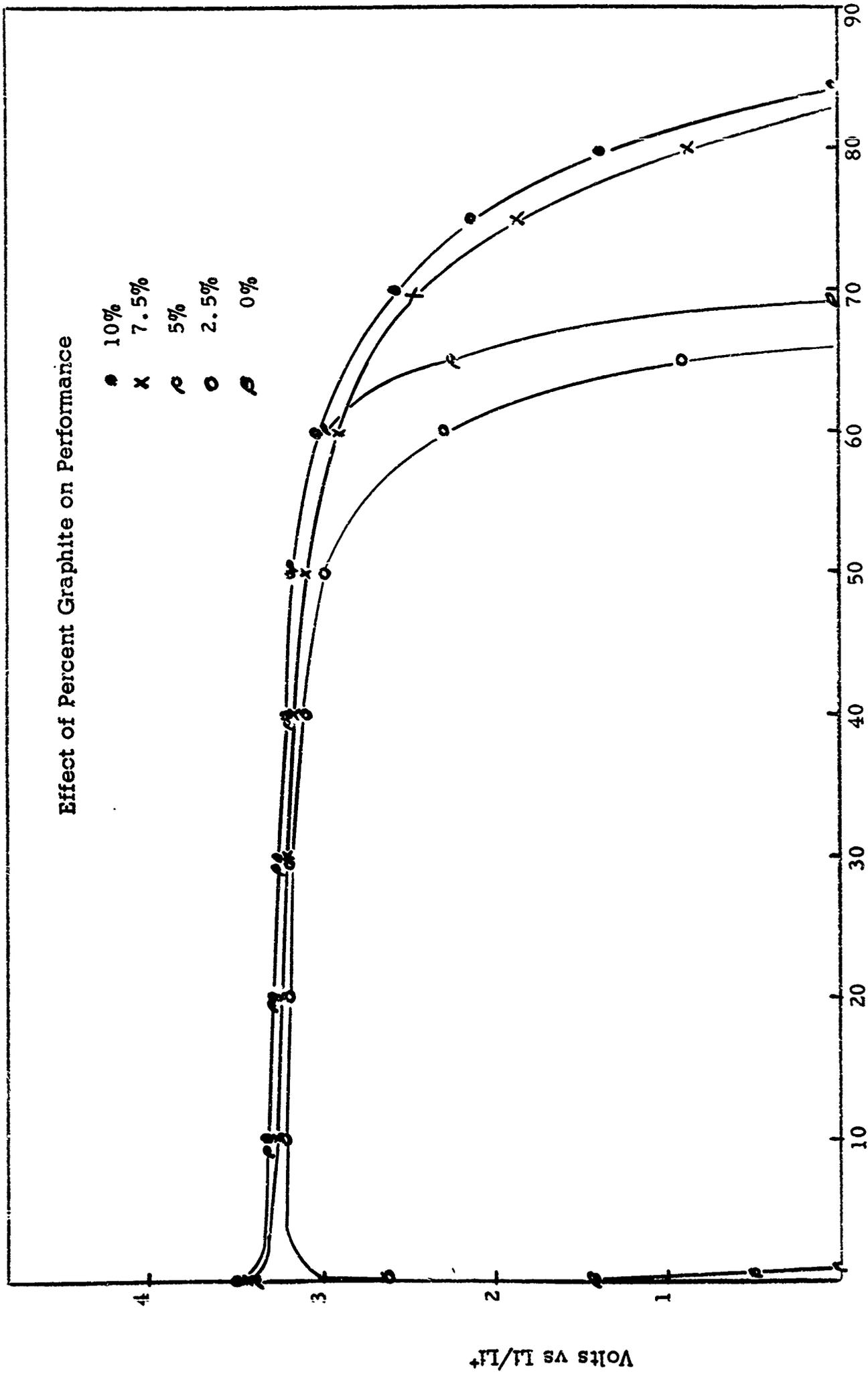
Percent Utilization of Cupric Fluoride

Figure 16



Watt-hours per Pound

Figure 17



Percent Utilization of Cupric Fluoride

Figure 18

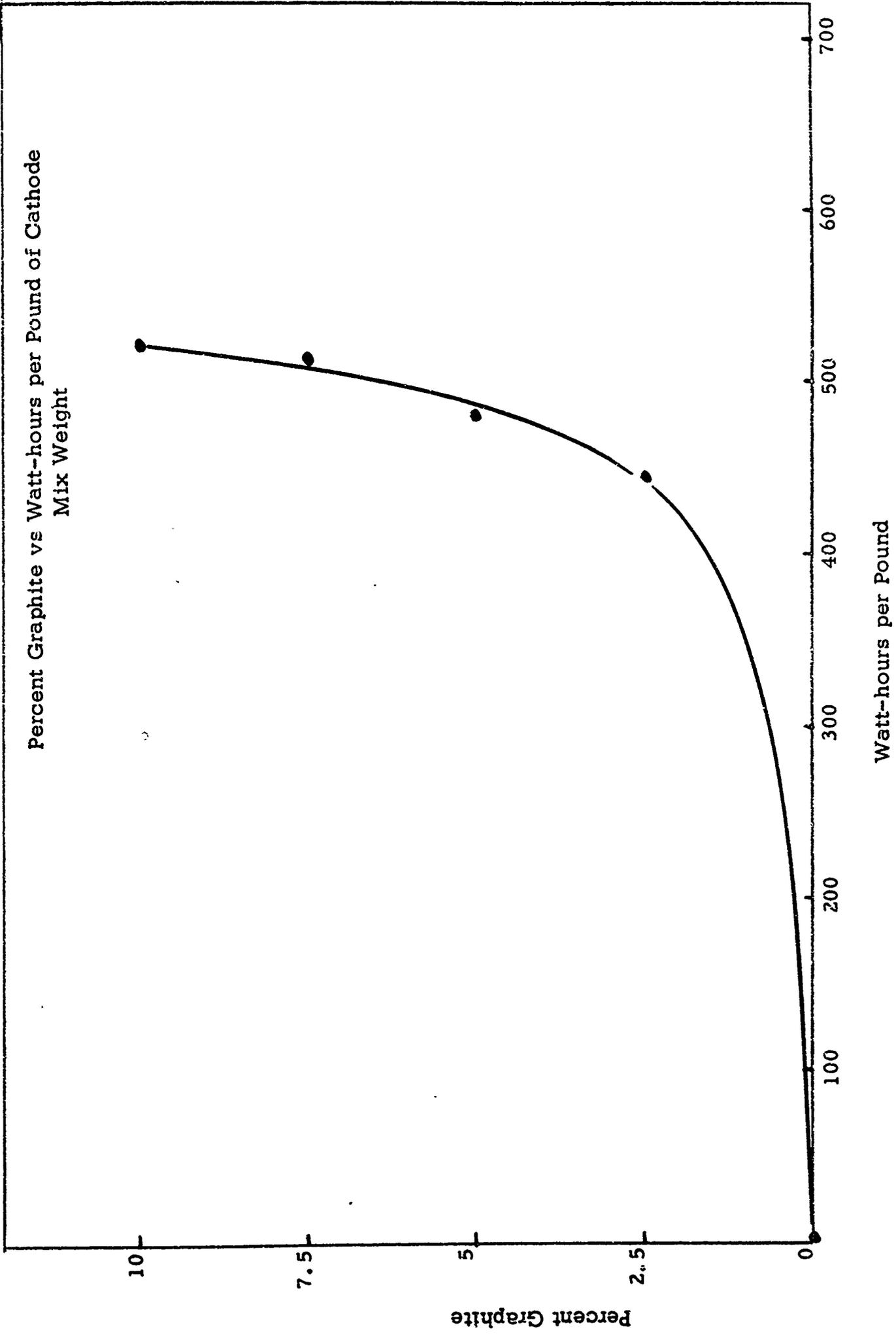
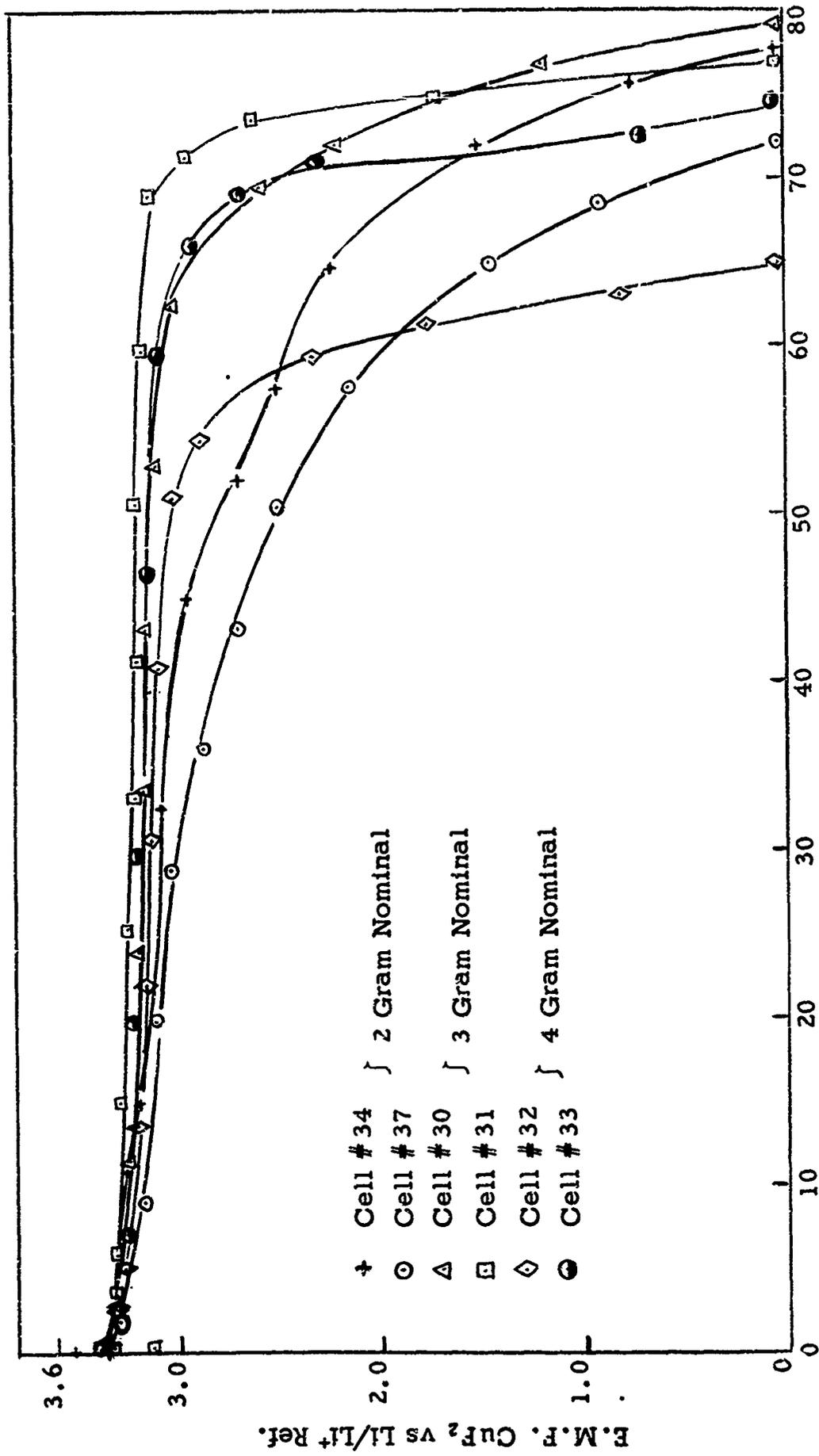


Figure 19

Effect of  $\text{CuF}_2$  Cathode Weight on Performance



Percent  $\text{CuF}_2$  Utilized

Figure 20

Discharge Characteristics of Li-CuF<sub>2</sub> Cells  
with 2 Gram Nom. Cathodes

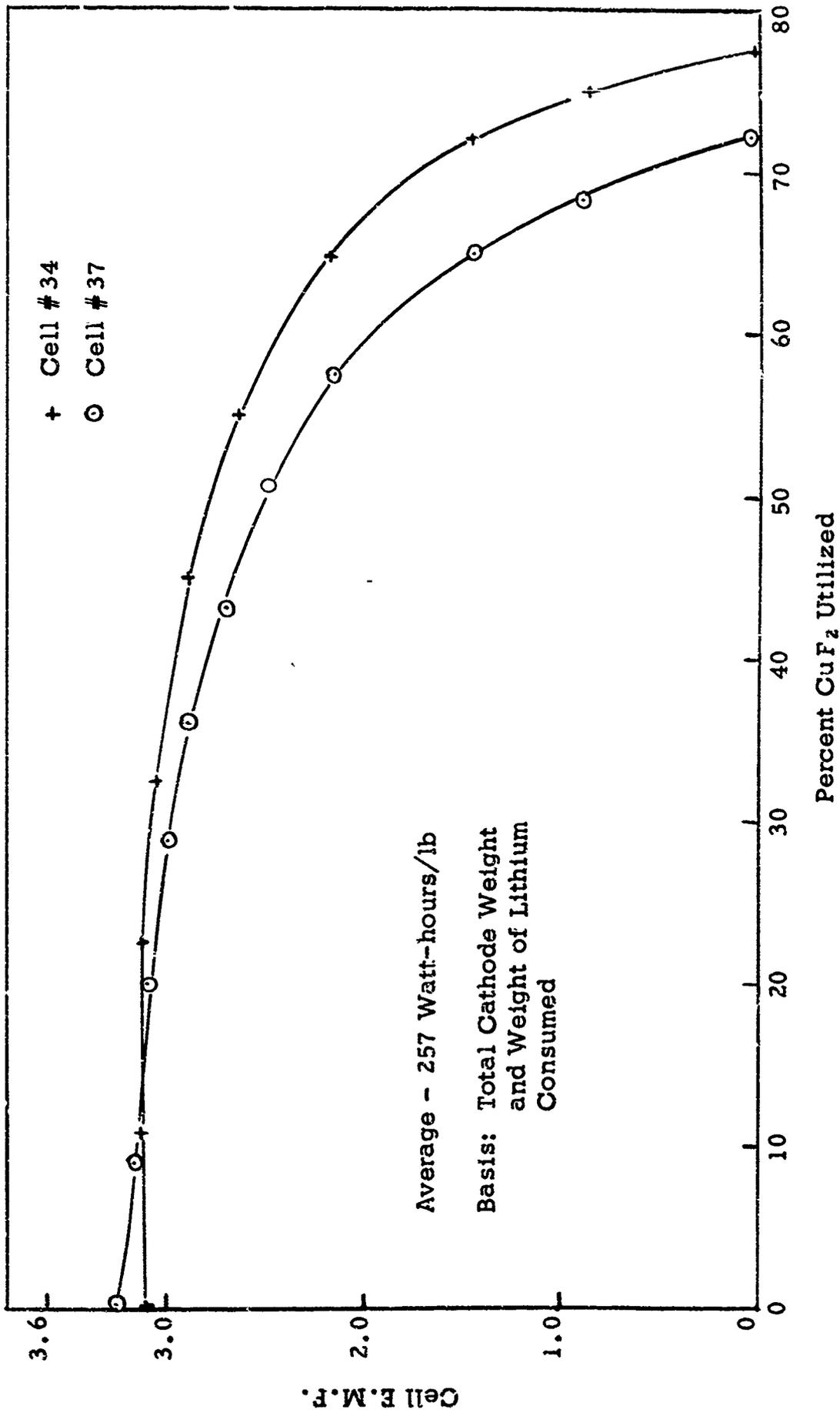
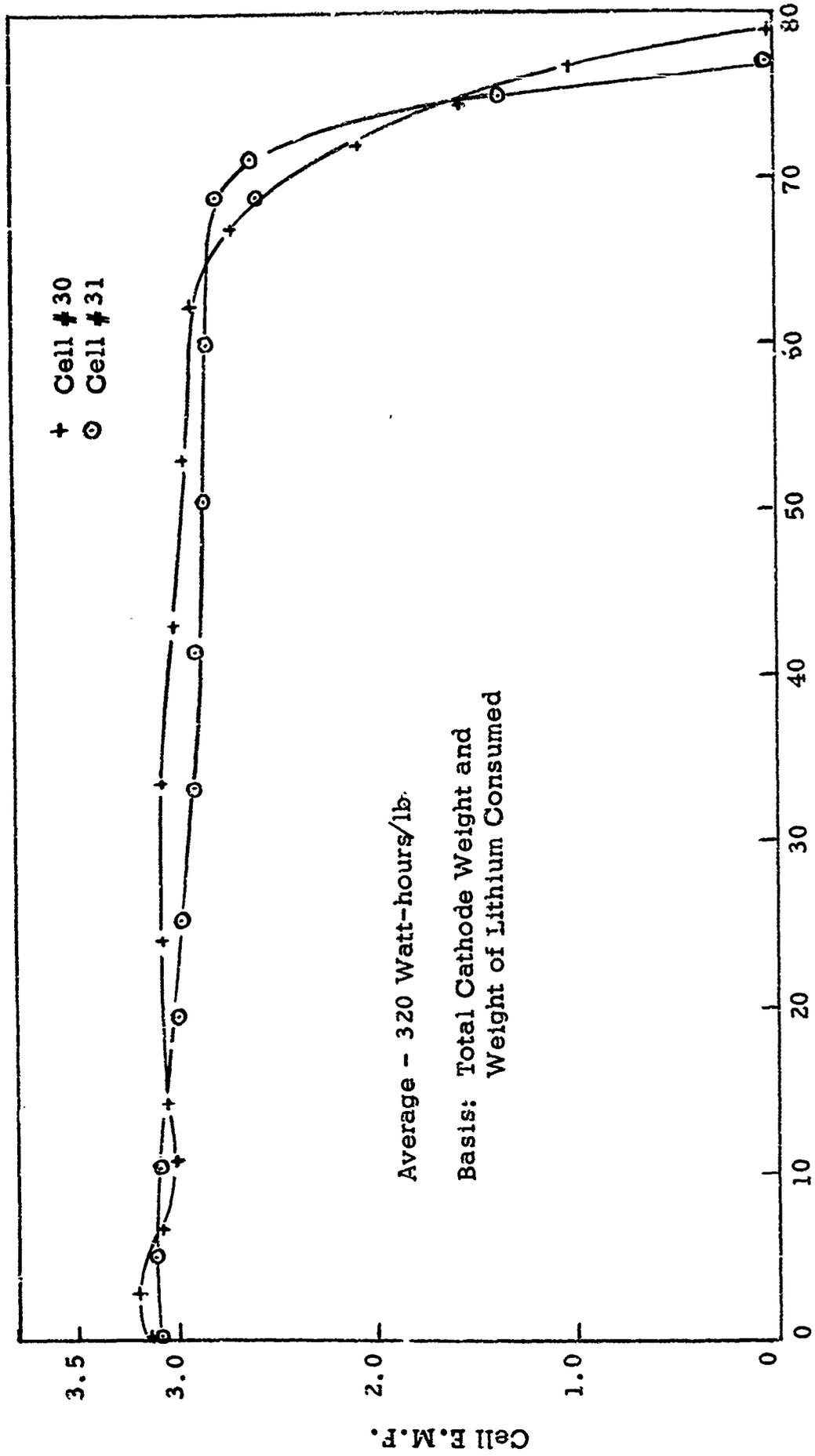


Figure 21

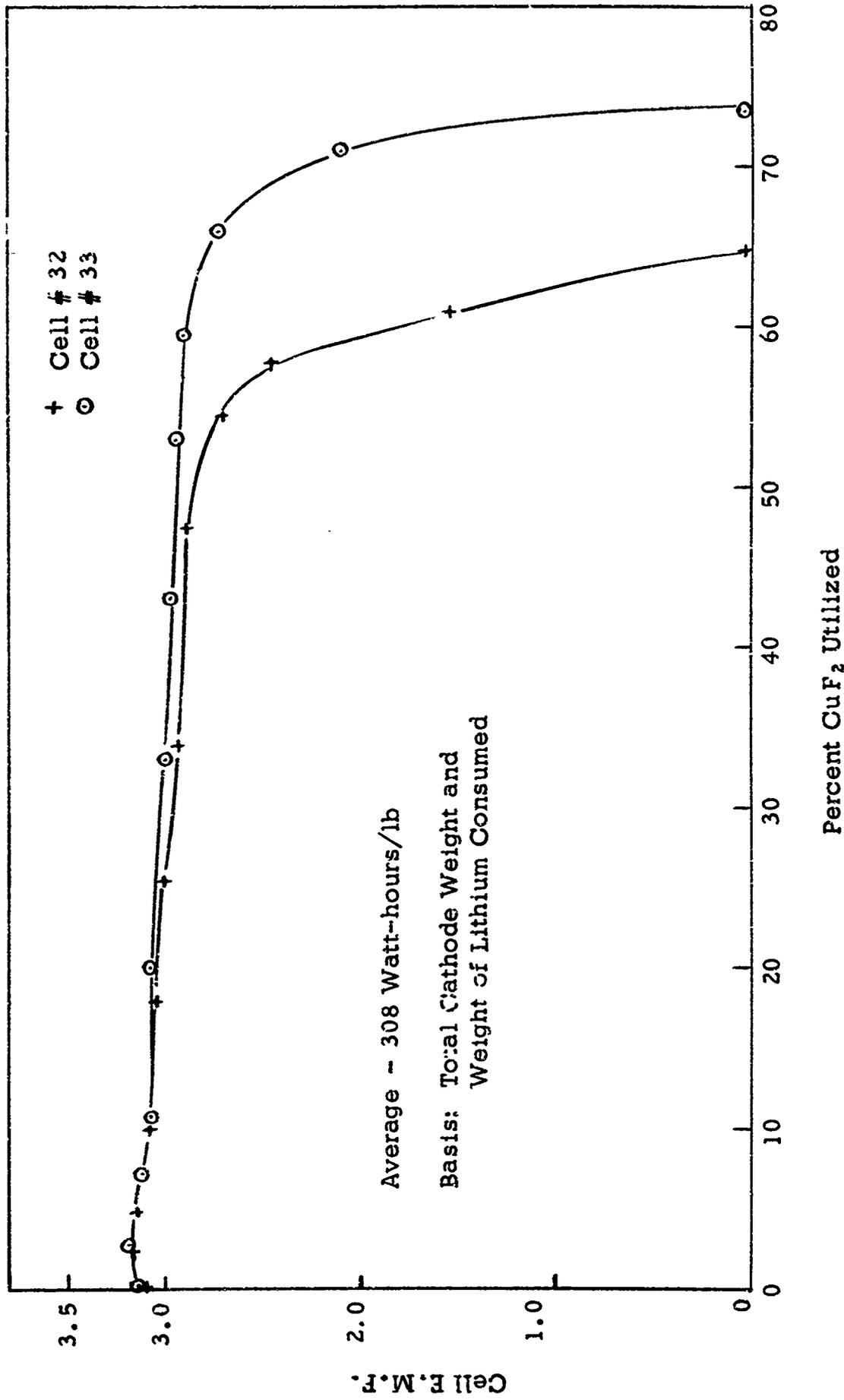
Discharge Characteristics of LiCuF<sub>2</sub> Cells  
with 3 Gram Nom. Cathodes



Percent CuF<sub>2</sub> Utilized

Figure 22

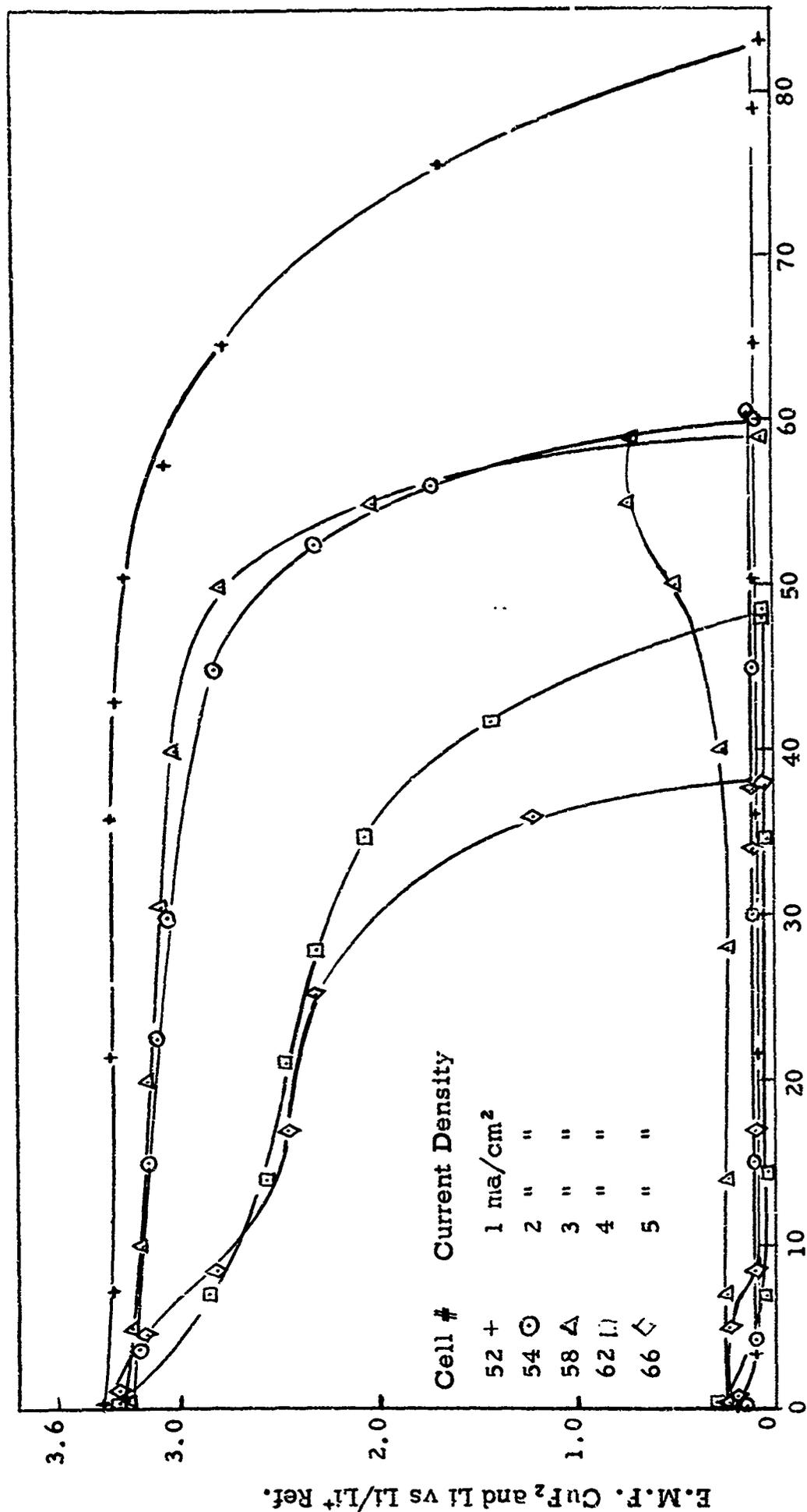
Discharge Characteristics of LiCuF<sub>2</sub> Cells  
with 4 Gram Nom. Cathodes



Percent CuF<sub>2</sub> Utilized

Figure 23

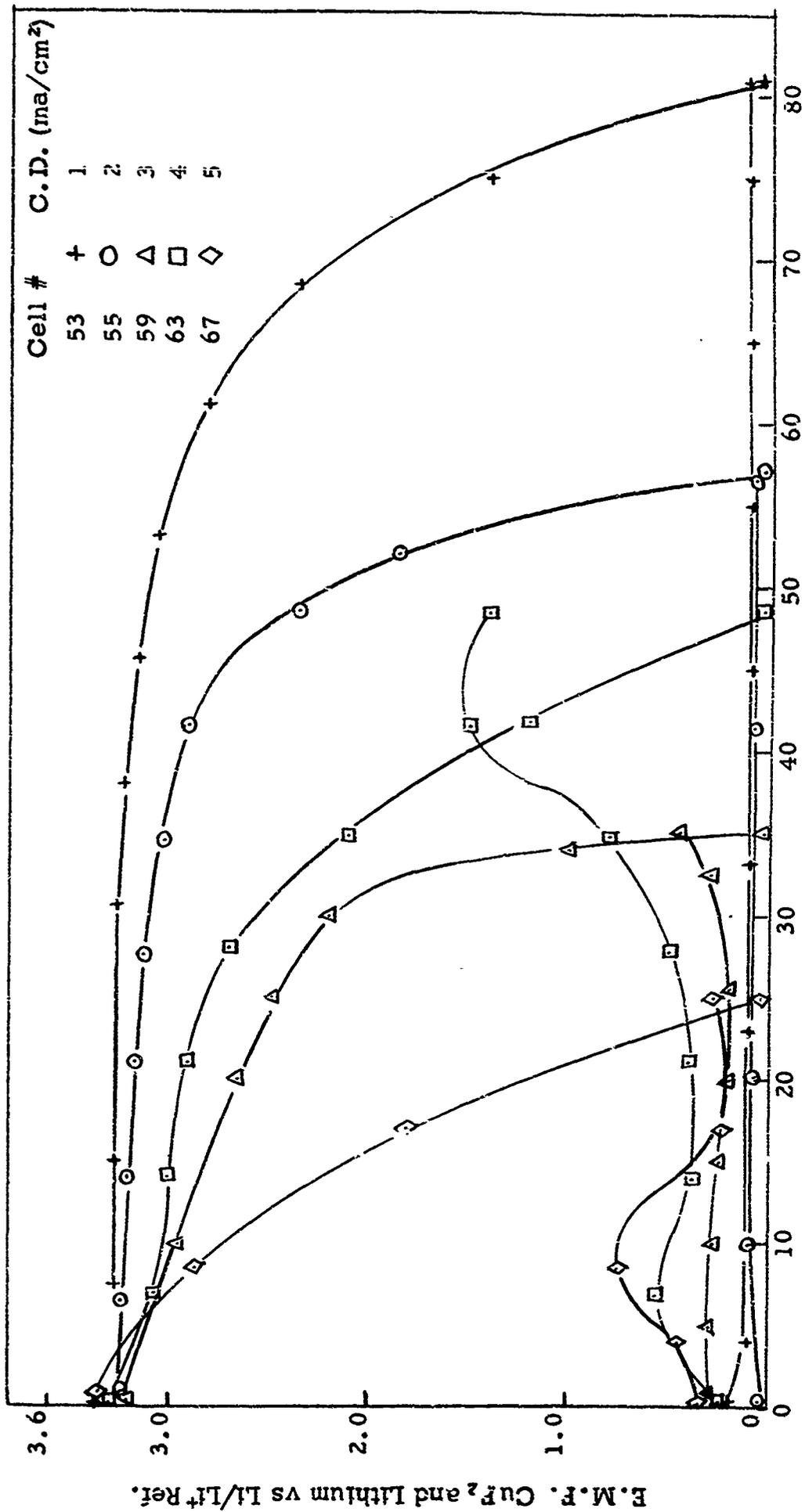
Effect of Discharge Current Density on Electrode Performance



Percent  $\text{CuF}_2$  Utilized

Figure 24

Effect of Discharge Current Density on Electrode Performance



Percent CuF<sub>2</sub> Utilized

Figure 25

E.M.F. CuF<sub>2</sub> and Lithium vs Li/I<sup>+</sup> Ref.

**Effect of Electrolyte Concentration on  $\text{CuF}_2$**   
**Cathode Performance**  
**Discharge Current Density  $2 \text{ ma/cm}^2$**   
**Solutions of  $\text{LiClO}_4$  in Distilled Propylene Carbonate**

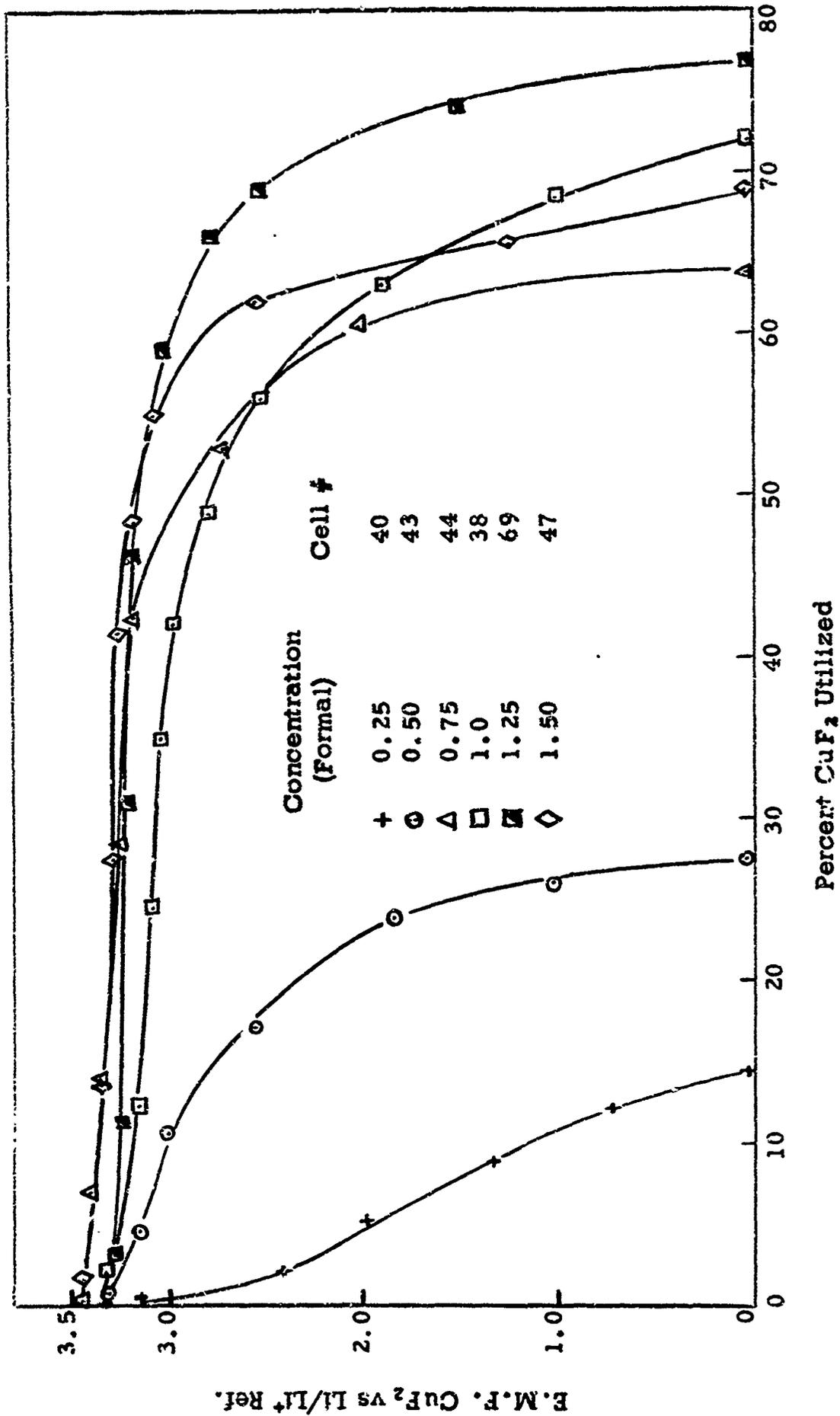


Figure 26

Effect of Electrolyte Concentration on  $\text{CuF}_2$   
 Cathode Performance  
 Discharge Current Density 2 ma/cm<sup>2</sup>  
 Solutions of  $\text{LiClO}_4$  in Distilled Propylene Carbonate

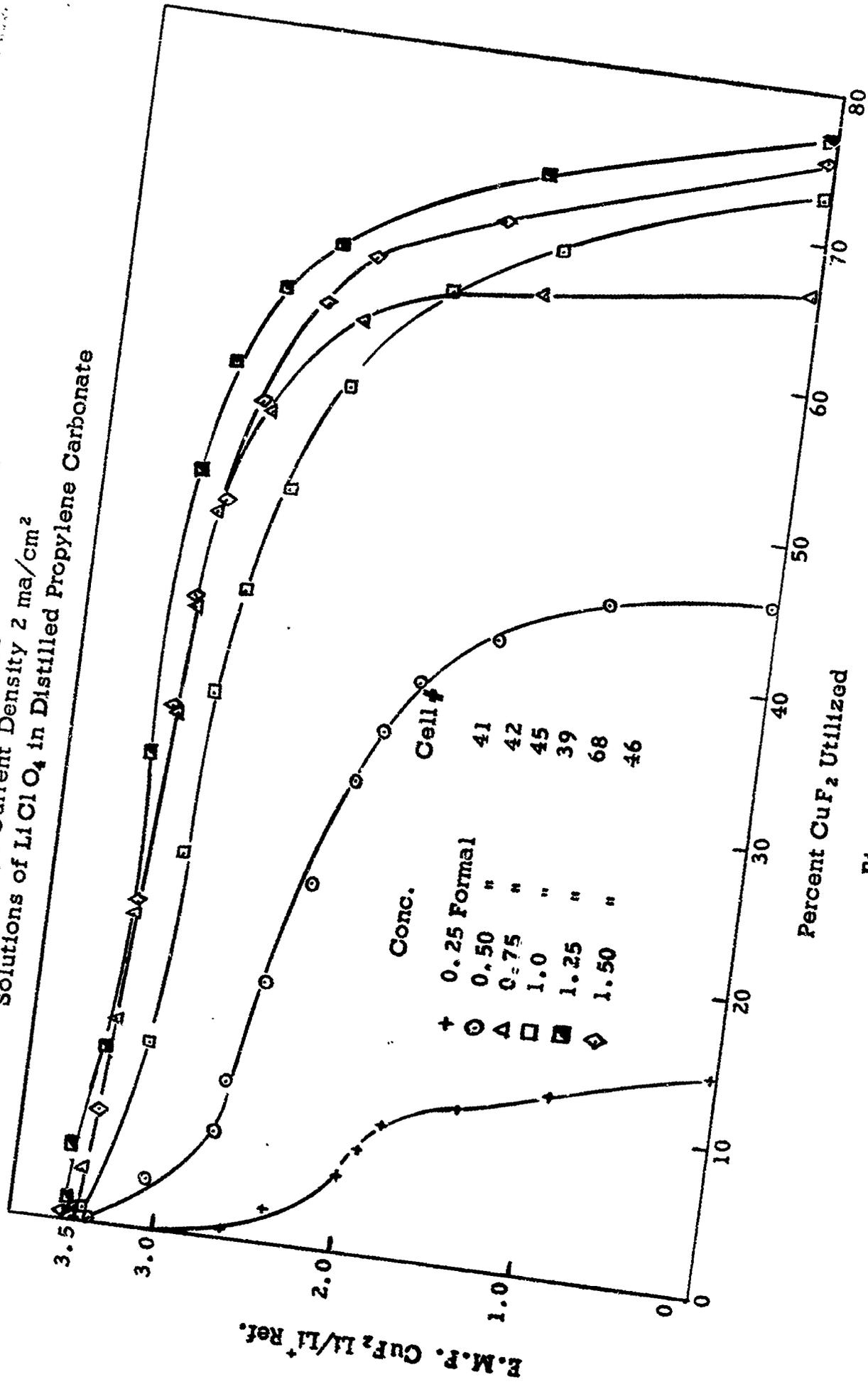


Figure 27

Effect of Electrolyte  
Concentration on  $\text{CuF}_2$  Cathode Performance

Solutions of  $\text{LiClO}_4$  in Distilled  
Propylene Carbonate

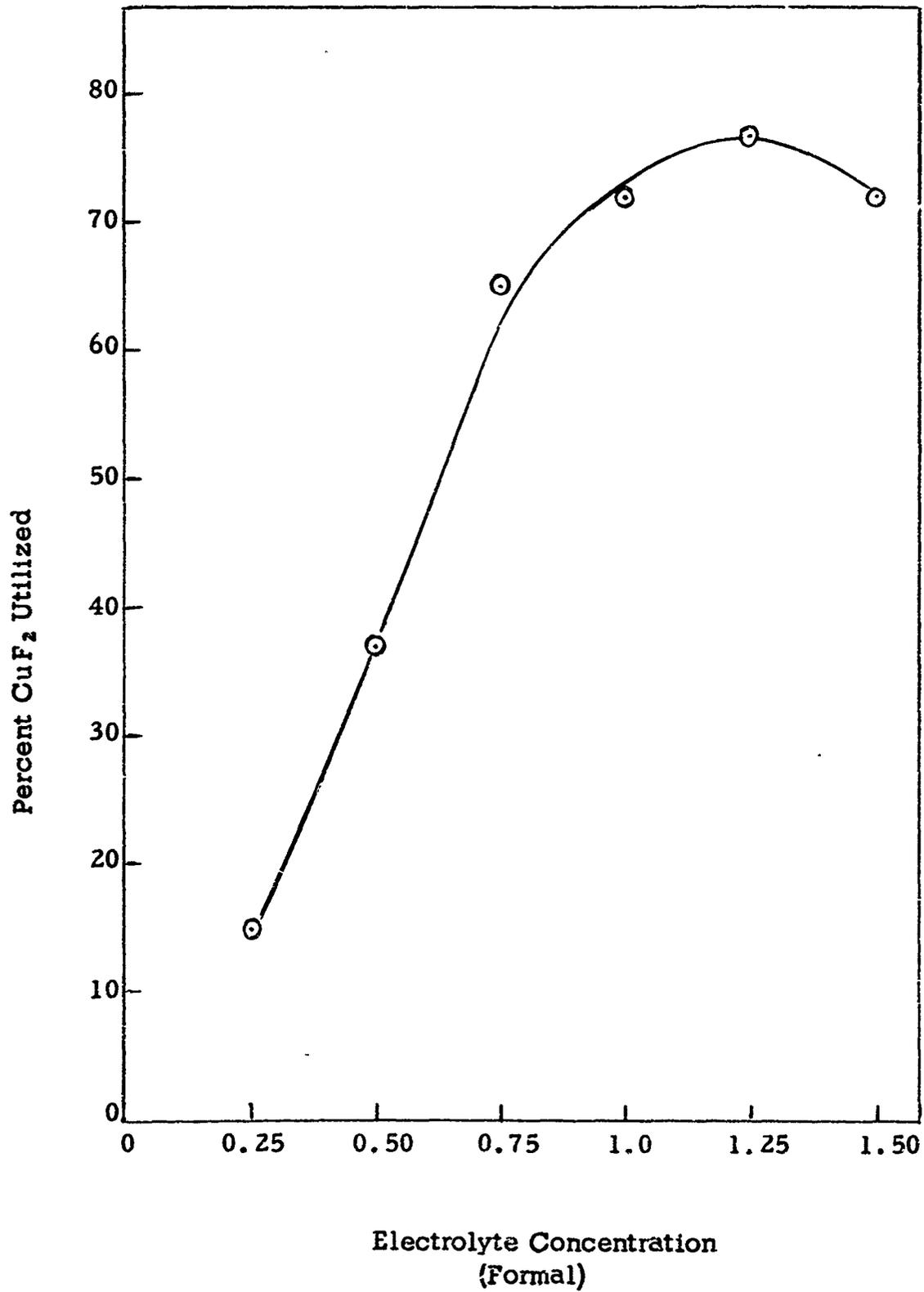


Figure 28

Effect of Storage in Paraffin Oil on Performance  
of Pressed Lithium Ribbon Anodes

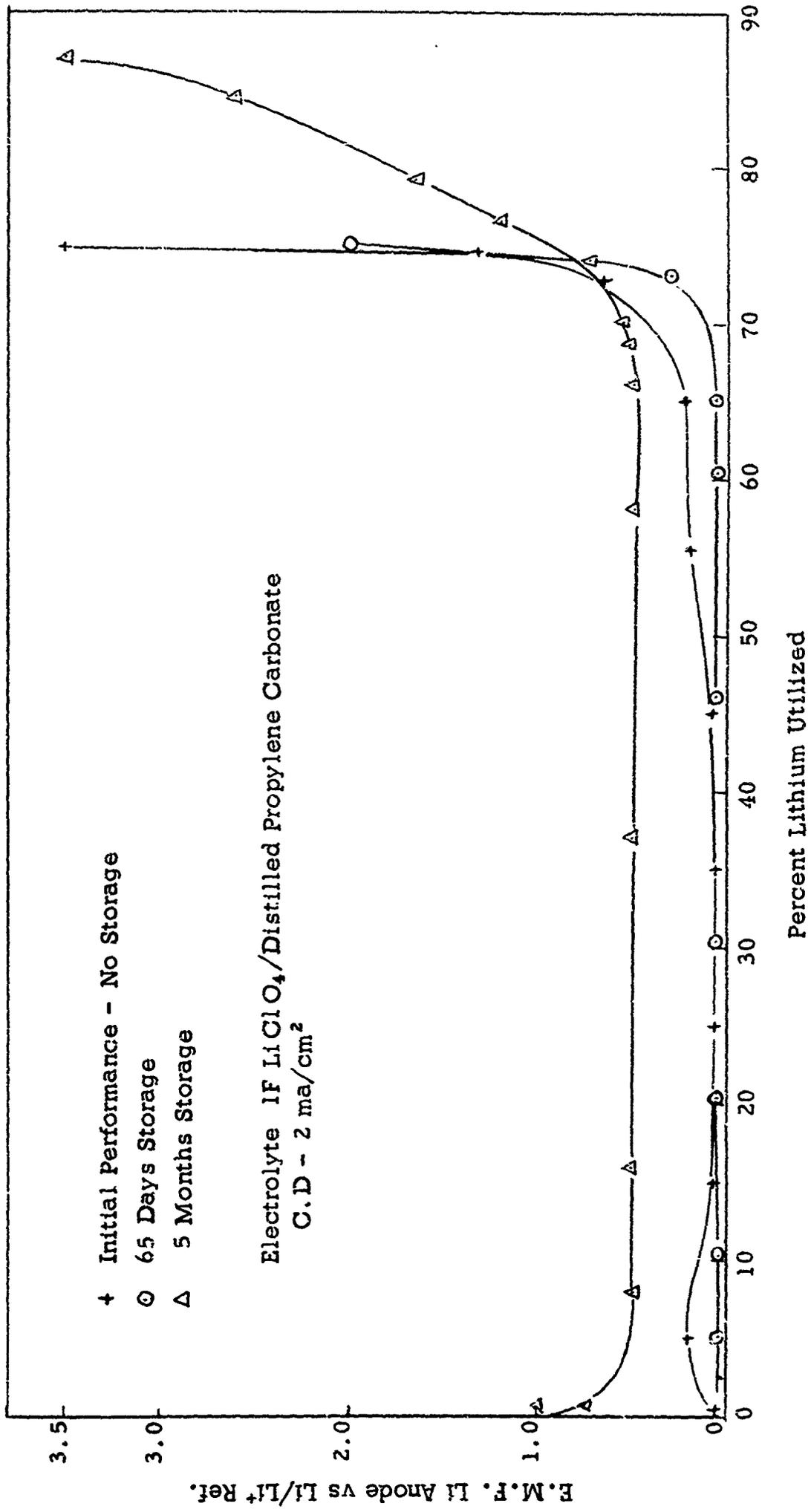
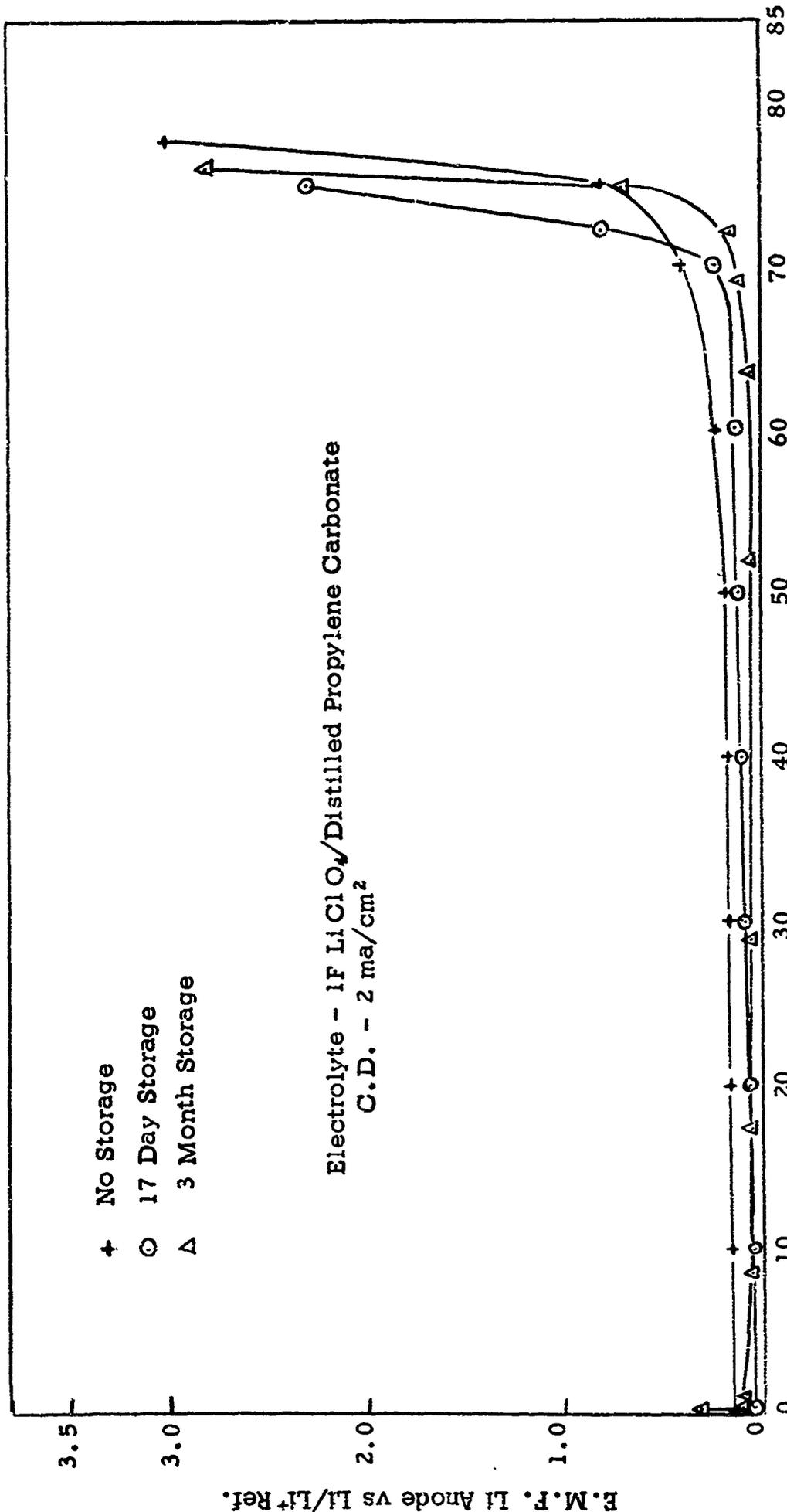


Figure 29

Effect of Storage in Electrolyte on Performance  
of Pressed Lithium Ribbon Anodes



Percent Lithium Utilized

Figure 30

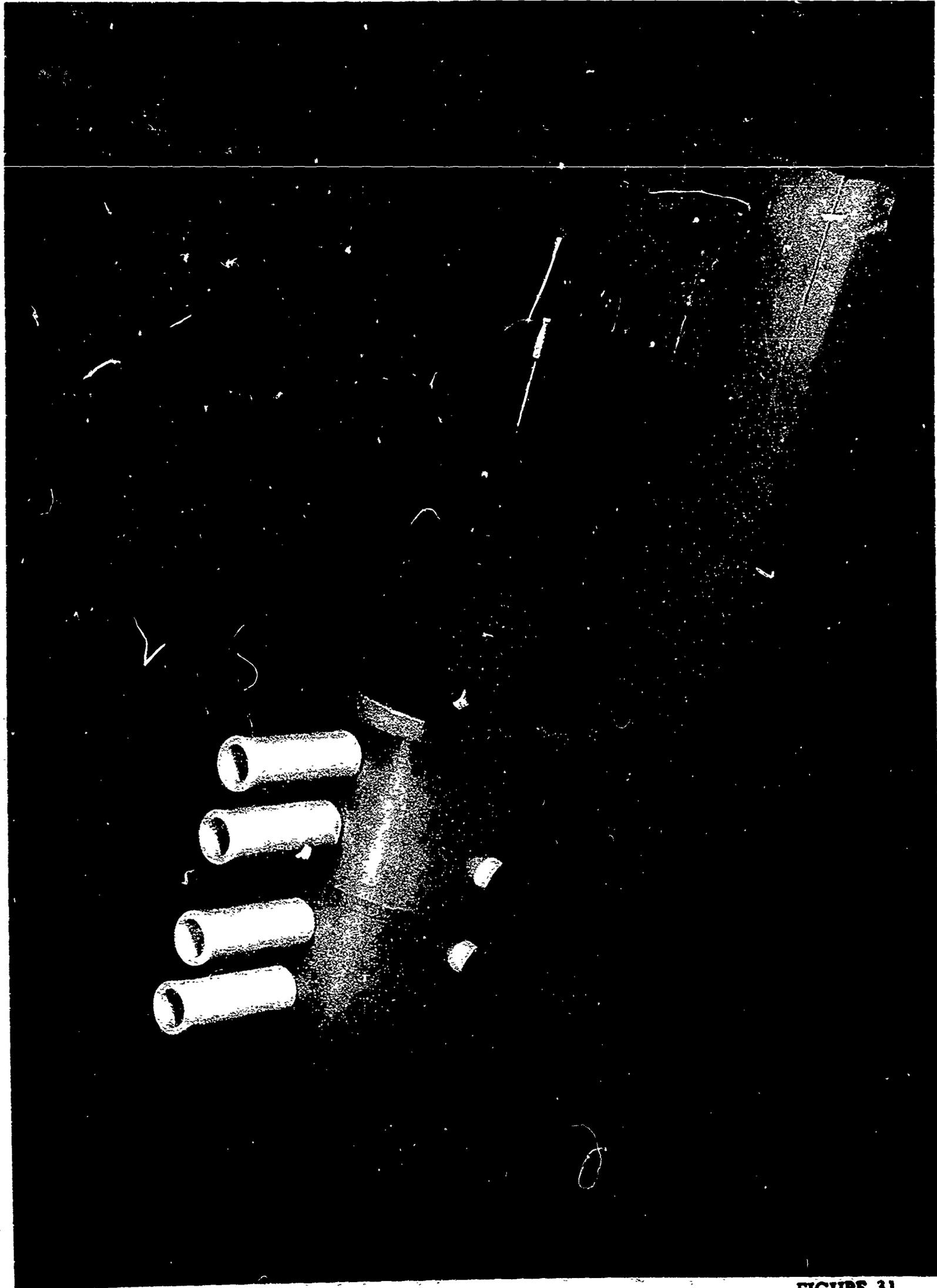
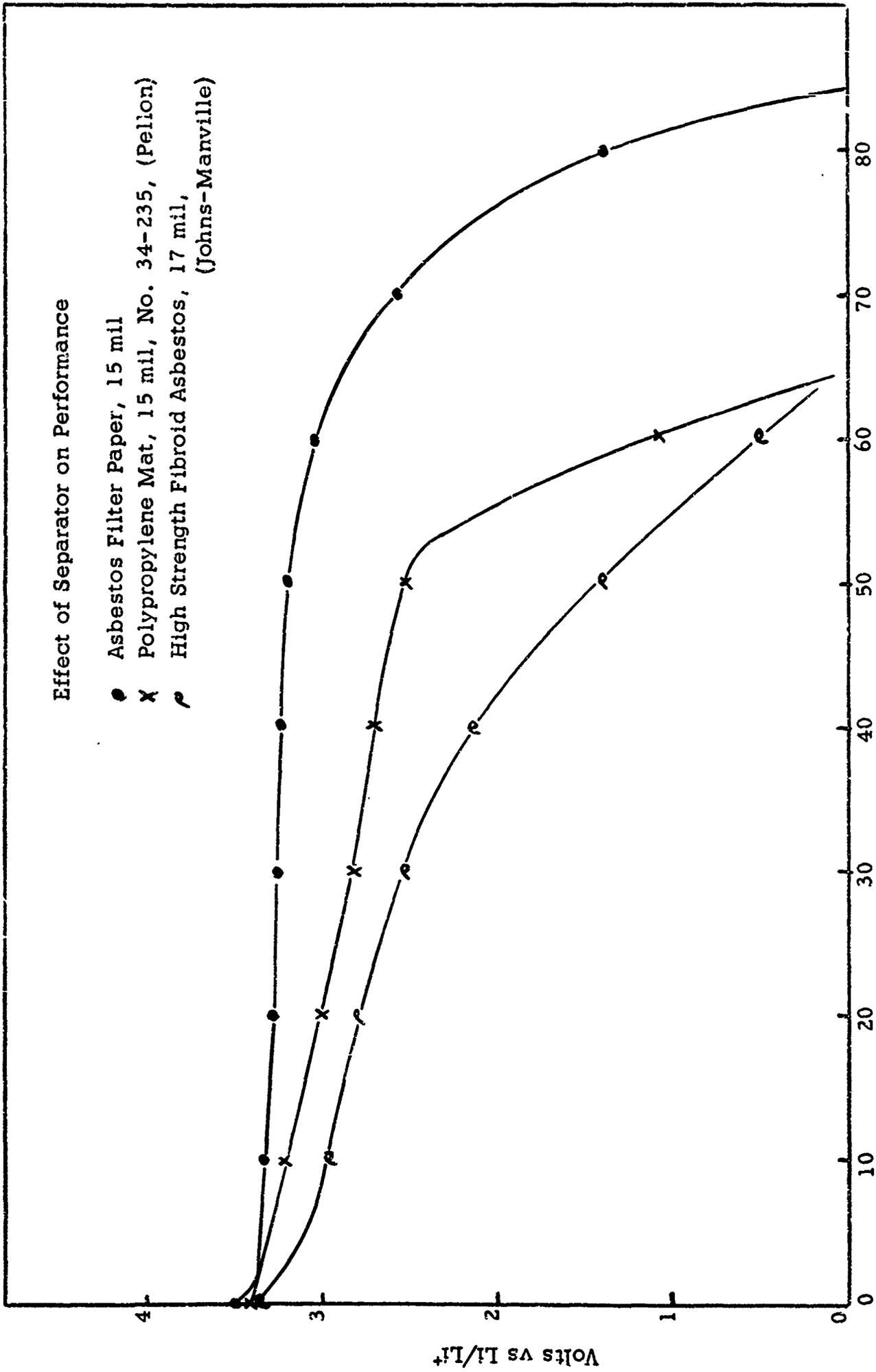


FIGURE 31

Effect of Separator on Performance

- Asbestos Filter Paper, 15 mil
- X Polypropylene Mat, 15 mil, No. 34-235, (Pellon)
- ρ High Strength Fibroid Asbestos, 17 mil, (Johns-Manville)



Percent Utilization of  $\text{CuF}_2$

Figure 32

Effect of Separator on Performance

- Glass Mat, 30 mil, (Hydromatic Packing)
- X Porous Polyethylene, 5 mil, (ESB Co.)
- Ⓟ Analytical Filter Paper, No. 589, (Schleicher and Schuelli Co.)

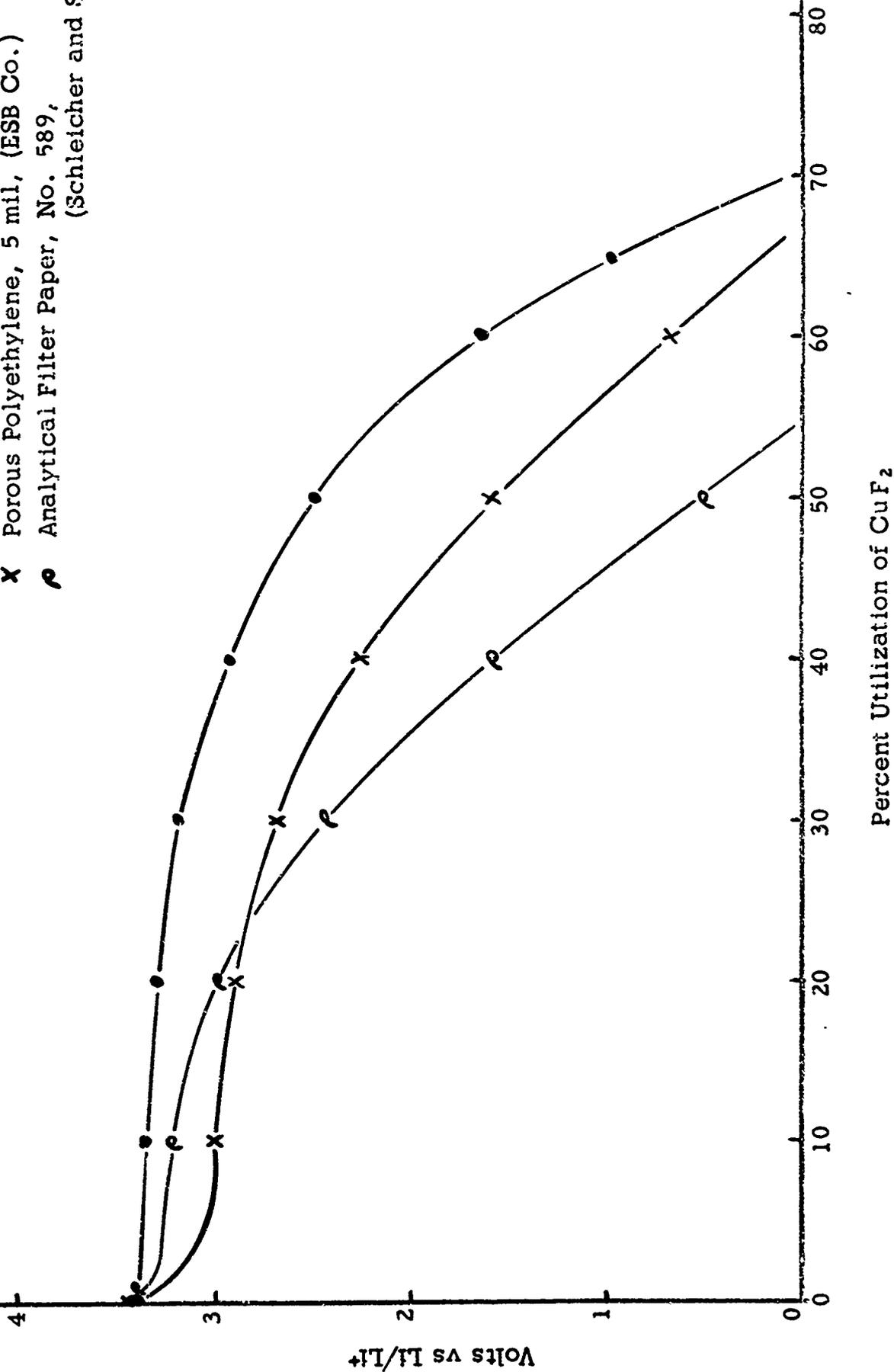
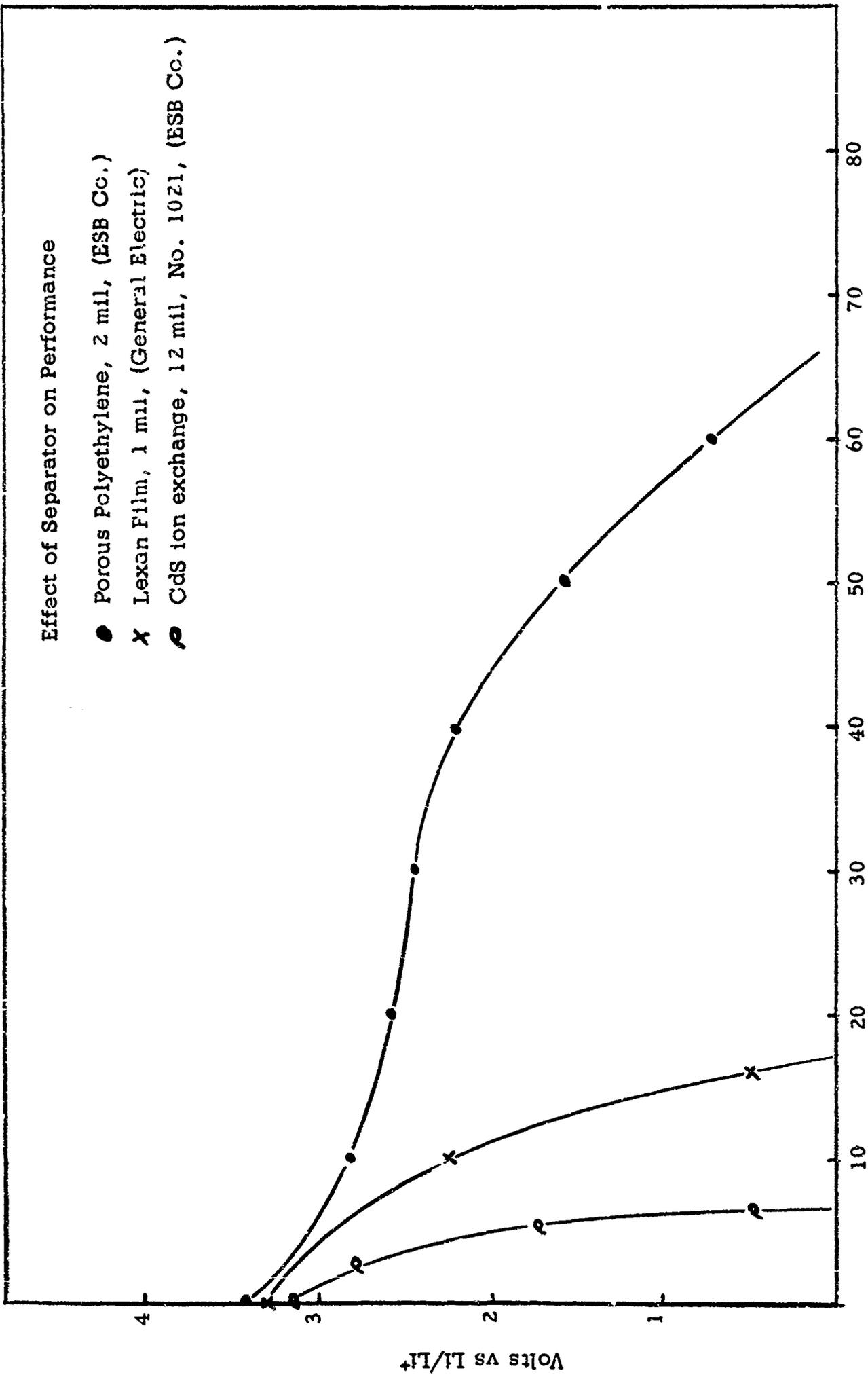


Figure 33

Effect of Separator on Performance

- Porous Polyethylene, 2 mil, (ESB Co.)
- X Lexan Film, 1 mil, (General Electric)
- Cds ion exchange, 12 mil, No. 1021, (ESB Co.)



Percent Utilization of CuF<sub>2</sub>

Figure 34

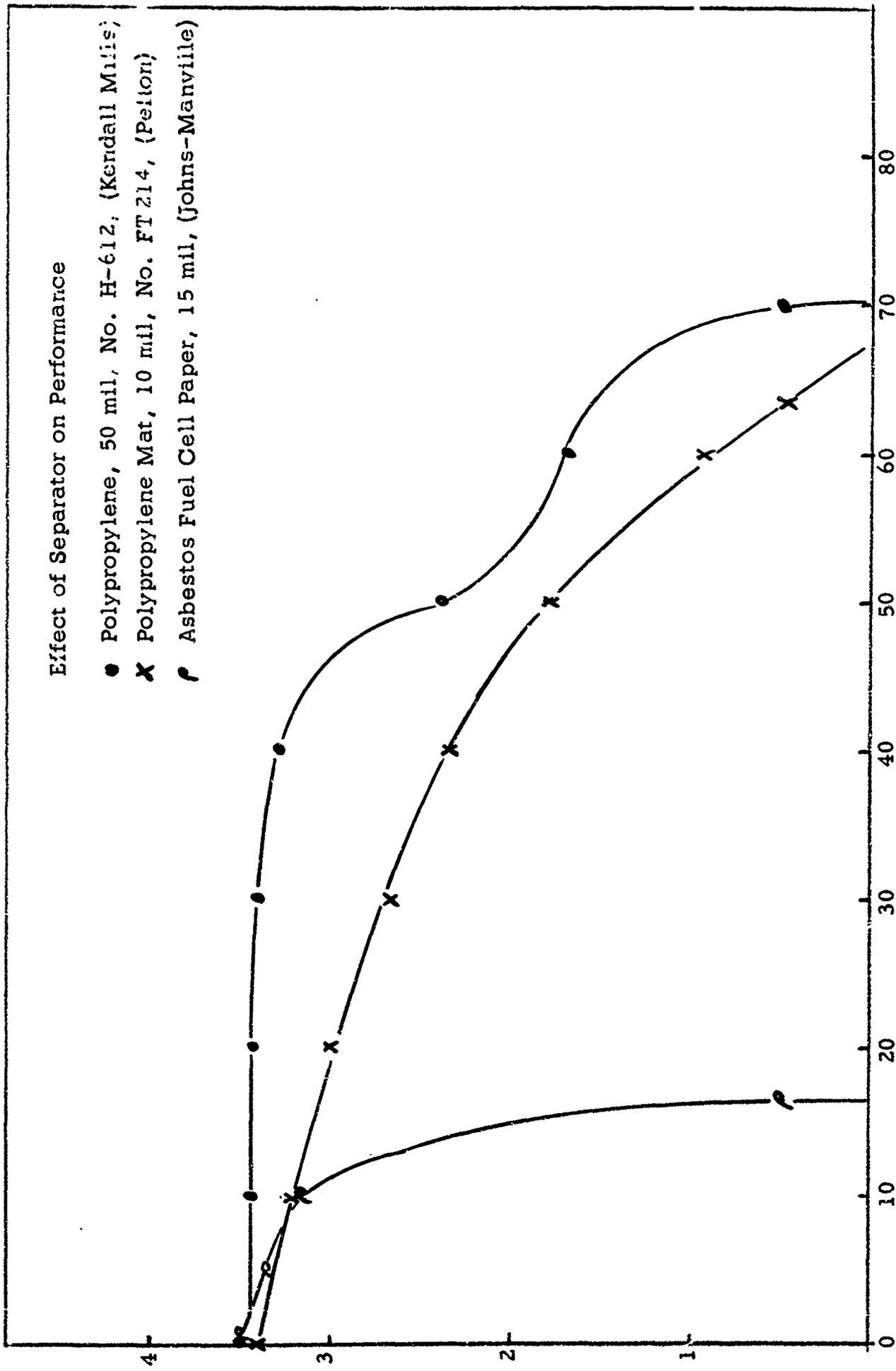
Effect of Separator on Performance

- Polypropylene, 50 mil, No. H-612, (Kendall Mills)
- X Polypropylene Mat, 10 mil, No. FT 214, (Pelton)
- Asbestos Fuel Cell Paper, 15 mil, (Johns-Manville)

Volts vs Li/Li<sup>+</sup>

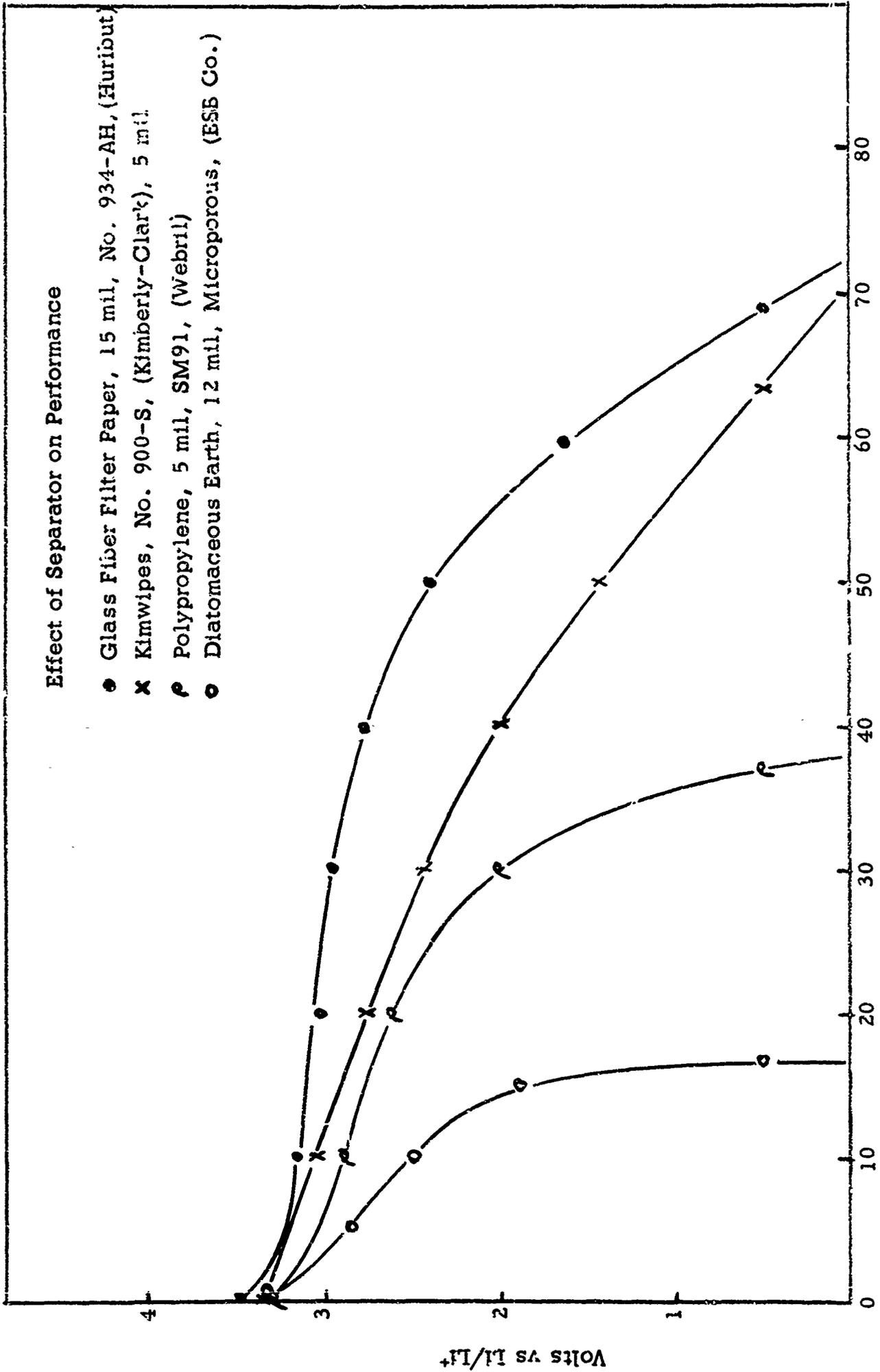
Percent Utilization of CuF<sub>2</sub>

Figure 35



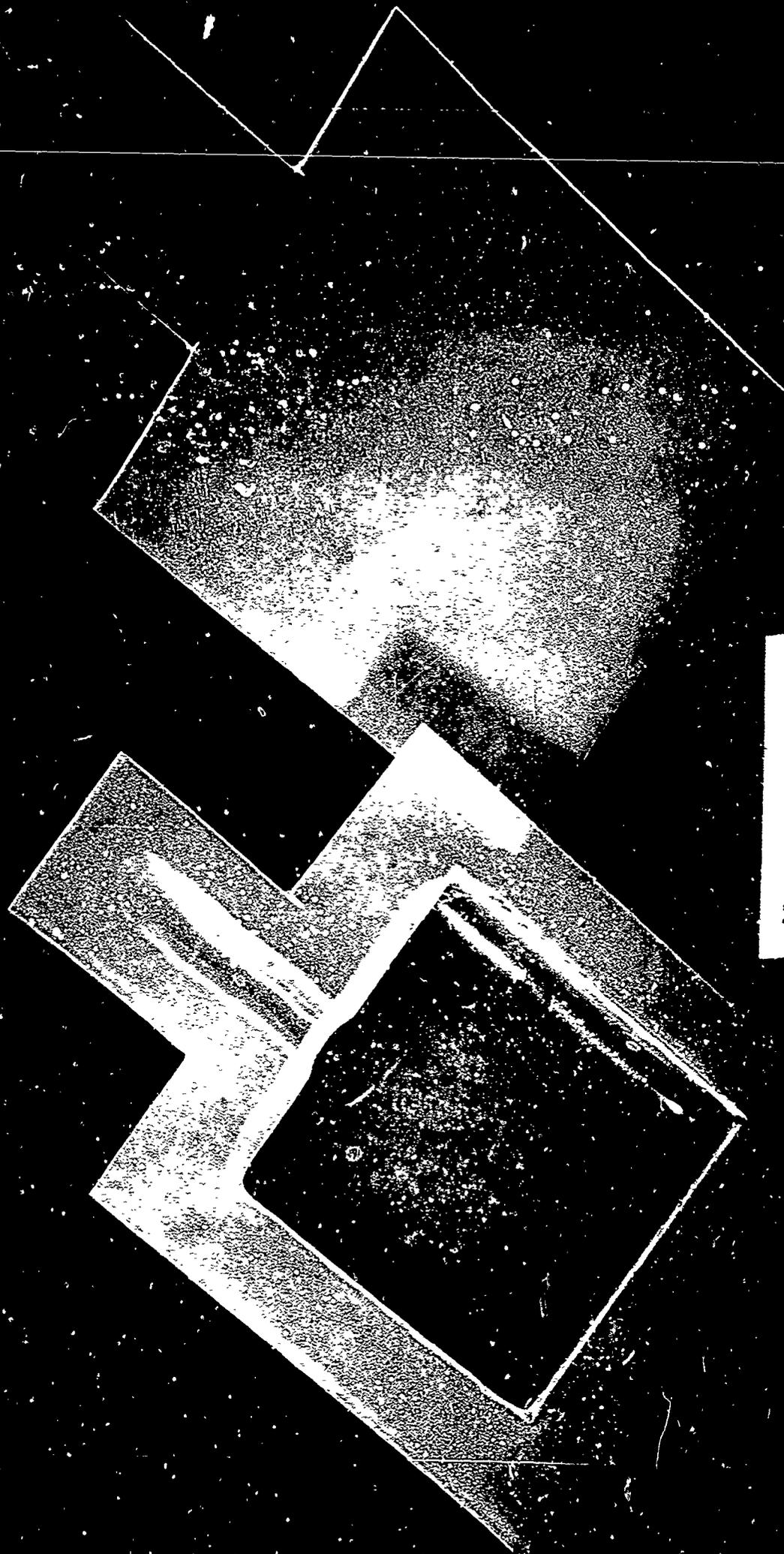
Effect of Separator on Performance

- Glass Fiber Filter Paper, 15 mil, No. 934-AH, (Hurlbut)
- × Kimwipes, No. 900-S, (Kimberly-Clark), 5 mil
- Ⓟ Polypropylene, 5 mil, SM91, (Webril)
- Diatomaceous Earth, 12 mil, Microporous, (ESS Co.)



Percent Utilization of CuF<sub>2</sub>

Figure 36



Vacuum Molded  
Polyethylene Jar  
and Cover

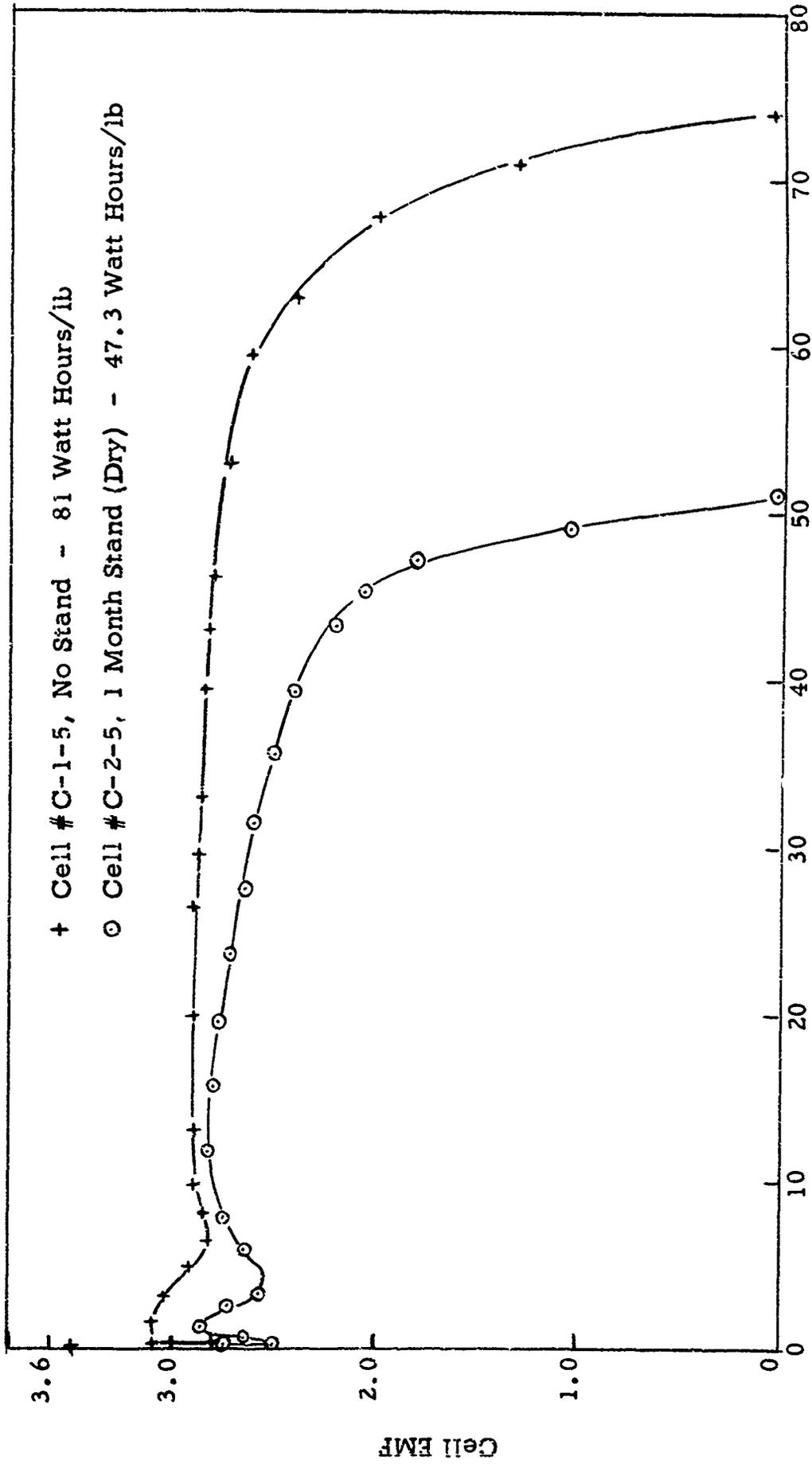
FIGURE 37



**Li - CuF<sub>2</sub> Cell**  
**5 Electrodes**  
**3.5 amp hrs**

**FIGURE 38**

Discharge Characteristics - Li-CuF<sub>2</sub> Cells  
Lightweight Polyethylene Container



Percent CuF<sub>2</sub> Utilized

Figure 39

Discharge Characteristic of Li-CuF<sub>2</sub> Cell C-1-7  
Lightweight Polyethylene Container  
7 Electrodes

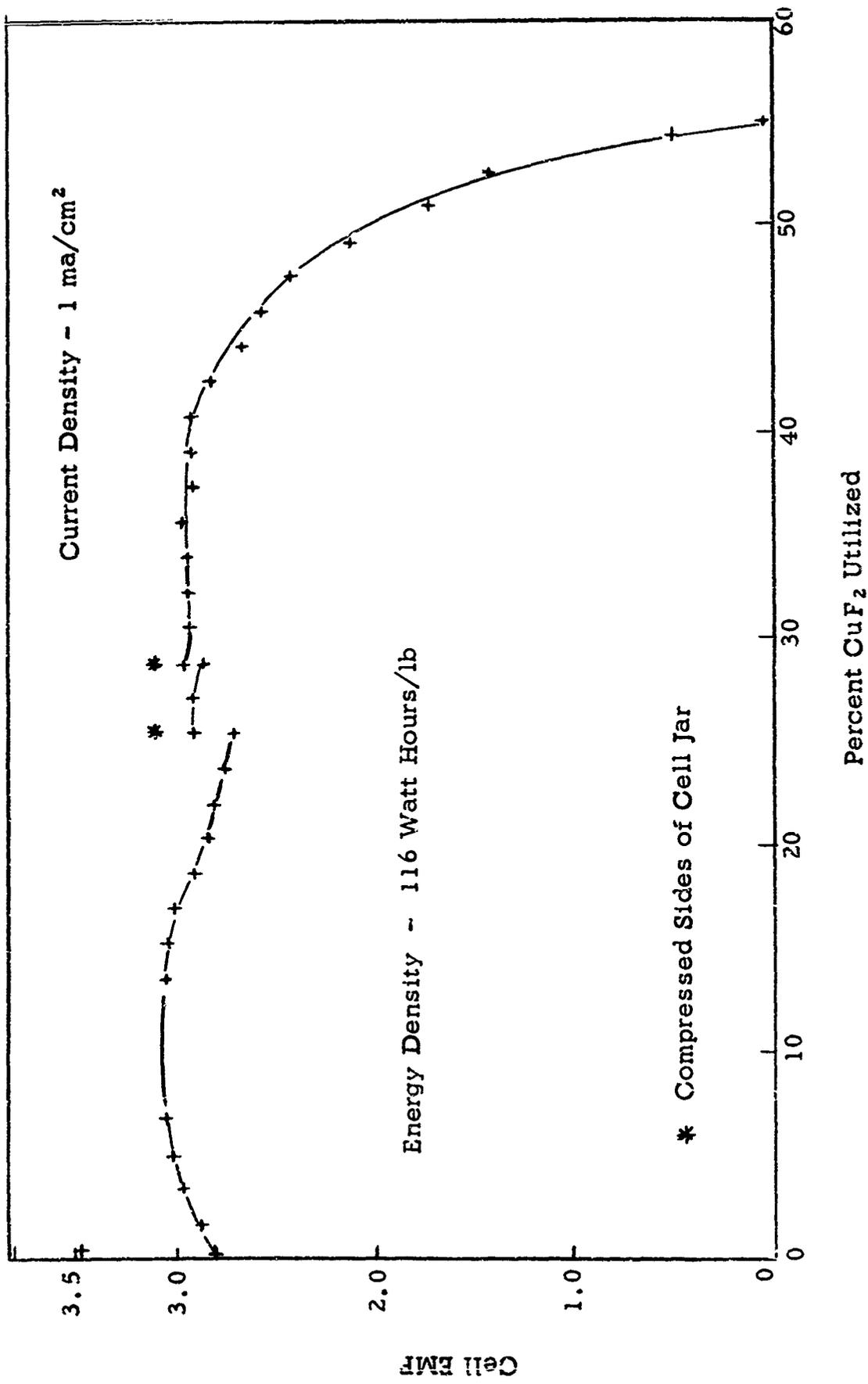
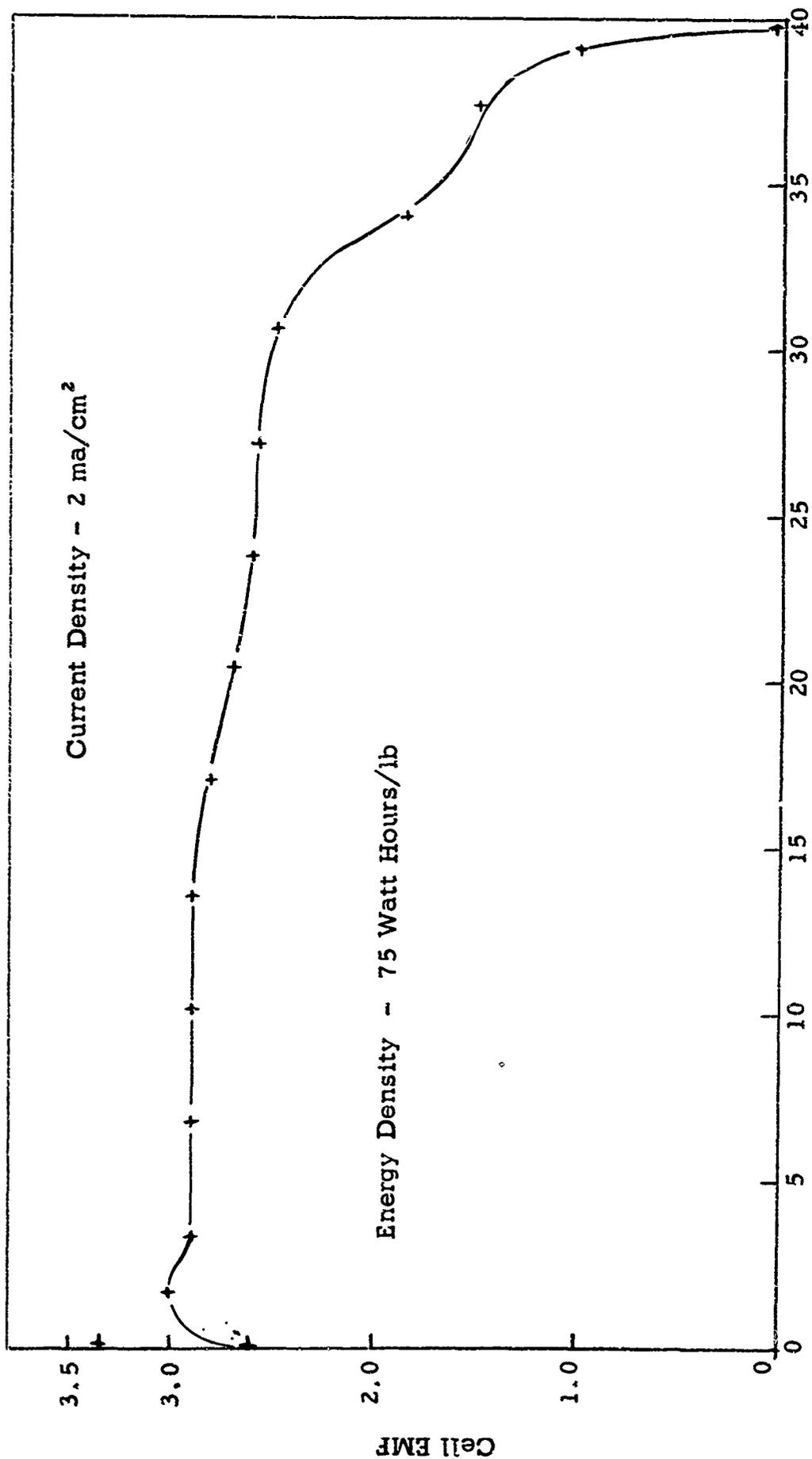


Figure 40

Discharge Characteristics of Li-CuF<sub>2</sub> Cell # C-1-9  
Lightweight Polyethylene Container  
9 Electrodes



Percent CuF<sub>2</sub> Utilized

Figure 41

## DOCUMENT CONTROL DATA - R&amp;D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) The Electric Storage Battery Company The Carl F. Norberg Research Center Yardley, Pennsylvania		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE  HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Quarterly - 15 December 1965 to 15 March 1966			
5. AUTHOR(S) (Last name, first name, initial)  Boden, D. P.; Buhner, H. R.; Spera, V. J.			
6. REPORT DATE June 1966		7a. TOTAL NO. OF PAGES 91	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. DA 28-043 AMC-01394(E)		9a. ORIGINATOR'S REPORT NUMBER(S) Report No. 3	
8b. PROJECT NO. 106 22001 A 053		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) ECOM-01394-3	
c. Task No. -02			
d. Subtask No. -32			
10. AVAILABILITY/LIMITATION NOTICES  Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES:		12. SPONSORING MILITARY ACTIVITY Commanding General U.S. Army Electronics Command Fort Monmouth, N.J. ATTN: AMSEL-KL-PB	
13. ABSTRACT The study of high energy density systems in the third quarter included: continued investigation of new electrolyte solvents; corrosion and solubility studies of cathode and anode materials in various electrolytes; a study of the reversibility of glass electrodes in non-aqueous electrolytes; continued efforts to optimize $\text{CuF}_2$ cathode performance; a study of the effect of electrolyte concentration and discharge current density on cathode performance; lithium anode storage tests; evaluation of various separator materials; construction and testing of $\text{Li-CuF}_2$ cells in lightweight polyethylene cases. In the evaluation of new electrolyte solvents, the highest specific conductance was obtained with solutions of $\text{LiClO}_4$ in 2-Pentanone, ethyl acetate, 2-Chloroethanol, and 2-4-Pentanedione, with values close to that obtained with propylene carbonate. However, none of the solvents tested this quarter was comparable to propylene carbonate with regard to compatibility with lithium. When compared to $\text{LiClO}_4$ , solutes such as $\text{KCNS}$ , $\text{AlCl}_3$ , and $\text{KPF}_6$ were found to yield higher specific conductance, in propylene carbonate, but poor cathode performance was obtained in these electrolytes. A study of the glass electrode showed that it was reversible to alkali metal ions in purely non-aqueous media, and should therefore be a useful reference electrode in non-aqueous electrochemistry. In addition, since no ions penetrate the glass, it should be stable over a long period of time.			

(Continued on Attached Sheet)

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High Energy Density Batteries Non-Aqueous Electrolyte Batteries Rate Capability Self-Discharge Charged Stand Capability Lithium Anode Copper Fluoride Cathode Separators Energy Density						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Abstract (DA 28-043 AMC-01394(E)) (Contd)

Continued efforts to optimize  $\text{CuF}_2$  cathode performance have shown that, consistent with good handling characteristics, an electrode material containing 87.5%  $\text{CuF}_2$ , 2.5% polyethylene, and 10% graphite, is the best thus far evaluated.

For a  $1\frac{1}{2}$  in. by 1-5/8 in. structure, it was found that the  $\text{CuF}_2$  cathode weight could be increased from two grams to three and four grams with an improvement of 20 to 24% in energy density.

In the evaluation of the effect of current density on cathode performance, the percent utilization of  $\text{CuF}_2$  was found to decrease from 82% at 1 ma/cm<sup>2</sup> to 32% at 5 ma/cm<sup>2</sup>.

A study of the effect of electrolyte concentration ( $\text{LiClO}_4$ /distilled propylene carbonate) on cathode performance revealed maximum efficiency at 1.25F. There was however, only a slight difference in efficiency in electrolytes ranging from 1.0 to 1.5F. Below about 0.75F performance was very poor.

Storage tests of pressed lithium foil anodes revealed that these electrodes could be stored for at least three months in paraffin oil or 1F  $\text{LiClO}_4$ /distilled propylene carbonate, with no appreciable loss in electrode discharge efficiency.

Separator screening tests have shown that lightly compacted, fibrous separators, such as glass or asbestos filter papers, and asbestos fuel cell papers are the best for use in the Li- $\text{CuF}_2$  cell.

Li- $\text{CuF}_2$  cells have been constructed having a maximum capability of 80 watt hours per pound, at a current density of 2 ma/cm<sup>2</sup>, and based on total cell weight, including case.

The stand characteristics of Li $\text{CuF}_2$  cells have been improved by the addition of complexing agents to the electrolyte. Copper dendrite formation can be prevented but all of the complexing agents thus far tested severely affect cathode performance, resulting in poor cell discharge performance, even in the absence of storage.