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HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

FINAL REPORT

BY

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

SEPTEMBER 1967

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TECHNICAL REPORT ECOM-02304-F

SEPTEMBER 1967

HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

FINAL REPORT

15 JUNE 1966 TO 14 JUNE 1967

REPORT NO. 8

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Prepared by

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For

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

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ABSTRACT

This report describes, in summary, the work conducted from June 15, 1966 to June 14, 1967 on Contract DA-28-043-AMC-02304(E) "High Energy System"(Organic Electrolyte). The major goal of this work was to improve the activated storage life and discharge rate capability of the Li/CuF₂ cell developed under Contract DA-28-043-AMC-01394(E). In addition, the scope was extended to include the investigation of new cathode material and electrolytes.

Electrolyte studies indicated that very few of the many prospective organic solvents and solutes tested were suitable, either because of low electrolytic conductances or incompatibility with the cell components. The most promising new solvents appeared to be propylene glycol sulfite and diethylene sulfite.

A reduction of more than an order of magnitude, in the solubility of CuF₂ in LiClO₄/P.C. solution, was effected by purification of LiClO₄ by recrystallization twice from distilled water and from anhydrous diethyl ether according to the method of Berglund and Sillen.

Studies of the rate of dissolution of CuF₂ in LiClO₄/P.C. electrolytes have not been conclusive, but it appears that the copper concentration increases with time over a period of one month, the longest interval thus far tested. It appears that a reaction between the electrolyte and the CuF₂, rather than a simple solubility function, may possibly be involved.

Studies of the CuF₂ cathode revealed that certain impurities in the graphite, used as a conducting additive, adversely affected performance on activated stand. This led to the purification of the graphite and the subsequent finding that activated stand was improved. A study of Li/CuF₂ cells with cathodes containing purified graphite then revealed that activated storage of cells was improved, but at the expense of high cathode polarization.

A program of separator and ion exchange membrane evaluation revealed that conventional microporous separators were incapable of preventing the transfer of soluble copper species and subsequent galvanic deposition of copper on the Li anode and resultant cell failure on activated storage. Ion exchange membranes were found to have prohibitively high resistivities, apparently because of inability to swell and absorb organic electrolytes.

The results of kinetic studies of the CuF₂ cathode discharge mechanism appear to indicate that the reaction is diffusion controlled. The high viscosity of the organic electrolyte (LiClO₄/P.C.) apparently adversely affects ionic mass transport of the species required to sustain the electrode reaction.

ABSTRACT (Cont'd.)

Voltammetric studies involving the use of a mercury pool cell were initiated to determine the copper species present in solution of CuF_2 in LiClO_4 / P. C. electrolyte. Preliminary results appear to indicate that the equations developed for aqueous system may be applied to organic systems.

LIST OF TABLES

1. Properties of Non-Aqueous Solvents
2. Solubility of CuF_2 in Various Electrolytes
3. Solubility of CuF_2 in Solutions of $\text{LiClO}_4/\text{P. C.}$
4. Theoretical Energy Densities of Various Couples
5. Coulombic Efficiency of Organic Cathodes
6. Results of Latin Square Experiment on Glass Floc Cathodes
7. Analyses of Results of Latin Square Experiment on Glass Floc Cathodes
8. Regression Equation for Effect of Floc on Utilization
9. Effect of Partially Hydrated CuF_2 on Cathode Performance
10. Spectrographic Analysis of Purified Graphite
11. Ion Exchange Membrane Characteristics in Organic Electrolyte
12. Characteristics of Polymer Films in Organic Electrolyte
13. Effect of Electrolyte Concentration and Current Density on Transition Time
14. Variation of Wave Height with Scanning Rate
15. Comparison of Various Inorganic Cathode Materials
16. Effect of Current Density on AgO Cathode Performance
17. Comparison of Organic Cathode Materials
18. Effect of Cathode Weight and Compacting Pressure on m-DNB Cathode Performance
19. Effect of Electrolyte and Current Density on CuF_2 Cathode Performance
20. Effect of Complexones and Activated Storage on CuF_2 Cathode Performance
21. Effect of Graphite Treatment, Compacting Pressure, and Activated Storage on CuF_2 Cathode Performance

LIST OF FIGURES

<u>Figure</u>	
1, 2	Conductance of LiClO_4 in Various Organic Solvents
3	Conductance of Solutions of Various Solutes in Propylene Carbonate
4	Conductance of $\text{BF}_3/\text{P.C.}$ Solutions
5	Conductance of LiClO_4 in $\text{BF}_3/\text{P.C.}$ Solutions
6	Conductance of LiClO_4 in $\text{BF}_3/\text{THF}/\text{P.C.}$ Solutions
7, 8, 9	Corrosion of Lithium in Various Electrolytes
10, 11	Rate of Dissolution of CuF_2 in Electrolyte
12, 13, 14, 15	Performance of Various Cathode Materials
16	Effect of Current Density on AgO Cathode Performance
17	Performance of AgO Cathodes in Various Electrolytes
18	Effect of Activated Storage on Li/AgO Cell Performance
19, 20	Evaluation of Various Organic Cathode Materials
21	Effect of Cathode Weight on Performance
22	Effect of Compacting Pressure on m - DNB Cathodes
23	Regression Line for the Effect of Percent Floe on CuF_2 Performance
24	Regression Line for the Effect of Compacting Pressure on CuF_2 Cathode Performance
25, 26, 27, 28, 29	Performance of CuF_2 Cathodes in Various Electrolytes
30	Effect of Ethylene Diamine Complexone on CuF_2 Cathode Performance

LIST OF FIGURES (Cont'd.)

<u>Figure</u>	
31	Effect of Diethylene Triamine Complexone on CuF_2 Cathode Performance
32	Effect of Complexones on Activated Storage of Li/ CuF_2 Cells
33	Effect of Water on CuF_2 Cathode Performance
34	Effect of CuF_2 Particle Size on Performance
35	Effect of Activated Storage on Cathode Performance
36	Effect of Activated Storage on Cathode Performance
37	Effect of Activated Stand on Cathode Performance - Nitric Acid treated Graphite
38	Effect of Activated Stand on Cathode Performance - HCl treated Graphite
39	Effect of Activated Stand on Cathode Performance - HCl/ HNO_3 treated Graphite
40, 41, 42	Effect of Graphite Purification on Activated Cell Stand Performance
43, 44, 45	Chronopotentiograms of CuF_2 Cathode Discharge
46	Typical Potential - Time Transient
47, 48, 49, 50	Current Sweep Voltammetric Curves
51	Mercury Pool Cell
52	Voltage - Time Sweep Apparatus
53	Block Diagram of Voltammetric Apparatus
54	Residual Current Curves in Various Electrolytes
55	Peak Current vs (Scanning Rate) ^{1/2}
56	Copper Concentration vs Diffusion Current

TABLE OF CONTENTS

Abstract.....	i
List of Tables.....	iii
List of Figures.....	iv
Introduction.....	1
Experimental.....	1
1. Electrolyte Studies.....	1
1.1 Choice of Organic Solvents.....	1
1.2 Investigation of New Electrolyte Solutes.....	2
1.3 Determination of Conductance.....	2
1.4 Corrosion and Solubility Studies.....	3
1.4.1 Corrosion of Lithium in Various Electrolytes	4
1.4.2 Solubility of CuF_2 in Various Electrolytes	4
1.4.3 Solubility of CuF_2 in $\text{LiClO}_4/\text{P.C.}$ Solution.....	4
1.4.4 Rate of Dissolution of CuF_2 in $1\text{F LiClO}_4/\text{P.C.}$ Solution..	5
2. Cathode Studies.....	6
2.1 Selection of Cathode Materials for Screening.....	6
2.2 Screening tests of Inorganic Cathode Materials.....	7
2.3 Extended Evaluation of AgO Cathodes.....	7
2.4 Screening Tests of Organic Cathode Materials.....	9
2.5 Studies of CuF_2 Cathodes.....	11
2.5.1 Optimization of Cathodes Containing Glass Floc.....	11
2.5.2 Effect of Various New Electrolytes on CuF_2 Cathode Performance.....	17

TABLE OF CONTENTS (Cont'd.)

2.5.3	Effect of Complexones on CuF_2 Cathode Performance....	13
2.5.4	Effect of Water on CuF_2 Cathode Performance.....	14
2.5.5	Effect of CuF_2 Particle Size on Cathode Performance....	14
2.5.6	Effect of Storage in Electrolyte on CuF_2 Cathode Performance.....	15
2.5.7	Purification of Graphite.....	16
2.5.7.2	Effect of Graphite Purification on Cathode Activated Stand.....	16
2.5.7.3	Effect of Graphite Purification on the Activated Storage of Li/CuF_2 Cells.....	17
3.	Separator Studies.....	19
3.1	Evaluation of Porothene Separators.....	19
3.2	Evaluation of Ion Exchange Membranes.....	20
3.3	Evaluation of Polymeric Films as Membranes.....	20
4.	Kinetic Studies of the CuF_2 Cathode.....	21
4.1	Chronopotentiometric Method.....	21
4.2	Current Sweep Voltammetry.....	22
5.	Voltammetry in a Quiet Mercury Pool.....	23
	Appendix A - Purification of LiClO_4	25
	Appendix B - Purification of Propylene Carbonate.....	29
	Appendix C - Rate of Corrosion of Lithium.....	30
	Appendix D - Determination of Solubility of CuF_2	1
	Appendix E - Cathode Fabrication; Anode Fabrication.....	32

TABLE OF CONTENTS (Cont'd.)

Appendix F - Cathode Testing 33

Appendix G - Purification of Graphite 34

List of Materials and Suppliers..... 35, 36, 37

List of References..... 38

INTRODUCTION

This report describes the work done on Contract DA-28-043-AMC-02304 (E) High Energy System (Organic Electrolyte). Lithium/cupric fluoride cells were developed in a previous contract (DA-28-043-AMC-01394 (E)) which, activated with 1 F LiClO₄/propylene carbonate electrolyte, were capable of delivering about 120 watt-hrs./lb. of total cell. However, this system had the disadvantages of a short activated storage life and discharge rates limited to about 2 ma/cm².

The present program was initiated to solve the aforementioned shortcomings, and to extend the scope of investigations to other promising cathode materials and electrolyte systems. Studies were made of the rate and extent of solubility of CuF₂ in LiClO₄/propylene carbonate solution, in an attempt to reduce the solubility to the lowest level. The kinetics of the CuF₂ discharge reaction were investigated to understand the rate limiting process. Various separators and ion exchange materials were evaluated in an effort to find a material capable of improving the activated storage life of the Li/CuF₂ cell.

Techniques were developed for purifying the electrolyte and graphite used in these studies.

EXPERIMENTAL

1. Electrolyte Studies

Although superior to other organic electrolytes in certain respects, there are two important disadvantages of LiClO₄/propylene carbonate electrolyte when used with the Li/CuF₂ couple. Good electrode performance is allowed only at low rates (2 ma/cm²), the performance decreasing rapidly as the current density is increased. It was thought that an electrolyte with a lower viscosity and a higher conductivity would allow higher cathode efficiencies than obtained previously. Another problem, associated with the CuF₂ cathode, has been the insolubility of LiF formed at the cathode during discharge. This results in a blockage of the pores which limits mass transfer of electrolyte species to the reaction sites and results in a reduced cathode efficiency. Therefore, a search was made for other solvents and electrolyte salts in an attempt to find a system with high conductivity, low viscosity, inertness toward the electrode materials and a capability of dissolving the cathode reaction products.

1.1 Choice of Organic Solvents

The solvents selected for study were chosen on the basis of their physical properties, particularly their dielectric constants and viscosities, the most important parameters influencing the conductance of solutions. In addition, several solvents were selected on the basis of work done by other investig-

ators of nonaqueous electrolytes (1, 2) The physical properties of the solvents chosen are shown in Table 1.

1.2 Investigation of New Electrolyte Solutes

A large number of organic and inorganic salts have been found to be soluble in organic solvents to give conducting solutions. Only a few of these electrolytes have been found to have the combination of characteristics required of a solution to be used in a high energy system such as the Li/CuF₂ couple.

In an attempt to produce an electrolyte having the desired properties, electrolyte studies were extended to include the following solutes: LiBF₄, Mg(ClO₄)₂, Mg(SCN)₂, LiPF₆, Li₂CO₃, Li₂SO₄, CaCO₃, CaCl₂, CaSO₄, MgCO₃, MgSO₄, MgCl₂, AlF₃ and (CH₃)₄NBF₄. Also, because of the finding that LiF will dissolve in a solution of BF₃ in propylene carbonate (3), it was decided to investigate BF₃ as a new solute.

1.3 Determination of Conductance

1.3.1 Solutions of LiClO₄ in Various Solvents

In evaluating the solvents selected for study, only LiClO₄ was used as a solute. The solvents were the purest commercially available and were not further purified. In the work with the following solvents the LiClO₄ was not purified, but was simply dried at 120°C under vacuum for 16 hours: diethyl sulfite, 1-chloro-2-propanone, methyl cyanoacetate, crotonitrile, 1-nitropropane, 2-nitropropane, 2,2-dichloro diethyl ether, methyl nitrate, and lactonitrile. The LiClO₄ used in the remaining solvents was purified as described in Appendix A.

It was found that methyl nitrate, 1-nitropropane, 2-nitropropane, 2,2-dichlorodiethyl ether, and 1,4-dioxane were poor solvents, dissolving less than 0.1 F. LiClO₄, and their use was discontinued. It was found that d-xylitol and succinonitrile were solids at room temperature and it was thought to be impractical to consider them as solvents.

Solutions were prepared over a wide concentration range and their conductivities were measured using a Kraus and Bray type cell in conjunction with a 1000 cycle A.C. Bridge (E. S. 1 Universal Impedance Bridge, Model 290 R).

The results of this experiment are shown in Figures 1 and 2. The highest conductivities, about 10^{-2} ohm⁻¹cm⁻¹, were obtained in lactonitrile, 1,3-dioxolane, and 1,2-propylene glycol sulfite. Conductivities comparable to that obtained in propylene carbonate, about 7×10^{-3} ohm⁻¹cm⁻¹, were obtained in 2,5-dihydrofuran, tetramethylurea and 1-chloro-2-propanone. A high solubility of LiClO₄ was found in triethyl phosphite (about 3F), and the

conductivity was found to increase steadily over this range of concentration. However, the highest conductance was only about $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$.

1.3.2 Solutions of Various Electrolyte Solutes in Propylene Carbonate

In the investigation of new electrolyte solutes, the salts were the purest commercially available. They were dried at 110°C under vacuum for 16 hours before use. Solutions were prepared over a wide concentration range using distilled propylene carbonate (appendix B) as the solvent. The solubility of Li_2CO_3 , Li_2SO_4 , AlF_3 , CaCO_3 , CaCl_2 , CaSO_4 , MgCO_3 , MgSO_4 and MgCl_2 was found to be poor, and the use of these materials was discontinued. The specific conductance of the solutions was measured as described in section 1.3.1.

The results of this experiment are shown in Figure 3. The highest conductivities were obtained with LiPF_6 and $\text{Mg}(\text{ClO}_4)_2$, (5 to $6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$), followed by LiBF_4 and $(\text{CH}_3)_4\text{NBF}_4$ (2.5 to $3.5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$) and finally by $\text{Mg}(\text{SCN})_2$ with a conductivity of about $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. With $(\text{CH}_3)_4\text{NBF}_4$, saturation was reached at about 0.25F concentration.

Boron trifluoride (BF_3) was obtained in two forms: (i) as a c. p. grade gas and (ii) as a complex in a 1:1 molar ratio with tetrahydrofuran (THF). Solutions of the BF_3/THF complex and of gaseous BF_3 respectively were made in purified propylene carbonate. These solutions were found to have a poor conductivity, with a maximum of $4 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ in a 2F solution. It was therefore decided to add LiClO_4 to these solutions as a supporting electrolyte in order to obtain higher conductivities. Solutions of LiClO_4 in 5, 10 and 20 volume percent BF_3/THF in propylene carbonate and in 2F $\text{BF}_3/\text{propylene carbonate}$ were made over a range of LiClO_4 concentrations.

The results of these experiments are shown in Figures 4, 5, and 6. The conductivity of solutions of $\text{BF}_3/\text{P.C.}$ increases as the concentration of solute increases, reaching a maximum of about $3.4 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ in 2F solution, and then decreases as the solution concentration is further increased. Addition of LiClO_4 to $\text{BF}_3/\text{P.C.}$ solutions results in a large increase in conductivity, reaching a maximum of about $3.4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in solutions containing about 0.75F LiClO_4 in 2F $\text{BF}_3/\text{P.C.}$ Generally, the same behavior is observed in solutions of LiClO_4 in BF_3/THF complex in propylene carbonate. It can be seen that an increase in BF_3 concentration reduces the conductance of solutions with the same LiClO_4 concentration.

1.4 Corrosion and Solubility Studies

For any electrochemical couple, it is important that the electrodes and electrolyte be compatible, especially with regard to an activated stand application. The activated storage life of the Li/CuF_2 cell has been seriously curtailed by excessive solubility of the CuF_2 in all of the electrolytes evaluated, with consequent galvanic deposition of copper on the anode and re-

sultant cell failure. In other instances the lithium anode has been found to be rapidly attacked by the electrolyte. Therefore, it is essential that corrosion and solubility studies be conducted to determine the overall system compatibility.

1.4.1 Corrosion of Lithium in Various Electrolytes

The rate of corrosion of lithium in the electrolytes described above was determined using the microgassing technique described in Appendix C.

The results of this study are shown in Figures 7, 8, and 9. The corrosion rate was high in the majority of electrolytes, and would preclude their use in cells having activated storage applications. Among the new solvents, the only materials comparable to propylene carbonate, with regard to compatibility with lithium, were propylene glycol sulfite and diethyl sulfite. Among the new solutes, the only one comparable to LiClO_4 was $\text{Mg}(\text{ClO}_4)_2$.

1.4.2 Solubility of CuF_2 in Various Electrolytes

The solubility of CuF_2 was evaluated in various electrolytes, using the technique described in Appendix D. The results of this experiment are shown in Table 2. With one exception, the solubility of CuF_2 was much higher in the new electrolytes than in 1F $\text{LiClO}_4/\text{P.C.}$ In $\text{Mg}(\text{ClO}_4)_2/\text{P.C.}$ the CuF_2 solubility was about a half of that found in the $\text{LiClO}_4/\text{P.C.}$ solution. In the BF_3/THF complex in $\text{LiClO}_4/\text{P.C.}$ solution, the CuF_2 solubility increased about 50% as the concentration of complex was increased from 5% to 10%. It should be noted that the LiClO_4 used in this study was not purified. The solubility of CuF_2 has been found to be higher in solutions containing impure LiClO_4 compared to those containing purified LiClO_4 .

1.4.3 Solubility of CuF_2 in Solutions of LiClO_4 /propylene carbonate

A still unresolved problem is the solubility of CuF_2 in $\text{LiClO}_4/\text{P.C.}$ solution. This solubility has been shown to adversely affect the activated storage capability of the Li/CuF_2 cell. Therefore, experiments were conducted to determine if the CuF_2 is inherently soluble in the electrolyte, or whether certain impurities in the LiClO_4 and/or the propylene carbonate promote this solubility.

1.4.3.1 Purification of Materials

In this study two methods of purifying LiClO_4 were investigated. In one method (designated as Method #1 LiClO_4) the salt was treated as described in Appendix A-1 and A-2. In another method (designated as Method #2 LiClO_4) the salt was prepared according to techniques described in Appendix A-1 to A-4. The ether treatment was used to produce a more completely anhydrous salt, according to the findings of other investigators(4).

The propylene carbonate used in the preparation of all solutions was purified as described in Appendix B.

1.4.3.2 Preparation of Solution

Solutions of LiClO_4 in propylene carbonate was prepared over a wide concentration range: 2×10^{-3} to 1.0 F. The anhydrous CuF_2 was treated at 60°C under vacuum to remove any volatile impurities. The CuF_2 was added to the respective solutions and the experiment conducted as described in Appendix D.

The results of this study are shown in Table 3. In general, there was an increase in CuF_2 solubility as the concentration of LiClO_4 was increased. A comparison of the results obtained with Method #1 and Method #2 LiClO_4 indicate that there is little difference in CuF_2 solubility due to the method of purifying the LiClO_4 . It appears that the ether treatment (Method #2) has little or no effect on CuF_2 solubility. Purification of the LiClO_4 , however, by recrystallization from water, does appear to be important in reducing CuF_2 solubility. Previous experiments have shown a CuF_2 solubility of 300 mg./liter in 1F LiClO_4 /P.C. in which the LiClO_4 was used as received, and in which the propylene carbonate was doubly distilled (5).

1.4.4 Rate of Dissolution of CuF_2 in 1F LiClO_4 /P.C.

This study was conducted to determine the rate of dissolution of CuF_2 in 1F LiClO_4 /P.C. electrolyte. It was thought that the results would give some indication whether the solubility was simply that of a sparingly soluble salt or due to a reaction between the electrolyte and the salt. It was assumed that a simple solubility mechanism would be shown by a solubility-time function, leading to a constant copper concentration after a relatively short time as the solution became saturated.

1.4.4.1 Experimental

The first experiment was conducted in the third quarter (6). Anhydrous CuF_2 was dispersed in 400 ml. of 1F LiClO_4 /P.C. (purified) in a one liter flask. The system was thermostated at 25°C in a water bath. Dry argon was bubbled through the solution to maintain dispersion of the CuF_2 , and to provide a dry, inert atmosphere over the solution. Samples, not replicated, were removed at intervals and filtered. The filtrate was analyzed to determine the concentration of dissolved copper. The results of this experiment are shown in Figure 10. It would appear from these results that the concentration continues to increase for a long period of time in a linear manner. However, in this experiment, the volume of solution was gradually depleted

as samples were withdrawn, and it was thought that this might have had an effect on solubility. If the rate of dissolution is dependent on the total volume of solution at any time, then the results might have been affected by this variable. Therefore, another experiment was designed in which the volumes of solution were invariant during the test. Approximately 40 ml. of 1F $\text{LiClO}_4/\text{P.C.}$ (purified) were placed in 50 ml. glass ampoules which were then flame sealed. The ampoules were then placed in a special holder in a water bath thermostated at 25°C. The holder rotated continuously at a constant rate, thereby maintaining dispersion of the CuF_2 . Samples, in replicates of two, were removed at intervals over a period of one month. The solutions were filtered twice, under argon, through highly retentive filter paper. The filtrate was then analyzed for dissolved copper (Appendix D). The results of this experiment are shown in Figure 11. There was a considerable scatter of data in certain areas which required that the results be analyzed by a Least Squares fit. In Figure 11, showing a linear relationship, the regression equation produced a line showing a much lower rate of dissolution than that obtained in the first experiment (Fig. 10). The scatter of data in the second experiment is not understood since the test was performed with care. This experiment will have to be repeated before interpretation is possible.

2. Cathode Studies

A major portion of the work in this contract involved the study and optimization of the CuF_2 cathode. However, it was considered advisable to examine other cathode salts so that the work would not encompass too narrow a spectrum, and thereby neglect possibly promising materials. Therefore, a rapid screening program was conducted to evaluate the relative electrochemical properties of various new inorganic and organic cathode materials.

2.1 Selection of New Cathode Materials for Screening

As an arbitrary criterion of acceptance, only cathodes with theoretical energy densities greater than 450 watt-hrs./lb., when coupled with lithium, were taken for consideration. The theoretical cell voltage and energy densities of various couples are shown in Table 4.

With regard to organic cathode materials, their cathodic properties are imparted by certain electron withdrawing substituents, the most powerful of which appears to be the nitro group, as contained for example in dinitrobenzene (DNB). Theoretically, a twelve electron change or about 1.9 ampere hours/gram of DNB is possible for this material. Other organic (cathode) materials of high coulombic capacity are picric acid, ADCA *, and BBFOS (bis benzofuroxane sulphone). The electrochemical characteristics of these materials are evaluated in non-aqueous electrolytes in this contract.

*a proprietary compound

2.2 Screening Tests of Inorganic Cathode Materials

The respective inorganic cathode materials (-170 mesh) were fabricated into electrodes as described in Appendix E and tested in three-plate cells as described in Appendix F. The cells were filled with 1F LiClO₄/P. C. (purified) and discharged at 2 ma/cm².

The results of this experiment are shown in Figures 12, 13, 14 and 15. Only a small percentage of the theoretical coulombic capacity was obtained in most instances, with the exception of AgO which yielded almost 100% of the theoretical capacity. Only AgO was considered to be worthy of further investigation on the basis of these screening tests.

2.3 Extended Evaluation of AgO Cathodes

The following experiments were conducted to evaluate the effect of fabrication and operating parameters on AgO cathode performance.

2.3.1 Investigation of Fabrication Parameters by the Latin Square Method

This study was conducted to determine the most significant factors in the preparation of AgO cathodes. A Latin Square experiment was conducted encompassing three variables, each at four levels. They were:

- (i) Compacting Pressure - 100, 300, 500, 700 #/cm²
- (ii) Percent Graphite - 2, 8, 14, 20
- (iii) Percent Polyethylene - 1, 3, 5, 7

Cathode fabrication and testing were as described in Appendices E and F, except for the blend ratios and compacting pressure variations as described above. Testing was done with 1F LiClO₄/P. C. (purified) at 2 ma/cm².

It was found in an analysis of the data, using the average energy density of two replicate electrodes as the criterion of performance, that all of the parameters were significant at a 95% confidence level. By the use of regression equations it was found that the variation of compacting pressures over the range tested was of little significance, and that an increase in both, graphite and polyethylene contents decreased performance.

2.3.2 Effect of Discharge Current Density on Performance

Cathodes were made as described in Appendix E using -170 mesh AgO. They were tested in cells made as described in Appendix F, using 1F LiClO₄/P. C. (purified) electrolyte. Discharges were conducted at 2, 3, 4 and 5 ma/cm², with replicates of two electrodes at the respective current densities.

The results of this test are shown in Figure 16. It can be seen that the per-

formance decreased as the current density was increased from a utilization of 95% at 2 ma/cm² to 46% at 5 ma/cm².

2.3.3 Effect of Various Electrolytes on AgO Cathode Performance

Electrolytes containing dimethyl carbonate and dimethyl sulfite, solvents with lower viscosities than propylene carbonate, were evaluated in this experiment. This was an attempt to increase mass transport of reactive electrolyte species and thereby improve cathode efficiency.

Cathodes were made as described in section 2.3.2 and tested in three plate cells made as previously described. Replicates of two cells were filled with respectively 1F LiClO₄/P.C. (purified), and 2F LiClO₄/dimethyl carbonate (purified LiClO₄), and 1.5F LiClO₄/dimethyl sulfite (purified LiClO₄). The electrodes were discharged at 2 ma/cm²

The results of this experiment are shown in Figure 17. The coulombic efficiency of AgO was almost identical in the three electrolytes, but cathode potentials were generally higher with electrolytes containing dimethyl carbonate and dimethyl sulfite. It appears that an improvement in the rate of ionic mass transport, as effected by the use of electrolyte solvents with lower viscosity than propylene carbonate, results in an improvement in cathode performance.

2.3.4 Effect of Activated Storage on Li/AgO Cell Performance

The activated storage capability of Li/AgO cells was determined using cells of three plate construction, filled with 1F LiClO₄/P.C. (purified) electrolyte. The cells, in replicates of two, were stored under argon, over a drying agent, for two weeks. After storage the cells were discharged at 2 ma/cm².

The results of this test are shown in Figure 18. Only about 10% coulombic efficiency was obtained, compared with the usual 90-100% for unstored cells. Upon cell inspection a heavy black deposit was found on the anodes and in the separator. This was interpreted to be silver.

In conclusion, AgO has been found to perform with almost 100% coulombic efficiency in electrolytes containing LiClO₄ in propylene carbonate, dimethyl carbonate or dimethyl sulfite. The cathode is limited to low rate discharges (about 2 ma/cm²) as was found for the CuF₂ cathode, when using LiClO₄/P.C. electrolyte. Apparently the cathode can be made using little or no binder or conductive graphite and perform very efficiently. The activated storage life of Li/AgO cells is poor, apparently because of the solubility of AgO, resulting in galvanic deposition of silver on the anode, penetration of the separator, and finally cell failure.

2.4 Screening Tests of Organic Cathode Materials

2.4.1 Preparation and Testing of Pasted Type Cathodes

A blend of equal parts by weight of organic cathode material and Columblan Carbon (Type SA-40-220) was made, and a paste formulated by the addition of 1F $\text{LiClO}_4/\text{P.C.}$ (purified) electrolyte. The paste was applied to an expanded copper screen (Appendix E-2). The electrode contained about 0.25 grams of organic cathode material. The cathodes, while wet, were insulated with 30 mils of glass fiber filter paper and assembled against lithium anodes. The cells were filled with 1F $\text{LiClO}_4/\text{P.C.}$ (purified) and discharged at 2 ma/cm². In another experiment the electrodes and cells were made as described above, but were discharged using 2F $\text{LiClO}_4/\text{dimethyl carbonate}$ electrolyte.

The results of these experiments are shown in Table 5 and Figures 19 and 20. A large increase in cathode efficiency was obtained when dimethyl carbonate was substituted for propylene carbonate as an electrolyte solvent. An apparent efficiency of 140% was obtained with BBFOS when discharged in 2F $\text{LiClO}_4/\text{DMC}$. The theoretical capacity of this material is based on reactions known to occur in aqueous electrolytes. This result appears to indicate that a greater degree of reduction can occur in non-aqueous environment.

In 2F $\text{LiClO}_4/\text{dimethyl carbonate}$ the best performance was obtained with m-DNB, with a fairly flat operating potential up to 1 amp. hr./gram, and then a gradually decreasing potential thereafter.

2.4.2 Effect of Cathode Weight on Performance (Pasted Electrodes)

Cathodes were made as described above, with replicates of two containing respectively 0.25 and 0.50 grams of m-DNB. They were discharged in three plate cells against lithium anodes, using 2F $\text{LiClO}_4/\text{dimethyl carbonate}$ electrolyte and a current density of 2 ma/cm².

The result of this experiment is shown in Figure 21. Cathode efficiency was greatly reduced when the weight of active material was increased. As a result, the capacity of electrodes containing 0.25 grams of m-DNB was about 40% greater than that of electrodes with twice as much active material. This unusual behavior has been attributed to a dependence of electrode efficiency on the ratio of electrolyte volume to active material weight. This may seriously limit the energy density of the Li/m-DNB couple if a large excess of electrolyte is required to efficiently discharge the cathode.

If the energy density of the Li/m-DNB cell is compared with that obtained from a typical Li/CuF₂ cell the following is obtained:

<u>Couple</u>	<u>Energy Density (watt-hrs. /lb.)</u>	
	<u>Active Materials Consumed</u>	<u>Total Electrode Material</u>
Li/CuF ₂	605	370
Li/ m-DNB	790	315

These values for m-DNB cathodes appear to be promising, but it must be considered that the weight of electrolyte has not been included in these calculations. If the organic cathode requires a large ratio of electrolyte volume/active material weight for maximum efficiency the energy density will be adversely affected in the final analysis.

2.4.3 Pressed Dry Powder Organic Cathodes

In this experiment m-DNB cathodes were made by die-pressing a blend of organic cathode material and Columbian carbon. This was an attempt to obtain better weight and thickness control than was possible with pasted electrodes. Also, with a dry cathode, there would be better handling and storage capability than was possible with pasted electrodes.

A dry blend containing equal parts by weight m-DNB and Columbian carbon was made. To this blend, dimethyl carbonate was added to produce a heavy paste. The m-DNB is soluble in the solvent and appears to be adsorbed by the activated carbon. The paste was then dried at room temperature under vacuum. Cathodes were made by die-pressing, at room temperature, one gram of dry blend (0.5 gm. m-DNB), using a retaining screen of 5 Cu 14-2/0 expanded copper with dimensions 1-1/2" x 1-5/8". Electrodes, in replicates of two, were made at each of the following compacting pressures: 133, 333 and 1000 lbs./cm². The electrodes were tested in three-plate cells of the type previously described. The cells were filled with 2F LiClO₄/dimethyl carbonate and discharged at 2 ma/cm².

The results of this experiment are shown in Figure 22. Maximum performance was obtained at 333 lbs./cm², with results comparable to those obtained with pasted m-DNB cathodes containing the same weight of active material. This technique has the advantages of ease of electrode fabrication and a storage capability for the cathodes.

In conclusion, it has been found that certain organic cathode materials will discharge in non-aqueous electrolytes with very high efficiencies. Dinitrobenzene yielded the highest coulombic capacity, 1.8 amp. hrs./gram, with an efficiency of 94%. The cathode efficiency appears to be a function of both the type of electrolyte and the amount of electrolyte per unit weight of cathode material. A much higher efficiency is obtained with dimethyl carbonate than with propylene carbonate as the electrolyte solvent. A high energy density

is obtained on the basis of active materials consumed for the Li/m-DNB couple: 790 watt-hrs./lb. as compared with 605 watt-hrs./lb. for the Li/CuF₂ cell. However, a large ratio of electrolyte volume to active material weight appears to be required for high efficiency, and this may adversely affect energy density in the final analysis.

2.5 Studies of CuF₂ Cathodes

2.5.1 Optimization of Cathodes Containing Glass Floc

This study was undertaken to determine which factors are the most significant in the preparation of CuF₂ electrodes containing glass floc, and to determine their effect on the performance of the electrode. A mix of CuF₂ (-170 mesh) and 10% graphite (Southwestern 1651) was used as the standard active cathode material. All work was done under argon, and the powders were mixed on a Fisher-Kendall mixer for 2.5 hours. The glass floc was prepared by chopping glass filter paper in a blender for 10 seconds. The prescribed amount of floc was added to the active cupric fluoride mix and blended (as above) for various time intervals. Three preparative variables, each at four levels, were investigated as shown below.

Percent Floc	0.25, 0.50, 1.0, 2.0%
Compacting Pressure	500, 1000, 2000, 3000 lbs./cm ²
Blending Time	5, 10, 15, 20 sec.

The blended powder was pressed onto 5 Cu 14 2/0 expanded copper screen at the various pressures, and room temperature. The electrodes (1-1/2 in. x 1-5/8 in.) contained approximately 1.9 gm. of active material; they were discharged in an electrolyte of 1M LiClO₄ in distilled propylene carbonate at a current density of 2 ma per square cm (60 ma). Replicates of two electrodes for each test variable were evaluated as described in Appendix F. The average percent utilization of two electrodes was used as the criterion of performance.

The results are shown in Table 6, and the analysis is shown in Table 7. It is concluded that the percent floc and the compacting pressure significantly affect the percent utilization whereas blending time has little effect. Confidence limits were computed with the result that the true average values lay within 8.4% of the experimental value.

To find the affect of changing the independent variable (% Floc, blending time, or compacting pressure) on the utilization, it was necessary to calculate and plot regression equations. The method is illustrated in Table 8 for electrodes containing different amounts of glass floc.

The regression equation for the effect of the % floc on the percent utilization was $y = 38.72 - 4.13 x$. The independent value x is the percent floc, and y is the percent utilization. This equation is plotted in Figure 23. An increase in the percent floc decreases the utilization.

The calculated equation for the effect of compacting pressure on performance was $y = 48.7 - 0.0085 x$.

y = percent utilization
 x = compacting pressure (lbs. per cm^2)

The regression equation is plotted in Figure 24 with observed average values. An increase in pressure causes a very noticeable decrease in utilization.

2.5.2 Effect of Various New Electrolytes on CuF_2 Cathode Performance

This experiment was conducted to determine the effect of several new electrolytes on the performance of the CuF_2 cathode. In certain instances also the effect of current density on performance was determined.

The following electrolytes were evaluated:

- i) 0.75F LiBF_4 / distilled propylene carbonate
- ii) 0.5F $\text{Mg}(\text{ClO}_4)_2$ / distilled propylene carbonate
- iii) 1.0F LiClO_4 in 5% BF_3 / THF complex in distilled P. C.
- iv) 1.0F LiClO_4 in 10% BF_3 / THF complex in distilled P. C.
- v) 2.0F LiClO_4 / dimethyl carbonate

Three-plate Li/CuF_2 cells were used in the evaluation of these electrolytes, with plate and cell construction as described in Appendices E and F. The cells, in replicates of two, were activated with the respective electrolytes and discharges, generally at $2 \text{ ma}/\text{cm}^2$, except where current density studies were made, i. e. 10% BF_3 / THF complex and dimethyl carbonate electrolytes.

The results of these experiments are shown in Figures 25 to 29 inclusive. In dimethyl carbonate solution the coulombic efficiency ranged from 80% at $3 \text{ ma}/\text{cm}^2$ to only 35% at $10 \text{ ma}/\text{cm}^2$. The performance obtained at $5 \text{ ma}/\text{cm}^2$ in this electrolyte was comparable to that found at $2 \text{ ma}/\text{cm}^2$ in LiClO_4 / P. C. electrolyte, or more than a 100% improvement in rate capability.

An average coulombic efficiency of about 32% was obtained in a solution of 0.75 LiBF_4 / P. C. electrolyte. This was only about half of that obtained in LiClO_4 / P. C. electrolyte.

The performance in $\text{Mg}(\text{ClO}_4)_2$ / P. C. electrolyte was very poor, with less than 2% coulombic efficiency of CuF_2 .

In electrolytes containing BF_3/THF complex, the performance was generally poorly reproducible, with cathode potentials fluctuating excessively, causing the result to be inconclusive in many instances. A 2 ma/cm^2 , a coulombic efficiency of about 52% was obtained in electrolyte with 5% BF_3/THF complex, and possibly a slightly higher performance in the 10% BF_3/THF solution, but this is uncertain, again because of difficulty in interpreting voltage data. The results of the experiment concerning the effect of current density, in solutions containing 10% BF_3/THF complex indicate generally a decrease in performance as current density was increased: approximately 100% coulombic efficiency at 4 ma/cm^2 to about 20% efficiency at 8 ma/cm^2 . There was again extreme voltage fluctuation making interpretation of data somewhat unreliable.

In conclusion, the results of evaluation of several new electrolytes, with respect to their effect on CuF_2 cathode performance, indicate that $\text{LiClO}_4/\text{dimethyl carbonate}$ solutions are the most promising. A rate improvement of more than 100% was obtained compared with the performance of CuF_2 cathode in $\text{LiClO}_4/\text{P.C.}$ electrolyte. Solutions of LiClO_4 in BF_3/THF complex in propylene carbonate may have some promise, but the extreme voltage fluctuations obtained in discharge make these solutions, as presently formulated, of somewhat questionable practical value.

2.5.3 Effect of Complexones on CuF_2 Cathode Performance

This work was done to improve the activated stand performance of cells. Complexones were added to the electrolyte to combine with copper ions; and therefore, the formation of copper dendrites in the separator could be prevented, and the activated stand life of the cell could be increased.

A search of literature revealed that the complexones, ethylene diamine and diethylene triamine, had high stability constants with cupric ion in aqueous solutions. These complexones were tested in Li/CuF_2 cells using purified electrolyte (1M LiClO_4 in P.C.) and purified graphite (Appendices A, B, and G). The complexone concentration in the electrolyte ranged from 0.01 to 0.5% by volume. The effect of various concentrations of ethylene diamine and diethylene triamine, respectively, on cell performance (no storage) is shown in Figures 30 and 31. In general, an increase in complexone concentration resulted in a large decrease in cell performance. There was approximately a 70% loss in utilization in going from 0.01 to 0.1% ethylene diamine, and about a 30% loss in going from 0.01 to 0.5% diethylene triamine.

The results obtained after a one week activated stand of cells containing 0.05% of the respective complexones in the electrolyte during storage are shown in Figure 32. The performance of control cells and that of cells with diethylene triamine and ethylene diamine was poor. Any beneficial effect of the complexones in improving the activated storage of Li/CuF₂ cells is minimal and would be of little practical value.

2.5.4 Effect of Water in CuF₂ on Cathode Performance

This study was conducted to determine the effect, on cathode performance, of the addition to the CuF₂ of small amounts of water. Since water is often present to some degree in either the electrolyte or the cathode salt, it was thought to be desirable to determine whether small amounts had any effect on the reproducibility and performance of the electrodes.

Anhydrous CuF₂ (-170 mesh) was placed in an evaporating dish over a steam bath and agitated continuously for various intervals, and the amount of water absorbed determined by weight difference. Various controlled amounts of water, between 0.25 and 2.0%, were added, and the partially hydrated salts were used to prepare cathode blends. The blend and cathode preparation was described in Appendix E. As a control test, anhydrous CuF₂ as received, and after heating under vacuum was used in preparation of electrodes. Replicates of two electrodes, for each variable tested, were discharged at 2 ma/cm², in three-plate Li/CuF₂ cells, using 1F LiClO₄/propylene carbonate (purified) electrolyte (see Appendix F).

The results of this experiment are shown in Table 9 and Figure 33. A comparison of the performance obtained with 2% water, with as-received and dried CuF₂, appears to indicate there is no significant effect due to slight hydration. Considering the large deviation in experimental results usually obtained in these studies, more than 10% between replicates at times, it might be concluded that the difference observed are within experimental error, and that the effect of water, at least in the range tested, is insignificant.

2.5.5 Effect of CuF₂ Particle Size on Cathode Performance

It is to be anticipated that the particle size of the CuF₂ used to prepare electrodes would have a significant bearing on the performance. As the particle size is reduced, the surface area will increase and reduce the true current density. In addition, more intimate contact with the graphite will be achieved with consequent improvement in the conductance.

The CuF_2 was sieved for 15 minutes on a mechanical shaker, and cathodes were fabricated from the various fractions collected and tested, as described in Appendices E and F. The performance curves for the various fractions are shown in Figure 34. Duplicate tests were run with each particle size and an average performance curve is given.

From the result it can be seen that the +170 mesh was too coarse for high utilization and that the smaller particle sizes (-170 to +325, and -325 mesh) definitely gave high performance. When the +170 was ground with a mortar and pestle, fine particles were produced which also gave high utilization. Generally, reducing the particle size increased the performance. This behavior might be expected, since an increase in the total surface area, as a result of progressive decrease in particle size for the same amount of material, should produce more reaction sites and consequently allow a more efficient discharge.

2.5.6 Effect of Activated Storage on CuF_2 Cathode Performance

This study was undertaken to determine the effect on performance of standing cathodes in electrolyte for various lengths of time. Electrodes were made from cupric fluoride (-170 mesh) and hot pressed at 3,000 lbs./cm², as described in Appendix E. The electrodes were soaked for a specified time in purified electrolyte which was 1M LiClO_4 in twice distilled propylene carbonate (Appendices A and B). They were discharged against two lithium anodes at 2 ma/cm² (60 ma) with a separator of two layers of 15 mil glass filter paper. Discharge was terminated when the potential of the cathode was 0.5v vs Li reference. The average percent utilization of two electrodes was used as the criterion of performance. The results are shown in Figure 35.

The longer the cathode stood in electrolyte, the lower the performance. After stand, electrodes were analyzed by x-ray diffraction to determine the electrode composition.

Two electrodes were soaked in purified electrolyte for two weeks and submitted for x-ray analysis; they contained, CuF_2 , polyethylene, LiF, and a trace of Cu_2O - no free copper was detected. There is apparently a reaction between CuF_2 and electrolyte, causing formation of LiF and undoubtedly, other reaction products not detected by x-ray, and which may be dissolved in the electrolyte.

When two electrodes were soaked as above but discharged after two weeks on stand, the x-ray analysis indicated the presence in the electrodes of CuF_2 , graphite, polyethylene, copper, LiF, and a trace of Cu_2O . The free copper formed on reduction of CuF_2 , but no cuprous fluoride compounds were detected.

2.5.7 Purification of SW 1651 Graphite

Studies of cathode activated stand revealed a loss in performance of CuF_2 electrodes after storage in electrolyte. Associated with this was the formation of LiF in the electrode as determined by x-ray diffraction. This behavior was attributed to certain impurities in the SW 1651 graphite used in the electrode construction. When high purity graphite (spectrographic grade) was used, LiF was not detected after stand. These observations indicated that degradation of the cathode salt occurred, by direct reaction with, or catalysis by, the graphite impurities.

The performance of Li/CuF_2 cells after activated storage has been generally unsatisfactory. This has been associated with solubility of the CuF_2 and consequent short-circuiting of the cells by copper dendrites. Cupric fluoride is soluble to some extent in the electrolyte, but it was thought that possibly certain impurities in the graphite used in the cathodes might increase the solubility and further aggravate the loss of cell efficiency on activated stand. Therefore, a program of work was initiated to purify the SW 1651 micronized graphite used in cathode fabrication and to determine the effect of this treatment on cathode activated storage.

2.5.7.1 Purification of SW 1651 Graphite by Various Methods

The following methods were used to purify SW 1651 micronized graphite:

- i) Nitric Acid Treatment
- ii) Hydrochloric Acid Treatment
- iii) Nitric/Hydrochloric Acid Treatment

The respective treatments are described in Appendix G.

Graphite purified according to the respective techniques described above was submitted for spectrographic analysis and the results are shown in Table 10.

The hydrochloric acid treatment was very effective in removing Fe, Ti, Ca, and the nitric acid treatment in removing Mg and Mo. The highest purity graphite was obtained by a combined HCl/HNO_3 treatment.

2.5.7.2 Effect of Graphite Purification on Cathode Activated Storage

This study was conducted to determine the effect on cathode activated stand of the various graphite purification techniques.

Cupric fluoride cathodes were made from blends of 85% CuF_2 (-325 mesh), as described in Appendix E. The various blends incorporated, respectively, impure, HNO_3 treated, HCl treated, and HCl/HNO_3 treated graphites. Two grams of the respective blends were die-pressed at 3000 lbs./ cm^2 for 3 minutes at 90°C.

Cathodes incorporating the various graphites were tested in cells, as described in Appendix F. The cells were filled with 1F LiClO_4 /propylene carbonate (purified) and discharged at 2 ma/ cm^2 to determine their initial (no stand) performance. In addition, cathodes were stored alone (dissociated from Li anodes) in electrolyte for two weeks in a dry argon atmosphere and then discharged. Additional cathodes representing the various graphite treatments were submitted for x-ray analysis after stand (undischarged).

The results of the various experiments are shown in Figures 36 to 39. Inspection of these results reveals that the effect of graphite purification was to improve the cathode utilization after activated storage, but also to increase the cathode polarization.

In those electrodes submitted for x-ray analysis (undischarged) after two weeks activated stand, LiF was found only in those containing unpurified graphite. No free copper was found in any of the electrodes. No compounds other than those originally present could be detected.

Apparently, the purification of SW 1651 graphite improves the activated storage capability of CuF_2 cathodes with regard to coulombic efficiency. However, there is a large decrease in discharge potentials after stand which is difficult to explain.

2.5.7.3 Effect of Graphite Purification on the Activated Storage of Li/ CuF_2 Cells

Cathode storage tests have shown that purification of SW 1651 graphite improves the activated storage capability of the CuF_2 electrode, at least with regard to coulombic efficiency. It was, therefore, decided to evaluate the effect of graphite purification on the activated storage performance of Li/ CuF_2 cells.

Cupric fluoride electrodes were made using blends containing respectively impure, HNO₃ treated, HCl treated, and HCl/HNO₃ treated graphite. Cathodes were prepared as described in Appendix E, using -325 mesh CuF₂. A few electrodes were prepared at 500 lbs./cm², but most of the work was done with cathodes pressed at 3000 lbs./cm². The cathodes were tested in three plate cells made as described in Appendix F and activated with 1F LiClO₄/P.C. (purified) electrolyte. The initial (no stand) performance was determined at 2 ma/cm² on replicates of two cells representing each of the respective graphite treatments.

Also, replicates of two cells for each of the respective graphite treatments were placed on activated storage for respectively 3 days and one week, after which they were discharged at 2 ma/cm².

The results of these experiments are shown in Figures 40, 41 and 42. An analysis of these curves reveals the following:

In general, for discharges conducted before stand, a high compacting pressure (3000 lbs./cm²) adversely affects the cathode operating voltages but not necessarily its coulombic efficiency, the overall effect being a loss in energy density. There is also some evidence to indicate that graphite purification may adversely affect the cathode potentials as shown by the results obtained with HNO₃ treated graphite (Figure 40). Regardless of the type of graphite treatment the performance after 3 days activated storage was only slightly less than that obtained initially. After one week of activated storage, for cathodes compacted at 3000 lbs/cm², the best performance was obtained from electrodes containing HCl treated graphite, which suffered only a slight increase in polarization but practically no loss in coulombic efficiency. Electrodes containing impure and HNO₃ treated graphite yielded very poor performance with only about 1% and 5% coulombic efficiency respectively. The combined treatment (HCl/HNO₃) appeared to be less effective than the HCl treatment alone, with combined treatment electrodes suffering a loss of about 15% in coulombic efficiency as well as a large increase in polarization.

Cathodes compacted at 500 lbs./cm² had poor activated storage performance, with high polarization, and losses of coulombic efficiency of 30% and 50% respectively after 3 days and one week. As a result, the performance of these electrodes was inferior to that of electrodes compacted at 3000 lbs./cm² after the respective storage periods.

After one week of activated storage, a post-discharge inspection of cells revealed the least copper dendrite penetration of separators in cells with cathodes containing HCl treated graphite, pressed at 3000 lbs./cm². For cells containing cathodes of the same composition (HCl treated graphite) but compacted at 500 lbs./cm², the copper dendrite formation was extensive, possibly causing internal short circuiting.

in conclusion, the purification of graphite (SW 1651) used in the CuF_2 cathode appears to effect a considerable reduction of capacity losses during storage of Li/CuF_2 cells. The most effective treatment is by HCl purification, with HNO_3 treatment practically ineffective and the combined HCl/HNO_3 treatment less effective than HCl alone. Associated with this is the effect of cathode compacting pressure, which appears to be a factor in determining activated storage. Initially (no stand) cathode performance is adversely affected by a high compacting pressure ($3000 \text{ lbs.}/\text{cm}^2$) because of high electrode polarization apparently resulting from poor electrolyte mass transport in the fine electrode pores. However, on activated storage the loss in performance of cells with cathodes pressed at $3000 \text{ lbs.}/\text{cm}^2$ is much less than that of cells with cathodes pressed at $500 \text{ lbs.}/\text{cm}^2$. An explanation for this behavior might be that the same mechanism causing high polarization with high compacting pressures, i. e., ionic mass transport, may in turn effect a reduction in diffusion of dissolved CuF_2 from within the electrode structure to the bulk electrolyte. Any CuF_2 dissolved in the electrolyte within the body of the cathode compacted at high pressure would encounter a greater resistance in diffusing into the bulk solution than would be the case in electrodes with larger pores (lower compacting pressures). This would result in a lower rate of self discharge caused by galvanic deposition of copper on the anodes and subsequent short-circuiting of the cell by dendrite penetration of the separator.

3. Separator Studies

Separator studies were conducted in an attempt to obtain a material with a capability of eliminating or retarding the migration of dissolved copper species from the CuF_2 cathode to the lithium anode. Investigations of microporous, ion exchange membrane, and polymer film materials were conducted in a search for materials with the desired selectivity toward the ionic species, and with a sufficiently high conductivity consistent with high cell efficiencies.

3.1 Evaluation of Porothene Separators

Porothene (ESB Inc.), a microporous polyethylene separator with a fine pore size and high porosity (approximately 70%) was selected for evaluation. This material is inert in most electrolytes, but has a resistivity about seven times that of the glass fiber filter paper which has been used in most of our investigations of the Li/CuF_2 system.

Three plate Li/CuF_2 cells, made as described in Appendices E and F, and insulated with 12 mils of Porothene, were filled with 1F $\text{LiClO}_4/\text{P.C.}$ (purified). Replicates of two cells were placed in a one week ac-

tivated storage. Another replicate of two cells was discharged from fill at 2 ma/cm². The results of this experiment revealed a 38% utilization of CuF₂ for cells discharged immediately from fill, and about 1% utilization after one week of activated storage. Inspection of the cells which had been on activated storage revealed almost completely discharged cathodes, and extensive copper dendrite deposits in the separator.

The results of this study indicate, as have previous studies, that microporous separator materials are incapable of preventing the migration of dissolved copper species and the consequent short-circuiting of cells on activated storage.

3.2 Evaluation of Ion Exchange Membranes

A program was undertaken to evaluate various ion exchange membranes as one phase of the separator study. It was intended to find a permselective type of membrane that would allow migration of the electrolyte species required by the cell reaction, while preventing the transfer of dissolved copper species. Several ion exchange membranes, proprietary to ESB, were evaluated. In addition, experiments were made with macroreticular strong base (IRA 904) and strong acid (Amberlite 200) ion exchange resins dispersed in a polyethylene matrix. The resins were dried at 140°F for 16 hours under vacuum. They were then reduced to a -325 mesh powder in a ball mill. Membranes were made with the respective resins by incorporating the material into a polyethylene binder on a rubber mill. The composition of the mixture was approximately 75% ion exchange and 25% polyethylene for each type of membrane. The mill temperature ranged from 260 - 265°F and the films were removed from the rolls at about 10 mils thickness. These membranes were very brittle and difficult to handle.

The membranes, of various types, were equilibrated in 1F LiClO₄ / P.C. (purified) and their absorption and resistivity measured. The results of this study are shown in Table 11. The resistivities were very high, with values greater than 10³ ohm-cm, or two to three orders of magnitude greater than that obtained with glass fiber filter paper. Also, it was noticed that an insignificant amount of swelling of the membranes occurred in the electrolyte. In aqueous system considerable swelling of the membranes is found, and this appears to be an important factor in obtaining good conductivity.

3.3 Evaluation of Various Polymeric Films as Membranes

Another phase of the separator study was concerned with the behavior of various polymeric materials, other than ion-exchange, in organic electrolyte. This was an effort to find a material with behavior analogous

to that of cellophane in aqueous media, i. e., in applications such as Ag/Zn or Ag/Cd alkaline cells. The desired characteristics are: (i) partial attack and swelling of the material in organic electrolyte, resulting in absorption of the solution to produce a conductive film, (ii) ionic selectivity - allow transfer of the electrolyte species while preventing transfer of the dissolved CuF_2 .

The results of testing of the various polymer films are shown in Table 12. The resistivity of all the materials was extremely high; about three orders of magnitude greater than that of glass fiber filter paper. Even for Orlex 310 which swelled considerably and absorbed an appreciable amount of electrolyte the resistivity was very high.

In conclusion, the results of experiments with microporous, ion exchange and polymer film materials reveal that none of the materials satisfy the prescribed separator requirements. Microporous separators are incapable of preventing transfer of dissolved copper species. The conventional ion-exchange membranes tested do not function satisfactorily in non-aqueous systems, probably because of their inability to swell and absorb electrolyte as in aqueous media. The resistivities of ion exchange and polymer film materials are extremely high and would be inconsistent with high energy density requirements, even at very low drains.

4. Kinetic Studies of the CuF_2 Cathode

Investigations of the kinetics of the CuF_2 discharge reaction were conducted in an effort to elucidate the factors which limit the reaction to fairly low rates. Two techniques were employed involving modified current sweep voltammetry and chronopotentiometry.

4.1 Chronopotentiometric Method

Cupric fluoride cathodes were tested in a glass three-compartment cell of the type previously described (7). The cell was maintained at 25°C in a thermostatically controlled oil bath. The cathodes were of the type described in Appendix E, except that they were $0.5'' \times 1''$, containing about 0.9 grams of blend and were pressed at 3000 lbs./cm^2 . The electrodes were discharged at various current densities in electrolytes of 0.25, 0.50 and 1.0 Formal LiClO_4 /propylene carbonate (purified). The electrolyte was not stirred in order to obtain a condition of semi-infinite linear diffusion.

The results of this experiment are shown in Figures 43, 44, and 45. The discharge characteristics were considerably different in the 0.25 and 0.50F as compared with the 1F electrolyte. The curves in the 1F solution show a fairly well defined transition time, whereas no trans-

ition time exists in the 0.25 and 0.5 F solutions. The product $i \tau^{\frac{1}{2}}$ was found to be approximately constant in the 1F solution as shown in Table 13. Since no transition time was observed in the dilute solutions it was decided to examine the relationship between the time at which the deposition of lithium occurs (as indicated) by leveling off of the curves) and the current density and electrolyte concentration. The results are shown in Table 13, where for the 0.25 and 0.50 F solutions τ is interpreted as the time at which lithium begins to deposit. It can be seen that there is a good constancy of the factor $i\sqrt{\tau}/c$. This would appear to indicate that the potential - time curves obey the Sand equation (8), and that the reaction is diffusion controlled. However, since the interpretation of the chronopotentiograms is difficult, especially in the dilute solutions, the agreement may be fortuitous.

4.2 Current Sweep Voltammetry

Another technique used to study CuF_2 cathode kinetics was a modified current sweep method. The glass three-compartment cell previously described was used in this work. Cupric fluoride electrodes were prepared as described in section 4.1 and were tested as follows:

A preset current was pulsed through the electrode using a 300 volt constant current power supply in conjunction with a time-delay switching system. The delay switch allowed an oscilloscope to trigger the trace before the current pulse was applied, thereby allowing the measurement of the open circuit potential. In this way the IR polarization could be determined at the instant the current pulse was applied. Measurements were obtained using a Tetrone type 535 Oscilloscope in conjunction with a camera attachment to record the potential transients. Polaroid film was used with designation B and W 3000 speed/type 107.

The test was conducted over a range of current densities in $\text{LiClO}_4/\text{P.C.}$ solution of various concentrations. The electrolyte was stirred by vigorous bubbling of dry argon through the solution. Cathode potentials were measured against a Ag/AgCl reference electrode.

A typical potential-time transient is shown in Figure 46. The time delay switch allows a recording of the open circuit potential for a few milliseconds before the pulse is applied. This allows the measurement of the IR component of polarization at the instant the current is applied, as shown by the break in the potential-time trace. Thereafter, polarization increases and includes components of diffusion and activation overpotential. The transient becomes linear after an initial curved portion, and this is an indication of diffusion control. The activation polarization is determined by extrapolating the linear portion of the trace (dashed line) back to an intersection with the vertical dashed line (time at instant current is applied). The activation polarization is then obtained by subtracting the IR compon-

ent from the total polarization (Δ mv from o. c. v. to intersection of dashed lines).

The results of this experiment are shown in Figures 47, 48 and 49. It is observed that the current density/potential behavior is linear over a wide range of current densities. Considerably more so than could be accounted for by the linear approximation to the electrokinetic equation.

The linear current-potential relationship is unusual in that, according to the modern treatments of the kinetics of porous electrodes, a logarithmic plot should be obtained (9). The linear current-potential behavior may be explained if it is assumed that the polarization is a function of the electrolyte resistance in the pores of the electrode. For example, the polarization characteristics of an irreversible electrode can be written as:

$$i = i_0 \left[\exp \frac{\alpha n F \eta}{RT} - \exp - \frac{(1 - \alpha) n F \eta}{RT} \right]$$

where the symbols have their usual significance. If $\alpha = 1/2$, as is often the case in practice, then

$$(1 - \alpha) = \alpha$$

and
$$i = i_0 \left[\exp \frac{\alpha n F \eta}{RT} - \exp \left(\frac{-\alpha n F \eta}{RT} \right) \right]$$

Using the Tafel terminology

$$\frac{RT}{\alpha n F} = b$$

therefore
$$i = i_0 \left[\exp \left(\frac{\eta}{b} \right) - \exp \left(\frac{-\eta}{b} \right) \right]$$

Since
$$\sinh \left(\frac{\eta}{b} \right) = 1/2 \left[\exp \left(\frac{\eta}{b} \right) - \exp \left(\frac{-\eta}{b} \right) \right]$$

the expression for the current-potential relationship can be written

$$i = 2i_0 \left[\sinh \left(\frac{\eta}{b} \right) \right]$$

The distribution of the potential inside the electrode, perpendicular to the electrode-electrolyte interface, is given by the Poisson equation

$$\frac{\partial^2 \kappa}{\partial x^2} = S \rho_i = 2S i_0 \rho \sinh\left(\frac{\kappa}{b}\right)$$

S = Surface Area

Integrating, using the boundary conditions

$$\kappa_x = \infty = 0$$

$$I_x = \infty = 0$$

gives
$$i = 2 \left(\frac{2S i_0 b}{\rho} \right)^{\frac{1}{2}} \sinh\left(\frac{\kappa}{2b}\right)$$

When $\kappa < 2b$, $\sinh\left(\frac{\kappa}{2b}\right) \approx \left(\frac{\kappa}{2b}\right)$ and the potential is a linear function of the current density. When $\kappa > 2b$, $\sinh\left(\frac{\kappa}{2b}\right) \approx \exp\left(\frac{\kappa}{2b}\right)$ and the potential should be a logarithmic function of the current with a slope equal to twice the normal Tafel value. Thus, one would expect a linear current-potential plot up to polarization of about 250 mv. where it should develop a curvature. This is indeed the observed result.

The experiment was repeated in the last quarter of this contract to test the above hypothesis. The electrodes were made as described in section 4.1 except that they were 1 cm square. The area of the electrode was reduced in order to obtain high current densities with the power supply equipment available. Replicates of two electrodes were tested at current densities of respectively 10 to 110 ma/cm², in increments of 10 ma/cm². In the previous test one electrode was discharged over the full current density range. It was thought that this might have changed the surface characteristics of the cathode with successive stages of discharge and thereby produced inaccurate results. It was assumed that a single rapid pulse, applied only once to each electrode would cause it to discharge only on the surface and thereby function essentially as a planar electrode. This would eliminate some of the complexities due to diffusion in porous electrodes. The electrodes were tested in the glass cell (4.1) in 1F LiClO₄/P.C. (purified).

The results of this experiment are shown in Figure 50. There was a considerable scatter of data, making analysis difficult, but it appears that

the current-potential relationship remains linear even at current densities twice as high as previously used. However, the maximum activation polarization was still under 250 mv, where the curvature should develop according to the theory described above. Possibly the new electrode construction and especially the modified testing technique might have affected the discharge characteristics, causing polarization to be lower than in the previous experiment. In any case, it appears that even higher current densities might be required to further test the hypothesis.

5. Voltammetry at a Quiet Mercury Pool Electrode

This study has recently been initiated to determine the nature of the copper species present in organic electrolyte solution.

The technique uses a specially designed cell incorporating a mercury pool of large surface area. A lower concentration of reducible species can be determined with this electrode than with the dropping mercury electrode because of the larger surface area. Also current fluctuations caused by the drop growth are absent. Information about this method can be found in literature (10 - 15).

A mercury pool cell with three electrodes was designed and built of polypropylene; the construction is shown in Figure 51.

A voltage-time sweep generator was designed and built and used to program the voltage in a potentiostat, this voltage was recorded on the X component of an X - Y Varian recorder. Current was measured with a resistor in series with the counter electrode. The voltage drop across the resistor being fed into the Y input of the recorder. A photograph and block diagram of the apparatus are shown in Figures 52 and 53 respectively.

Tests were made to determine the effect of electrolyte concentration on residual current. Reproducible results were obtained for 1.0, 0.5, and 0.1 F LiClO_4 in twice distilled propylene carbonate. At the lower concentration (0.1F), the current-potential curve was not smooth due to the high resistance of the solution. A scanning rate of 4.07 mv/sec was used for solution at room temperature. The pool was filled with fresh triple distilled, instrument grade mercury and degassed for 10 minutes with argon before each run. The residual current curves are shown in Figure 54. It was evident that as the concentration of LiClO_4 increased, the residual current increased, indicating that the electroactive impurities were present in the solute and not the solvent.

When 1.0 F electrolyte was electrolyzed with the mercury pool for one hour at -1.5 volts vs. Ag/AgCl to reduce impurities, the residual current was reduced appreciably compared to that obtained before electro-

lyzing; see Figure 54. This therefore appears to be a good method to purify the electrolyte for current-voltage studies.

When 0.5% water was added to electrolyte, there was a gradual but continuous rise in the residual current before the lithium decomposition potential. Large amounts of water (greater than 0.2%) can probably be detected by this method. A quantity of 0.05% water added to the electrolyte could not be detected.

In order to test the ability of this technique to give useful information in non-aqueous media, it was decided to determine whether the Randles-Sevcik equation (16 and 17) was obeyed as in aqueous solutions. The equation has the form

$$i_p = Kn ADCw^{\frac{1}{2}}$$

where

- i_p = peak current
- K = constant
- A = electrode area
- D = diffusion coefficient
- C = concentration
- w = sweep rate

Thus it is predicted that the peak current is directly proportional to the concentration of the electroactive species and also to the square root of the sweep rate.

In order to determine the relationship between peak current and scanning rate (11 and 12), solutions of $CuCl_2$ in 1F $LiClO_4$ in twice distilled propylene carbonate were used. The peak current was plotted against the scanning rate for three different concentrations of $CuCl_2$ in supporting electrolyte, (3.6×10^{-4} , 0.72×10^{-4} , and $0.072 \times 10^{-4}M$). The copper half peak potential was observed to be at -0.42 volts vs $Ag/AgCl$. See Figure 55 and Table 14. In each case a straight line was obtained. This is similar to the results of Streuli and Cooke (12) in water solution, who also found a linear relationship.

To determine whether the diffusion current was proportional to concentration, solutions of various concentrations of $CuCl_2$ in 1F $LiClO_4$ in twice distilled propylene carbonate were used. A plot of copper concentration vs diffusion current is given in Figure 56. Work was done at room temperature and a scanning rate of 26.7 mv/sec. A linear relationship between peak current and concentration was found but the data appeared to show more scatter at the very lowest concentration studied. More work will have to be done to find the reason for this be-

havior. However, it does appear that the Randles-Sevcik equation is obeyed in this electrolyte system which now opens the possibility of being able to study the constitution of the copper species in solution.

APPENDIX A

Purification of LiClO₄

- 1) Recrystallize 100 gm of LiClO₄ twice from 83 ml double distilled water (yield 80% LiClO₄).
- 2) Dry crystals under vacuum for 16 hours, with incremented increases in temperature of about 20°C, until a final temperature of 120°C is reached. The salt is held at this temperature for an additional 8 hours, under vacuum.
- 3) 80 gm. of LiClO₄ (from A-2) is refluxed in 250 ml diethyl ether (which has been dried over lithium) at 60°C for about 16 hours. The solution is then filtered under dry argon to remove insoluble material. The LiClO₄ is then crystallized by evaporation of the ether under vacuum at 60°C.
- 4) The ether treatment salt is dried at 120°C under vacuum for 16 hours (85% yield of LiClO₄ in steps 3) and 4).

APPENDIX B

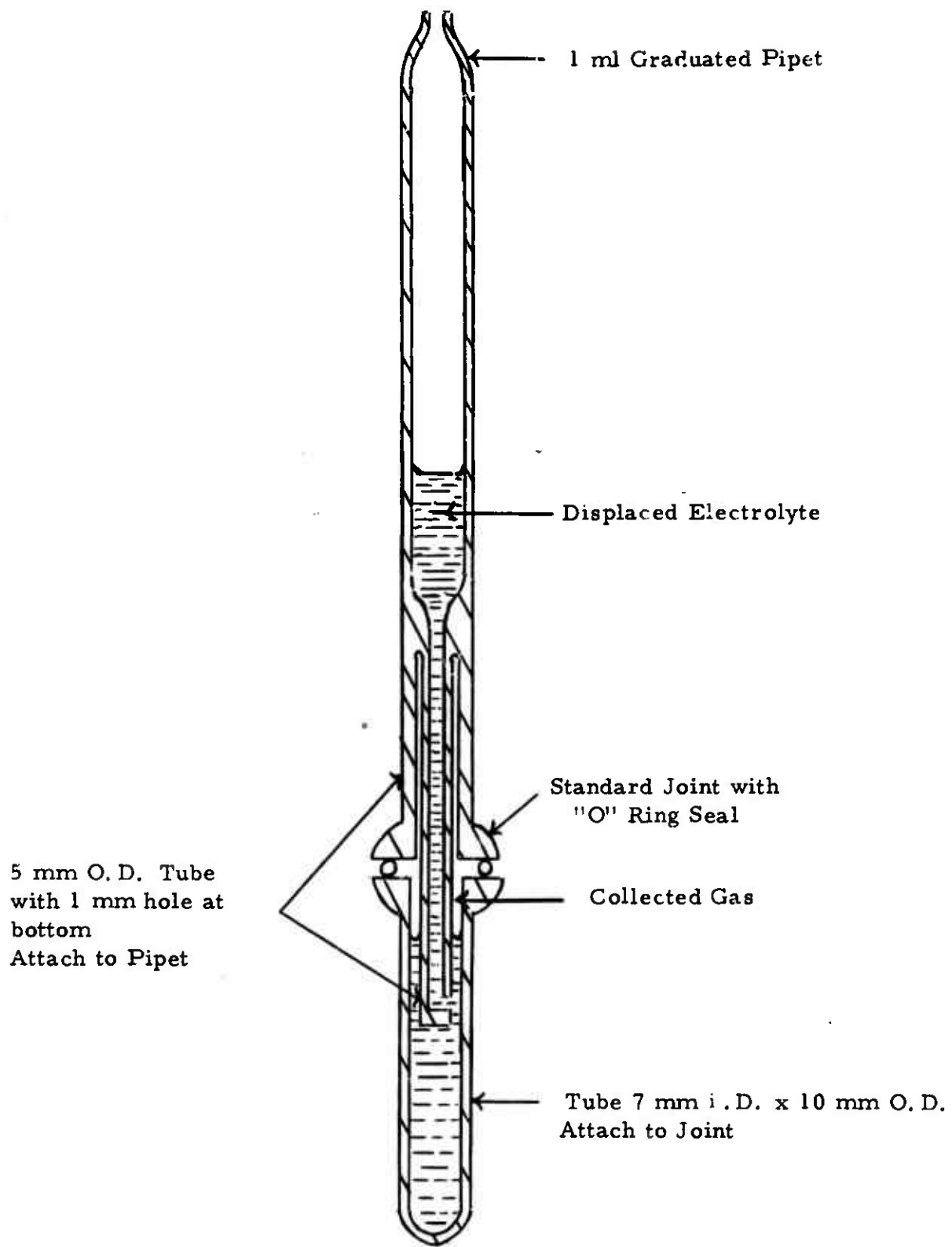
Purification of Propylene Carbonate

700 ml propylene carbonate is distilled over dried CaO at 1 mm. Hg pressure through a Vigreux column 12 inches long. The first fraction starts to come over at about 60°C, after which, the temperature increases to 70 - 72°C where the main fraction is distilled off. Distillation is terminated when the temperature exceeds 72°C. The middle fraction is collected, while the others are discarded. This process is then repeated on the middle cut from the first distillation (first fraction 150 ml; main fraction 400 ml; residue 150 ml).

APPENDIX C

Rate of Corrosion of Lithium by Microgassing Technique

The gas evolution pipet shown in Figure C-1 is used in this experiment. A piece of shiny lithium ribbon, 1/2 in. x 1/4 in. x 0.015 in. is degreased in n-hexane and placed in the tube. The tube is filled with the test electrolyte and the top inserted so as to expel all of the gas. The apparatus is then clamped, using an "O" ring to effect a seal. All operations are conducted under dry argon. The unit is maintained at 25°C in a thermostated water bath. The rate of gas evolution is determined by displacement of the meniscus.



Gas Evolution Pipet

FIGURE C-1

APPENDIX D

Solubility of CuF_2 in Various Electrolytes

1) Approximately 150 mg. of anhydrous CuF_2 is added to 50 ml. of electrolyte in a tightly stoppered flask. The solutions are agitated at regular intervals to disperse the salt. After two weeks, the dispersion is filtered through highly retentive filter paper, under dry argon, and the filtrate analyzed for dissolved copper.

2) Analysis of Solutions by Photometric Methods

This method is described in reference No. 18. Filtrate from D-1 is diluted with water and treated with hydroxylamine hydrochloride and sodium citrate, with the pH adjusted between 4 and 6. A solution of neocuproine (2, 9 dimethyl - 1, 10 phenanthraline) is added to give a yellow color indicating the presence of copper. The solution is extracted with chloroform and the absorbancy of the chloroform layer is measured at 454 nm.

APPENDIX E

Cathode Fabrication (General)

1) Blend Composition

85% Cathode material, 10% Southwestern 1651 micronized graphite, and 5% polyethylene powder (-100 mesh).

2) Grid Structure

Expanded copper, designated as 5 Cu 14-2/0, with dimensions 1-1/2 in. x 1-5/8 in., with a 0.020 in. dia. copper wire spot-welded to one corner.

3) Electrode Fabrication

Two grams of blend (E-1) are compacted into the grid in a steel pressing die. Standard conditions of consolidation are 500 lbs./cm² at 90°C for 3 minutes.

4) Anode Fabrication

The anodes are made by pressing a copper grid (expanded metal - 3 Cu 7-3/0) of dimensions 1-1/2 in. x 1-5/8 in. into 15 mil thick lithium ribbon. Pressing is done between 1/4 in. steel plates lined with Patapar release paper which is coated with petrolatum. The pressing is done at 10,000 lbs. total load.

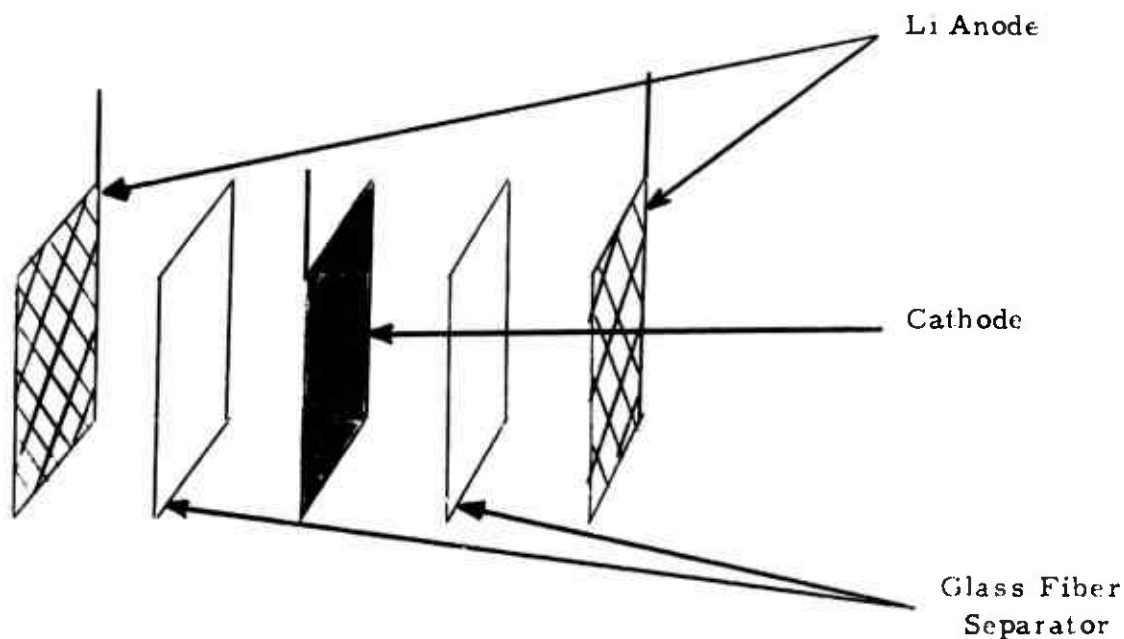
APPENDIX F

Cathode Testing

The cathodes are tested in cells of three plate construction against pressed lithium anodes. (Appendix E).

The cathode is positioned in a "U" shaped separator of 30 mil thick glass fiber filter paper, and the assembly then positioned between two lithium anodes. The element is then inserted into a polypropylene jar for testing. The jar is provided with a reference electrode well connected with a luggin capillary, the opening of which inside the jar is within 1/16 in. of the plate edges. The cell is filled with electrolyte (by vacuum filling in a vacuum desiccator) and discharged at the prescribed rate. Cathode potentials are measured against a Ag/AgCl reference electrode using a high impedance voltmeter. The cathode - Ag/AgCl potentials were converted to cathode-Li/Li⁺ for presentation in this report. The potential of the cell, Ag/AgCl/ 1M LiClO₄ -PC/Li/Li⁺ is = 3.50 V at 25°C

Cell Construction



APPENDIX G

Purification of SW 1651 Graphite*

i) Nitric Acid Treatment

Thirty grams of graphite was slurred with 600 ml of nitric acid solution (1:1, concentrated HNO_3 and water). The mixture was maintained at 60°C for 17 hours, with continuous stirring during the period. The slurry was then filtered, and the product washed with distilled water. The graphite was dried under vacuum, at 120°C for 10 hours. (Yield: 95%).

ii) Hydrochloric Acid Treatment

Thirty grams of impure graphite was leached in 600 ml of HCL solution (1:1, concentrated HCl and distilled water) at 70°C for 17 hours with continuous stirring. The product was washed thoroughly and dried at 130°C under vacuum. (Yield: 95%).

iii) Nitric/Hydrochloric Acid Treatment

- a) Thirty grams of impure graphite was leached in 600 ml of hydrochloric acid (1:1, concentrated HCl and distilled water) at 80°C for 17 hours with continuous stirring. The product was filtered and washed with 1 liter of distilled water.
- b) Step (a) was repeated.
- c) The graphite from step (b) was leached in 600 ml of nitric acid (1:1, HNO_3 and distilled water) at 70°C for 17 hours. The product was filtered and washed with 1 liter of distilled water.
- d) Repeat step (c).
- e) The product from step (d) was washed thoroughly in a filter and dried at 120°C under vacuum for 10 hours. (Yield: 90%).

* see Table 10 for data on impurity analysis

LIST OF MATERIALS AND SUPPLIERS

Nickelic Oxide	Fisher Certified Reagent - Fisher Scientific Co.	
Cobaltous Carbonate	" " " " " "	
Cupric Oxide	" " " " " "	
Cupric Chloride, anhyd.	" " " " " "	
Cupric Sulfate, anhyd.	" " " " " "	
Cupric Carbonate, basic	" " " " " "	
Cupric Sulfide	" " " " " "	
Ferric Oxide, anhyd.	" " " " " "	
Lithium Carbonate	" " " " " "	
Calcium Chloride, anhyd.	" " " " " "	
Calcium Carbonate, basic	" " " " " "	
Magnesium Sulfate, anhyd.	" " " " " "	
Magnesium Carbonate, basic	" " " " " "	
Magnesium Perchlorate, anhyd.	" " " " " "	
m-Dinitrobenzene	" " " " " "	
Ferric Chloride, purified, anhyd.		
Chromic Chloride, purified, anhyd.		
Dimethyl Carbonate	Highest Purity	" " "
Dimethyl Sulfite	" "	" " "
Diethyl Sulfite	" "	" " "
Propylene Carbonate	Practical Grade	Jefferson Chemical Co.
Titanium Tetrafluoride	98-100%	Ozark-Mahoning Co.

LIST OF MATERIALS AND SUPPLIERS (cont'd)

Cupric Fluoride, anhyd.	99.5% Min	Ozark-Mahoning Co.
Titanium Trifluoride	Ca 95%	" " "
Chromium Difluoride	90-100%	" " "
Nickel Fluoride	95-100%	" " "
Manganese Difluoride	98-100%	" " "
Lithium Tetrafluoroborate, anhyd.	Ca 95%	" " "
Lithium Hexafluorophosphate		" " "
Manganese Sesquioxide		Pfaltz and Bauer
Nickelous Carbonate	Baker Analyzed Reagent	J. T. Baker Co.
Calcium Sulfate, anhyd.	" " "	" " "
Ferrous Carbonate		City Chemical Corp.
Lithium Sulfate, anhyd.	Purified	" " "
1-nitropropane	Practical	" " "
2-nitropropane	Practical	" " "
Calcium Perchlorate, anhyd.	90-95%	K and K Laboratories
Magnesium Chloride, anhyd.	90-95%	" " "
Magnesium Thiocyanate	90-95%	" " "
D-Xylitol	90-95%	" " "
Succinonitrile	90-95%	" " "
Methyl Cyanoacetate	90-95%	" " "
Crotonitrile	90-95%	" " "
Lactonitrile	90-95%	" " "

LIST OF MATERIALS AND SUPPLIERS (cont'd)

1-Chloro-2-Propanone	90-95%	K and K Laboratories
2-2'-Dichlorodlethyl Ether	90-95%	" " "
Methyl Nitrate	99.8%	" " "
Lithium Metal Ribbon	99.96%	Foot Mineral Company
Bis-benzo-furoxane Sulfone		American Cyanamid
Azodicarbonamide		" "
Aluminum Trifluoride, anhyd.		Matheson, Coleman and Bell
Tetramethyl, ammonium Tetrafluoroborate		Ozark-Mahoning Co.
1,4 Dioxane, Fisher Cert.		Fisher Scientific Co.
1,3 Dioxolane, Highest Purity		" " "
2,5 Dihydrofuran, Practical		" " "
Triethyl Phosphite, Practical		Matheson, Coleman and Bell
Tetramethyl Urea		K and K Laboratories
Propylene Glycol Sulfite		" " "
Boron Trifluoride, c.p		Matheson Co.
Lithium Perchlorate, anhyd.		G. F. Smith Company
Amberlite 200		Rohm and Haas
Ira 904		" "

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Table 1

Properties of Non-Aqueous Solvents

	Dielectric	Viscosity (Centipoise)	Density (g/cc)	Melting Point (°C)	Boiling Point (°C)
Diethyl Sulfite	41.9	0.829	1.083	-----	157.7
1-Chloro-2 propanone	30	1.44	1.15	-44	119
Methyl Cyanoacetate	28	2.628	1.123	-22	200
Crotononitrile	36	0.475	0.832	-84	119
1-Nitropropane	23.2	0.79	1.003	-108	132
2-Nitropropane	25.5	0.722	0.992	-93	120
2-2 Dichlorodiethyl ether	21.2	2.127	1.222	-50	178
Methyl Nitrate	23	0.493	1.217	-----	65 Exp.
Lactonitrile	38	2.289	0.992	-40	182
D-Xylitol	40	Solid at R.T.		93	216
Succinonitrile	56.5	Solid at R.T.	0.985	54.5	267
1,4 - Dioxane	2.2	1.184	1.035	11.7	101.5
1,3 - Dioxolane	----	0.603	1.060	----	78
2,5 - Dihydrofuran	----	0.535	0.940	----	68
Triethyl Phosphite	----	0.699	0.968	----	155.5
Tetramethyl Urea	23.5	1.38	0.972	----	170
Propylene Glycol Sulfite	33	1.76	1.296	-70	240

Table 2
Solubility of CuF₂ in Various Electrolytes

Electrolyte	Milligrams Copper Per Ml	P. P. M
0.75 F Li BF ₄ /P.C.	1.5	1500
1.25 F LiClO ₄ in 10% BF ₃ /THF in P.C.	3.0	3000
1.25 F LiClO ₄ in 5% BF ₃ /THF in P. C.	1.9	1900
0.5 F Mg (ClO ₄) ₂ /P.C.	0.16	160
1.0 F Mg (SCN) ₂ /P.C.	0.65	650
1.0 F LiClO ₄ /P.C.	0.30	300

Table 3

Solubility of CuF_2 in Solutions of LiClO_4 /P. C.

Concentration of Cu (mg/liter)

<u>Electrolyte Concentration (Formal)</u>	<u>Method No. 1 LiClO_4</u>	<u>Method No. 2 LiClO_4</u>
0.002	2.9	
0.0025		0.6
0.005	1.30	
0.01	0.75	1.3
0.025		1.7
0.05	1.0	2.1
0.10	1.73	1.8
0.25	1.40	3.1
0.50	1.90	
0.75		3.6
1.00	3.1	3.0

Table 4

Calculated Cell Volts and Energy Density of
High Energy Couples

<u>Couple</u>	<u>Cell Volts</u>	<u>Energy Density</u> <u>(W·hrs/lb)</u>
Li/TiF ₃	1.84	534
Li/NiO	2.38	489
Li/CrF ₂	2.35	550
Li/MnO ₂	1.69	715
Li/TiF ₄	2.29	735
Li/CuSO ₄	3.21	450
Li/FeCO ₃	2.37	447
Li/CrCl ₃	2.27	926
Li/CuO	2.24	582
Li/NiCO ₃	2.68	491
Li/NiF ₂	2.82	620
Li/CuCO ₃	3.17	563
Li/MnF ₂	2.17	498
Li/Fe ₂ O ₃	1.62	588
Li/AgO	2.95	520
Li/CoCO ₃	2.47	378

Table 5

Coulombic Efficiency of Organic Cathodes

Cathode Material	Ampere-Hrs/Gram		Coulombic Efficiency %	
	1 F LiClO ₄ /P.C.	2 F LiClO ₄ /DMC	1 F LiClO ₄ /P.C.	2 F LiClO ₄ /DMC
m-DNB	0.36	1.8	20	94
BBFOS	0.53	1.7	44	140
Picric Acid		1.5		70
ADCA	0.28	0.4	60	86

Table 6

Results of Latin Square Experiment on Glass Floc Cathode

		<u>Blending Time (sec)</u>				
		5	10	15	20	Total
Compacting Pressure (lbs per cm ²)	500	A41%	B62%	C37%	D33%	173
	1000	D43%	A39%	B53%	C36%	171
	2000	C21%	D30%	A27%	B38%	116
	3000	B28%	C23%	D20%	A26%	97
Total		133	154	137	133	557

A = 0.25% Glass Floc

B = 0.50% " "

C = 1.0 % " "

D = 2.0 % " "

Table 7

Analysis of Results of Latin Square Experiment
on Glass Floc Cathodes

	<u>Sum of Sq's</u>	<u>D. F.</u>	<u>Mean Sq.</u>	<u>F. Ratio</u>
Columns (blend. time)	75	3	25	0.904
Rows (comp. pressure)	1,117	3	372	13.44**
Treatments (% floc)	612	3	204	7.37 *
Residual	166	6	27.67	
<hr/>				
Total	1,970	15		

$F_{.95} (3:6) = 4.76$

* Significance at 95% confidence

+ Significance at 99% confidence

Table 8

Computation of Regression Equation for
Effect of Floc on Utilization

<u>% Utilization (av.)</u> y	<u>% Floc</u> x	<u>y²</u>	<u>x²</u>	<u>xy</u>
31.5	2.0	992	4	63
29.3	1.0	859	1	29.3
45.3	0.5	2052	0.25	22.7
33.3	0.25	1107	0.063	8.33
Total 139.4	3.75	5012	5.313	123.33

$$\begin{aligned}
 n &= 4 \\
 \Sigma x &= 3.75 \\
 \Sigma y &= 139.4
 \end{aligned}$$

$$\begin{aligned}
 \Sigma xy &= 123.3 \\
 \Sigma x^2 &= 5.31 \\
 \Sigma y^2 &= 5012
 \end{aligned}$$

$$b = \frac{\frac{\text{Slope}}{\Sigma xy - (\Sigma x)(\Sigma y)}}{\frac{\Sigma x^2 - \frac{(\Sigma x)^2}{n}}{n}} = -4.13$$

$$a = \frac{\text{Intercept}}{\frac{\Sigma y - b \Sigma x}{n}}$$

$$a = 38.72$$

Table 9

Effect of Partially Hydrated CuF₂ on Cathode Performance

<u>Percent Water Added to CuF₂</u>	<u>Percent Utilization of of CuF₂ (av.)</u>
No water added, CuF ₂ dried 17 hours at 100°C (vacuum)	75.5
No water added, CuF ₂ dried 17 hours at 60°C (vacuum)	74
No water added, CuF ₂ as received	70.5
0.25% water	62
0.50% water	67.5
1.0% water	58
2.0% water	71

Table 10

Spectrographic Analysis of Purified Graphite *

	SW 1651 (unpurified) ppm	SW 1651 (purified with HNO ₃) ppm	SW 1651 (purified with HCl) ppm	SW1651 (purified with HCl and and HNO ₃) ppm
Mg	1000	10	100	10
Si	1000	1000	1000	1000
Al	1000	1000	1000	100
Fe	1000	100	10	10
Mn	100	1	1	n.d.
Mo	500	10	500	n.d.
V	50	10	10	n.d.
Ti	100	50	10	10
Na	100	1000	1000	1
Ca	100	50	10	10
B	n.d.	50	10	50

* see Appendix G for purification methods

Table 11

Ion Exchange Membrane Characteristics in Organic Electrolyte

Electrolyte: 1 F LiClO₄/Propylene Carbonate

Membrane Designation	Thickness (mils)		Electrolyte Absorption (%)	Electrolyte Retention (1%)	Specific Resistance (ohm-cm)
	Dry	Equilibrated			
Amberlite 200	10	10	18	95	$> 2.8 \times 10^4$
IRA-904	8	8	27	42	$> 3.5 \times 10^4$
#396	16	16	23	54	2.5×10^3
#592	20	19	16	50	3.5×10^3
#677	8	9	23	6	$> 2.8 \times 10^4$
#164	20	20	9.7	60	1.1×10^4
#397	15	16	12	98	$> 1.7 \times 10^6$
#1054-F	5	5	40	57	$> 5.5 \times 10^6$
#1072	7	7	72	90	7.3×10^3
#1073	8	8.5	88	68	1.8×10^3
#1074	6	7	40	57	$> 3.5 \times 10^6$

Table 12Characteristics of Polymer Films in
1 F LiClO₄/Propylene Carbonate

Film Material	Thickness (mils)		Absorption (%)	Retention (%)	Specific Resistance (ohm-cm)	Remarks
	Dry	Equilibrated				
Teslar (PVF) Type 30 (DuPont)	1.5	1.5	13	30	$> 1.8 \times 10^5$	
Nylon 66 (Commercial Plastics Co.)	2	2.5	53	10	$> 1. \times 10^5$	
Phenoxy 8 (Union Carbide)	0.5	---	--	--		Dissolved
Orlex 310 (Nixon-Baldwin)	1	3	90	46	$> 1 \times 10^5$	
Borden C-2 (Borden Chem. Co.)	1.5	1.5	70	10	$> 1.8 \times 10^5$	
Borden C-3 (Borden Chem. Co.)	1.5	1.5	60	2	$> 1.8 \times 10^5$	
Capram Nylon 6 (Allied Chem. Corp.)	5	---	--	--		Dissolved

Table 13

Concentration LiClO ₄ / Propylene carbonate (formal)	Current Density (ma/cm ²)	τ Transition Time (min)	$i \sqrt{\tau/c}$
1.0	13.3	40	84
1.0	18.2	23.5	88
1.0	23.4	11.7	80
0.5	11.6	13	83.5
0.5	15	8	84.6
0.25	10	2.5	82.1
0.25	13.3	2.6	85
0.25	20.7	1.0	82.8

Table 14

Variation of Wave Height with Scanning Rate

3.6×10^{-4} MCuCl₂ in 1 F LiClO₄ in P.C.

<u>Scan Rate</u>	<u>(Scan)1/2 (Rate)</u>	<u>Peak Current (μa)</u>	<u>i_{max} (S. Rate) 1/2</u>
4.07 mv/sec	2.02	54	26.8
6.52 "	2.55	75	29.4
10.42 "	3.23	94	29.1
16.7 "	4.08	124	30.3
26.7 "	5.16	161	31.3

0.72×10^{-4} MCuCl₂ in 1 F LiClO₄ in P.C.

4.07 mv/sec	2.02	26	12.9
6.52 "	2.55	33	12.9
10.42 "	3.23	41	12.7
16.7 "	4.08	51	12.5
26.7 "	5.16	66.5	12.9

0.072×10^{-4} MCuCl₂ in 1 F LiClO₄ in P.C.

4.07 mv/sec	2.02	12.2	6.02
6.52 "	2.55	12.6	4.94
10.42 "	3.23	17.3	5.35
16.7 "	4.08	24.0	5.88
26.7 "	5.16	33.6	6.52

Table 15
Comparison of Inorganic Cathode Materials

Cathodes: 1.70 gms. Active Material; 0.20 gram graphite; 0.10 gram polyethylene powder pressed at 500 lbs./cm² at 90°C for 3 minutes

Electrolyte: 1F. LiClO₄/P.C. Current Density: 2 ma/cm² (Data from Figures 12, 13, 14, and 15)

Cathode Material	Amp. Hrs. / Gram Active Material		Coulombic Efficiency (%)	Open Circuit Voltage vs Li/Li ⁺	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)		Watt-Hrs / Lb Active Material		Watt-Hrs / Lb Battery (Estimated)
	Theor	Obs.				Theor	Obs.	Theor	Obs.	
TiF ₄	0.865	0.030	3.5	2.29	1.53	66.9	735	20.5	3.25	
TiF ₃	0.766	0.007	1.0	1.84	1.06	58	534	1.87	0.93	
CrF ₂	0.595	0.012	2.0	2.35	0.54	23	550	3.27	0.50	
CuSO ₄	0.335	0.015	4.5	3.21	0.84	26	450	5.45	1.05	
CuO	0.673	0.074	11	2.24	0.79	35	582	26.3	1.4	
NiCO ₃	0.415	0.045	11	2.68	1.00	37	491	21.3	4.0	
NiF ₂	0.554	0.066	12	2.82	0.98	35	620	30	5.2	
FeCO ₃	0.462	0.032	7	2.37	1.50	63	447	22.3	3.9	
CrCl ₃	0.507	0.045	9	2.27	0.80	35	926	15	5.8	
CuCO ₃	0.467	0.107	23	3.17	1.52	48	563	71	12.4	
Fe ₂ O ₃	1.0	0.31	31	1.62	0.73	45	588	102	16.4	
MnF ₂	0.576	0.161	28	2.17	0.54	25	498	39.8	6.9	
CuS	0.56	0.145	26	3.2	1.36	42.5	-	89	36	

Table 16
Effect of Current Density on AgO Cathode Performance

Cathodes: 1.70 AgO, 0.20 gm SW 1651 graphite, 0.10 polyethylene powder pressed 500 lbs./cm² at 90°C for 3 minutes

Electrolyte: 1F LiClO₄/P.C.

(Data from Figure 16)

Current Density (ma/cm ²)	Amp. hrs. /gram Active Material		Open Circuit Voltage vs Li/Li ⁺	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)	Watt hrs. /lb. Active Material		Watt hrs /lb. Battery (Estimated)
	Theor.	Obs.				Theor.	Obs.	
2	0.433	0.411	2.95	1.76	60	520	327	106.5
3	0.433	0.312	2.95	1.78	60	520	253	80.8
4	0.433	0.329	2.95	1.77	60	520	253	85.5
5	0.433	0.20	2.95	1.12	38	520	103	32.7

Table 17
Comparison of Organic Cathode Materials

Cathodes 0.25 grams Cathode Material and 0.25 grams Columbian Carbon
 Discharge Current Density - 2 ma/cm²
 (Data from Figures 19 and 20)

Cathode Material	Electrolyte	Amp. Hrs./Gram Active Material		Coulombic Efficiency (%)	Open Circuit Voltage vs Li/Li ⁺	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)	Watt hrs. / lb. Active Mat.		Watt Hrs. / lb. Battery (Estim.)
		Theor.	Obs.					Theor.	Obs.	
m-DNB	1F LiClO ₄ /PC	1.9	0.36	20	3.2	1.95	61	1860	325	47
m-DNB	2F LiClO ₄ /PC	1.9	1.8	94	3.2	1.95	61	1860	1580	125
Picric Acid	2F LiClO ₄ /DMC	2.14	1.5	70	3.36	1.59	47.2	2100	1080	83
ADCA	1F LiClO ₄ /PC	0.46	0.26	56	3.2	2.06	64	595	260	40
ADCA	2F LiClO ₄ /DMC	0.46	0.41	89	3.2	1.95	61	595	363	88
BBFOS	1F LiClO ₄ /PC	1.2	0.54	45	3.2	2.07	65	1330	510	116
BBFOS	2F LiClO ₄ /DMS	1.2	1.72	143	3.2	1.52	47.5	1330	1189	139

Table 18
Effect of Cathode Weight and Compacting Pressure on
m-DNB Cathode Performance

Cathodes: Pasted: Blend of 50% m-DNB and 50% Columbian Carbon (not pressed).
 Pressed: Blend of 50% m-DNB and 50% Columbian Carbon (0.5 gms. m-DNB/Electrode)

Electrolyte: 2F LiClO ₄ /DMC		Current Density: 2 ma/cm ²					(Data from Figures 21 and 22)			
Weight of m-DNB in Cathode	Compacting Pressure (lbs/cm ²)	Amp. Hrs/gm Active Material		Coulombic Efficiency (%)	Open Circuit Voltage vs Li/Li ⁺	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)	Watt Hrs/lb Active Material		Watt Hrs / lb Battery (Estimated)
		Theor.	Obs.					Theor.	Obs.	
0.25 gm	pasted	1.9	1.5	79	3.2	1.87	58	1860	1257	110
0.50 gm	"	1.9	0.54	28	3.2	2.10	66	1860	526	51
0.50 gm	133	1.9	0.44	23	3.2	2.18	68	1860	435	43
0.50 gm	333	1.9	0.62	33	3.2	2.24	70	1860	626	62
0.50 gm	1000	1.9	0.52	27	3.2	2.14	67	1860	503	50

Table 19
Effect of Electrolyte and Current Density
on CuF_2 Cathode Performance

Cathodes: 1.70 gm CuF_2 ; 0.20 gm graphite, 0.10 gm polyethylene pressed at 500 lbs/cm² and 90°C for 3 minutes.

(Data from Figures 25, 26, 28, and 29)

Electrolyte	Current Density (ma/cm ²)	Amp. Hrs. / gram of Active Mat.		Open Circuit Voltage vs Li/Li ⁺	Coulombic Efficiency (%)	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)	Watt. Hrs. / lb. of Active Mat.		Watt-Hrs/lt of Total Battery Weight (Estimated)
		Theor.	Obs.					Theor.	Obs.	
2F LiClO_4 - DMC	3	0.528	0.408	3.50	78	2.33	66.5	746	435	128
"	5	0.528	0.366	3.50	70	2.52	72	746	420	123
"	7	0.528	0.301	3.50	58	2.34	67	746	320	95
"	10	0.528	0.175	3.50	34	2.09	60	746	164	48
0.75 F LiBF_4 -PC	2	0.528	0.172	3.50	33	2.90	82	746	227	67
1F LiClO_4 -PC, 5% BF ₃ /THF	2	0.528	0.295	3.50	56	2.40	69	746	326	87
1F LiClO_4 -PC, 10% BF ₃ /THF	2	0.528	0.343	3.50	65	2.43	70	746	378	102
"	4	0.528	0.528	3.50	100	2.75	79	746	658	177*
"	6	0.528	0.216	3.50	48	2.17	62	746	192	50
"	8	0.528	0.100	3.50	23	1.66	47	746	72	19

* Not Reproducible

Table 20
Effect of Complexones and Activated Storage
on CuF_2 on Cathode Performance

Cathodes: 1.70 gm CuF_2 , 0.20 gm graphite, 0.10 gm polyethylene powder.
 Pressed at 500 lbs/cm² and 90 °C for 3 minutes.

Electrolyte: 1F $\text{LiClO}_4\text{-P.C.}$ Current Density: 2 ma/cm²

(Data from Figures 30, 31, and 32)

Complexone (added to electrolyte)	Storage Time	Amp. - Hr/ gram of Active Mat.		Oper Circuit Voltage vs Li/Li ⁺	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)	Watt-Hr/ lb. of Active Mat.		Watt-Hrs/lb. of Total Battery Weight (Estimated)
		Theor.	Obs.				Theor.	Obs.	
no complexone	0	0.528	0.348	3.50	2.78	79	746	436	116
"	1 wk.	0.528	0.021	3.50	0.66	19	746	5.5	1.7
0.05% of Ethylene Diamine	0	0.528	0.321	3.50	2.90	83	746	423	114
"	1 wk.	0.528	0.084	3.50	1.22	35	746	46	13
0.01% Diethylene Triamine	0	0.528	0.332	3.50	2.73	78	746	409	110
0.05% Diethylene Triamine	1 wk.	0.528	0.016	3.50	0.56	16	746	4	1.1

Table 21
Effect of Graphite Treatment, Compacting Pressure,
and Activated Storage on CuF₂ Cathode Performance

Cathode: 1.70 gm CuF₂, 0.20 gm graphite, 0.10 gm polyethylene powder.
 Pressed at 90°C for 3 minutes at pressure indicated.
 Electrolyte: 1 F LiClO₄-PC Current Density: 2 ma/cm²
 (Date from Figures 40, 41, and 42)

Treatment	Pressure (lb/cm ²)	Storage Time	Amp-Hrs. / gram of Active Mat.		Open Circuit Voltage vs Li/Li ⁺	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)	Watt-Hrs / lb. of Active Mat.		Watt-Hrs/lb of Total Battery Weight (Estimated)
			Theor.	Obs.				Theor.	Obs.	
Untreated	3,000	0	0.528	0.216	3.50	3.10	89	746	277	82
Untreated	3,000	1 wk	0.528	0.053	3.50	0.4	11	746	1	0.3
HNO ₃ (i, Appen- dix G)	3,000	0	0.528	0.327	3.50	1.73	49	746	235	68
HNO ₃	3,000	3 days	0.528	0.337	3.50	1.56	45	746	217	65
HNO ₃	3,000	1 wk.	0.528	0.032	3.50	0.6	17	746	8	2.3
HCl (ii, Appen. G)	3,000	0	0.528	0.354	3.50	1.61	46	746	270	69
HCl	3,000	3 days	0.528	0.348	3.50	1.46	42	746	237	62
HCl	3,000	1 wk.	0.528	0.370	3.50	1.53	44	746	265	69
HCl-HNO ₃ (iii, Appen. G)	3,000	0	0.528	0.406	3.50	1.48	42	746	273	72
HCl-HNO ₃	3,000	3 days	0.528	0.380	3.50	1.49	43	746	258	69
HCl-HNO ₃	3,000	1 wk.	0.528	0.306	3.50	0.91	26	746	403	104

(continued)

Table 21 (contd)

Treatment	Pressure (lb/cm ²)	Storage Time	Amp-Hrs. / gram of Active Mat.		Coulombic Efficiency (%)	Open Circuit Voltage vs Li/Li ⁺	Average Voltage vs Li/Li ⁺	Voltage Efficiency (%)	Watt-Hrs. / lb. of Active Mat.		Watt-Hrs /lb. Total Battery Weight (Estimated)
			Theor.	Obs.					Theor.	Obs.	
HCl (ii Appen. G)	500	0	0.528	0.327	62	3.50	2.61	75	746	403	104
HCl	"	3 days	0.528	0.216	41	3.50	1.68	48	746	171	44
HCl	"	1 week	0.528	0.132	25	3.50	1.00	29	746	64	16

Specific Conductance of LiClO_4 in Various Solvents

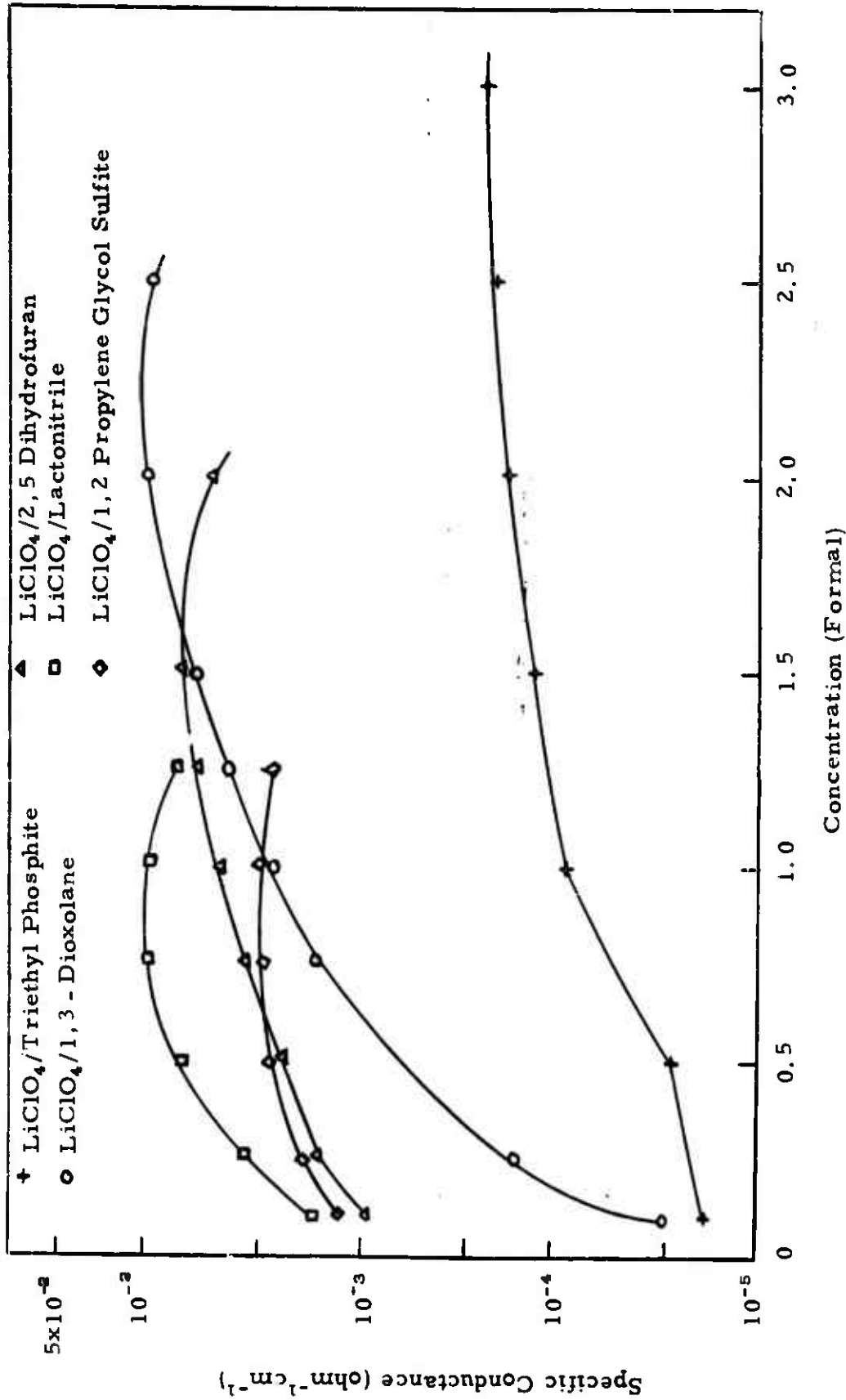


FIGURE 1

Conductance of Solutions of LiClO_4 in Various Organic Solvents

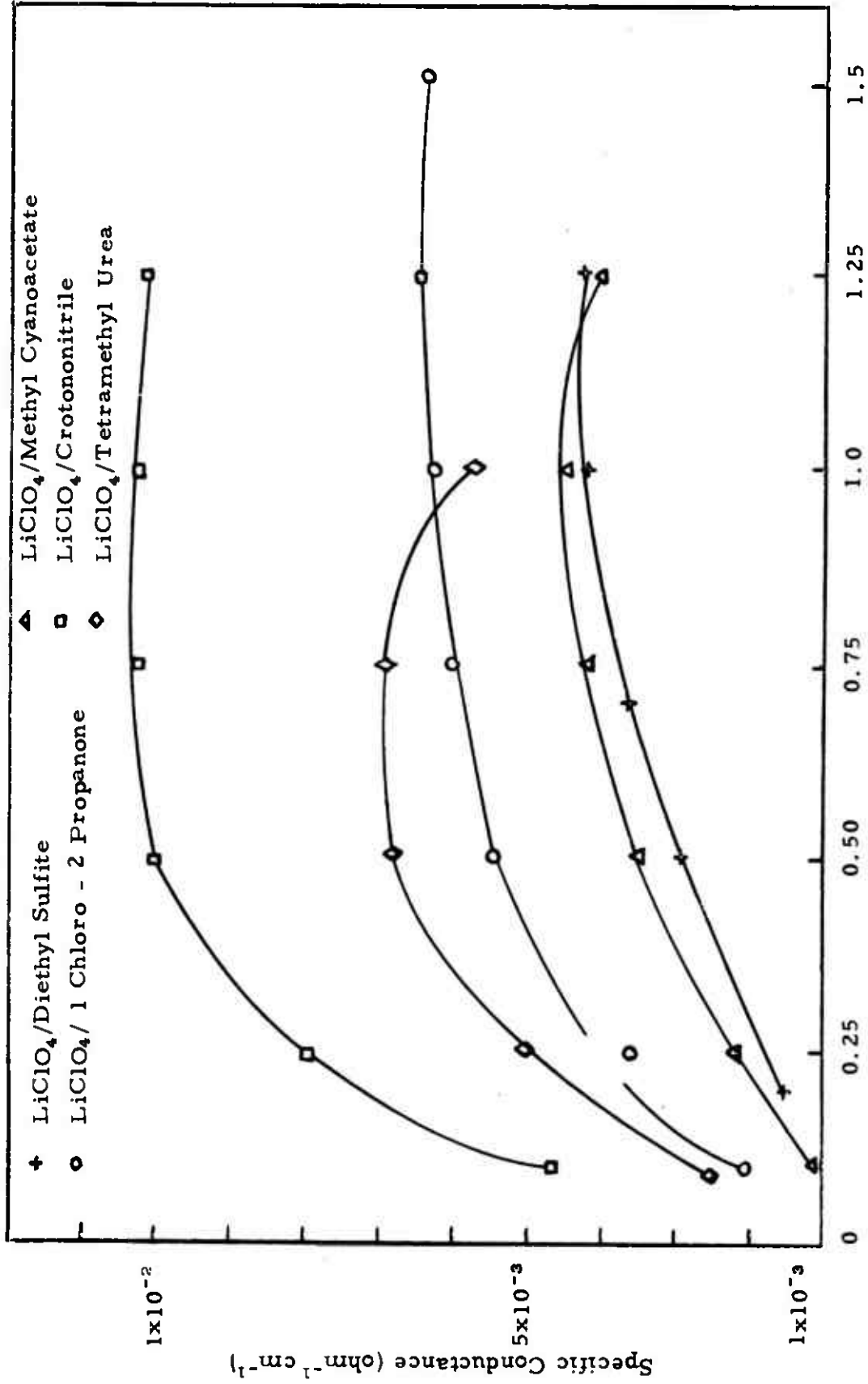


FIGURE 2 Concentration (Formal)

Conductance of Solutions of Various Solutes in Propylene Carbonate

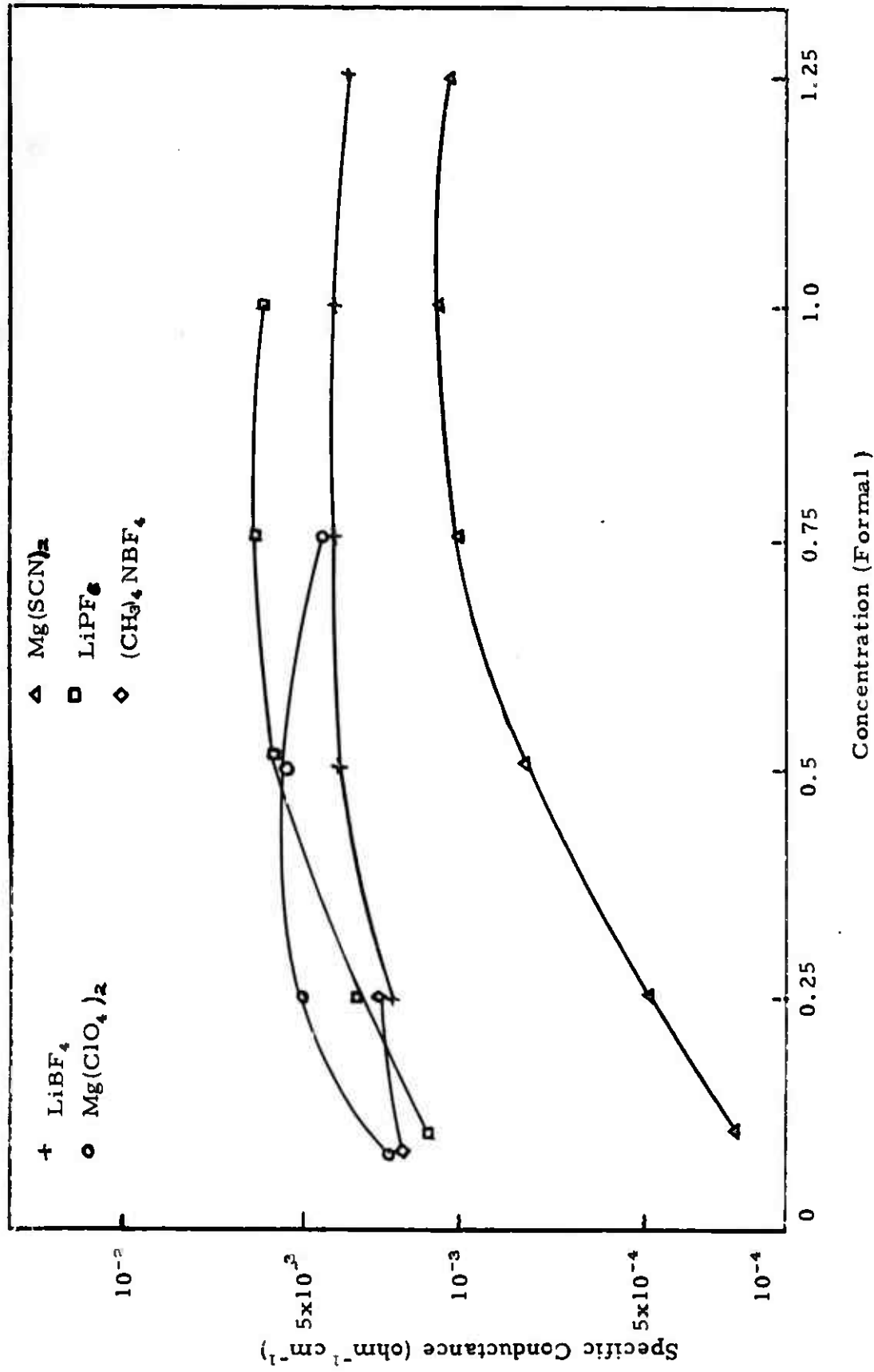


FIGURE 3

Specific Conductance of BF_3 /propylene carbonate solutions

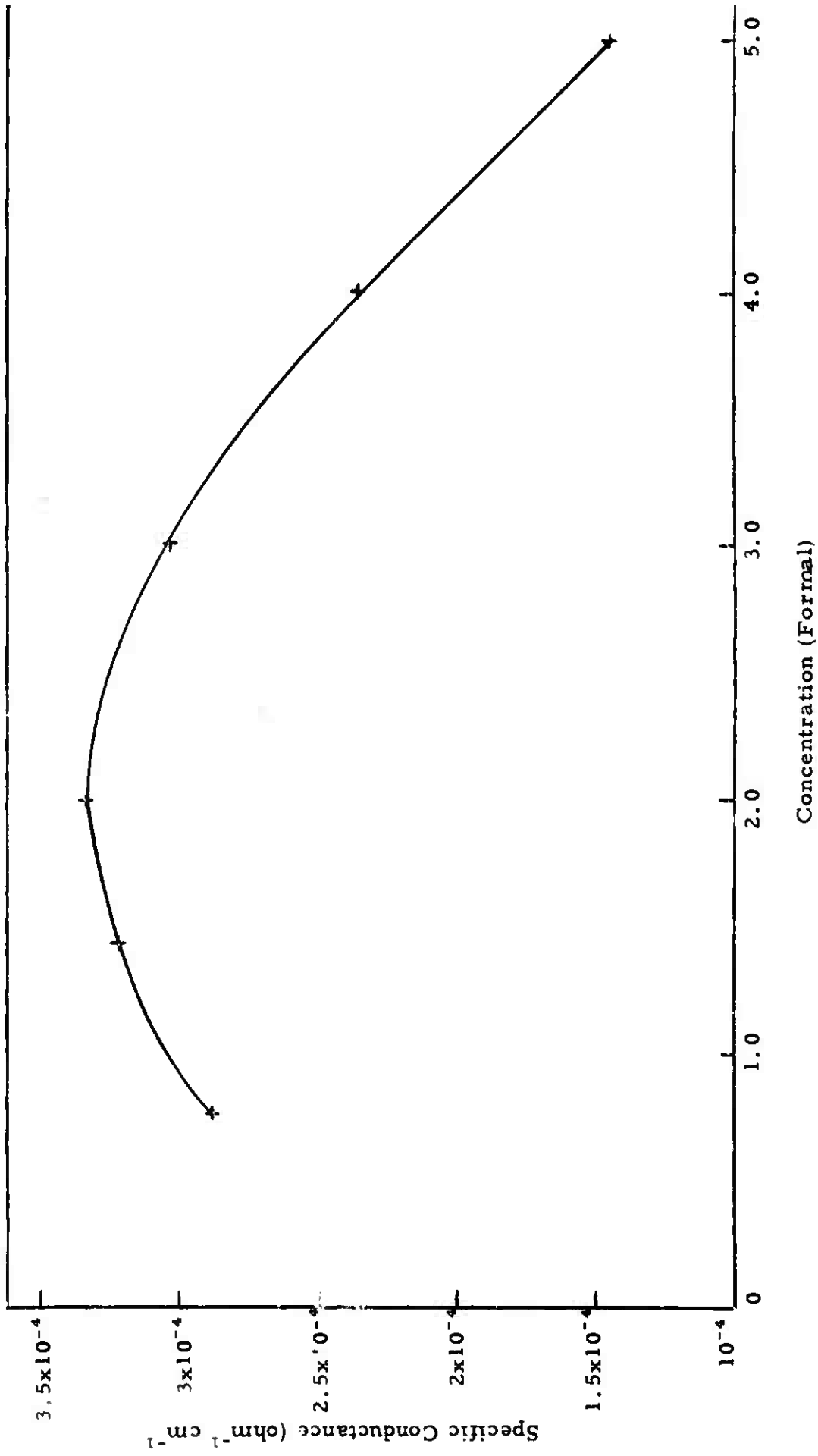


FIGURE 4

Specific Conductance of LiClO_4 in 2F BF_3 / propylene carbonate

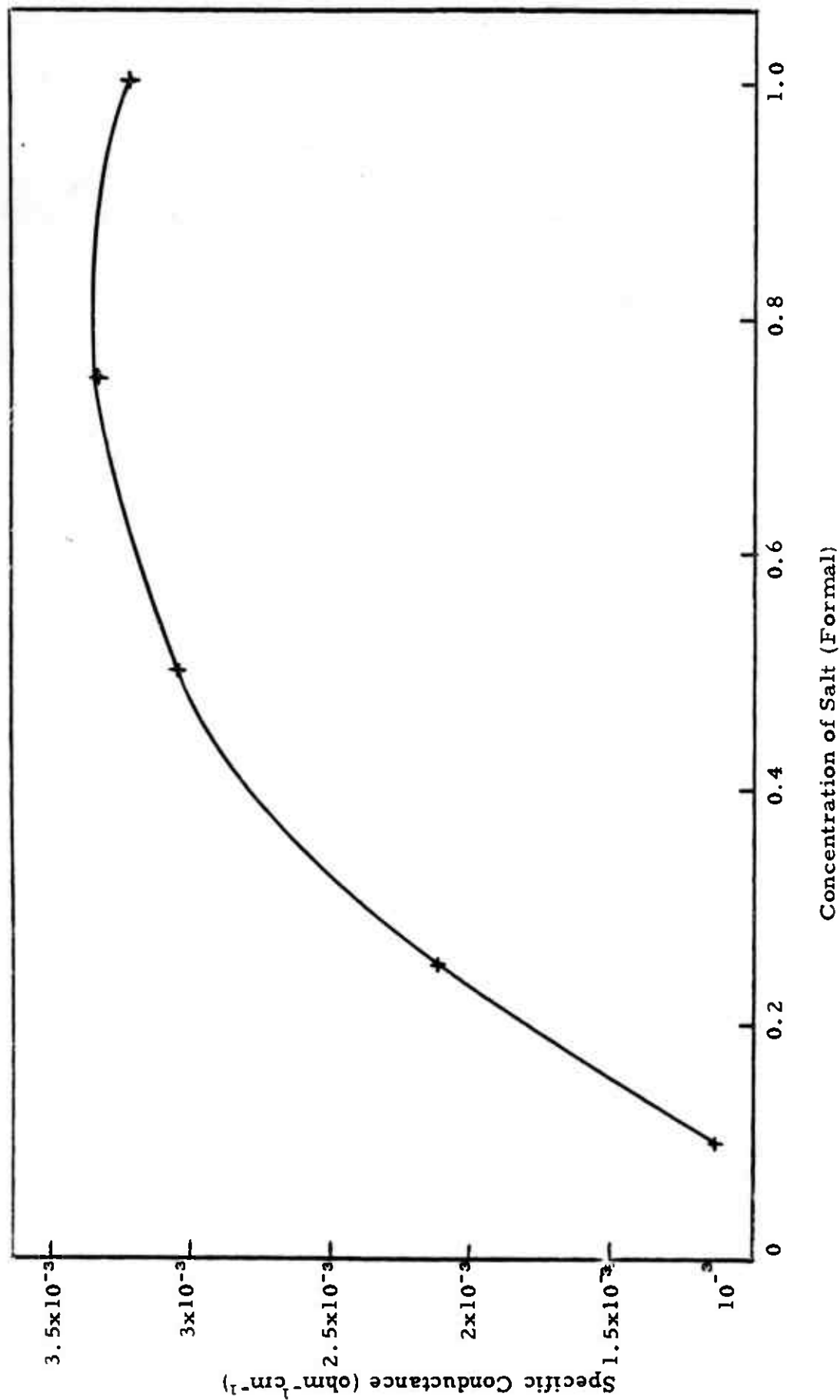


FIGURE 5

Conductance of LiClO_4 in Propylene Carbonate Containing BF_3/THF Complex

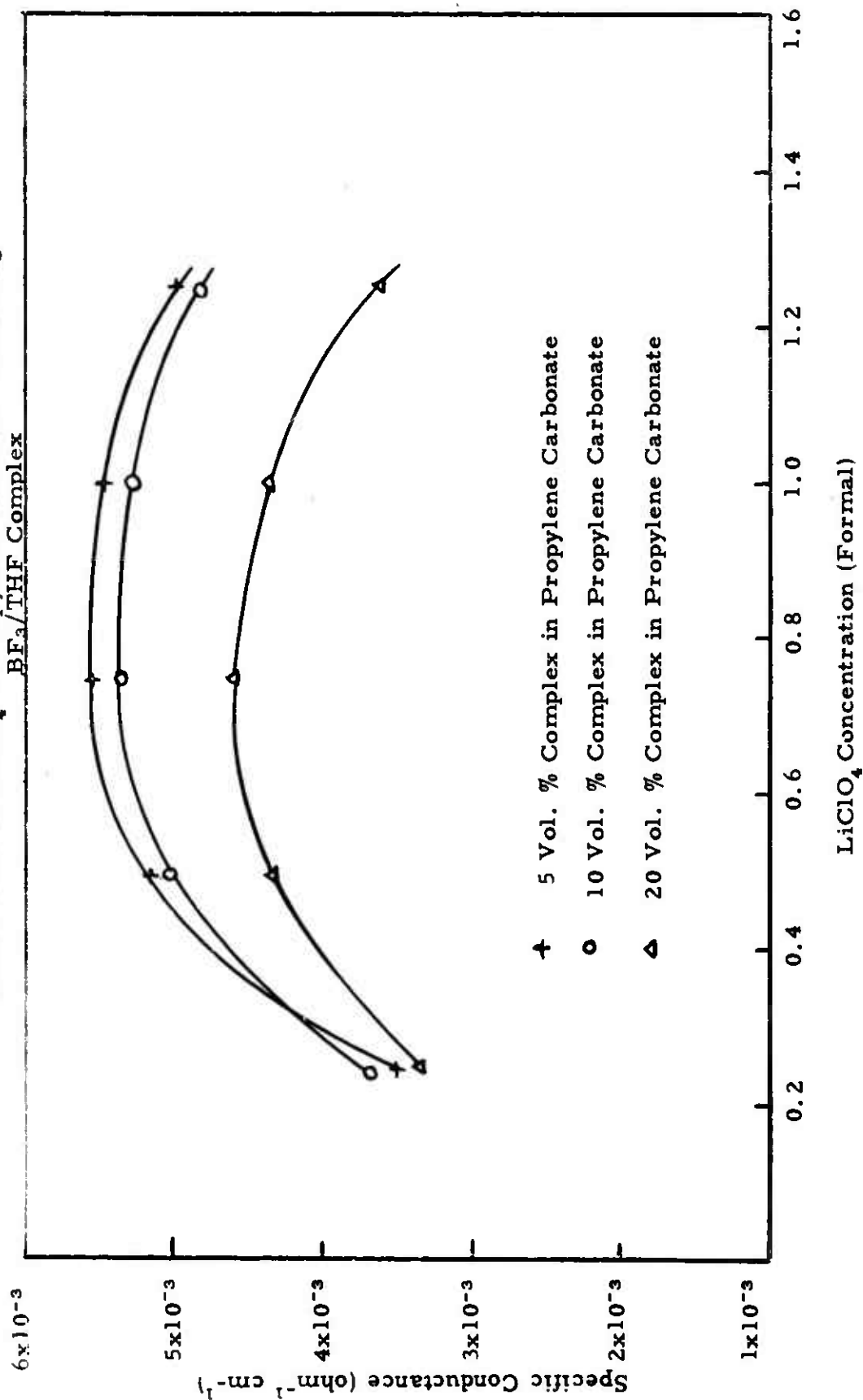


FIGURE 6

Corrosion of Lithium in Various Electrolytes

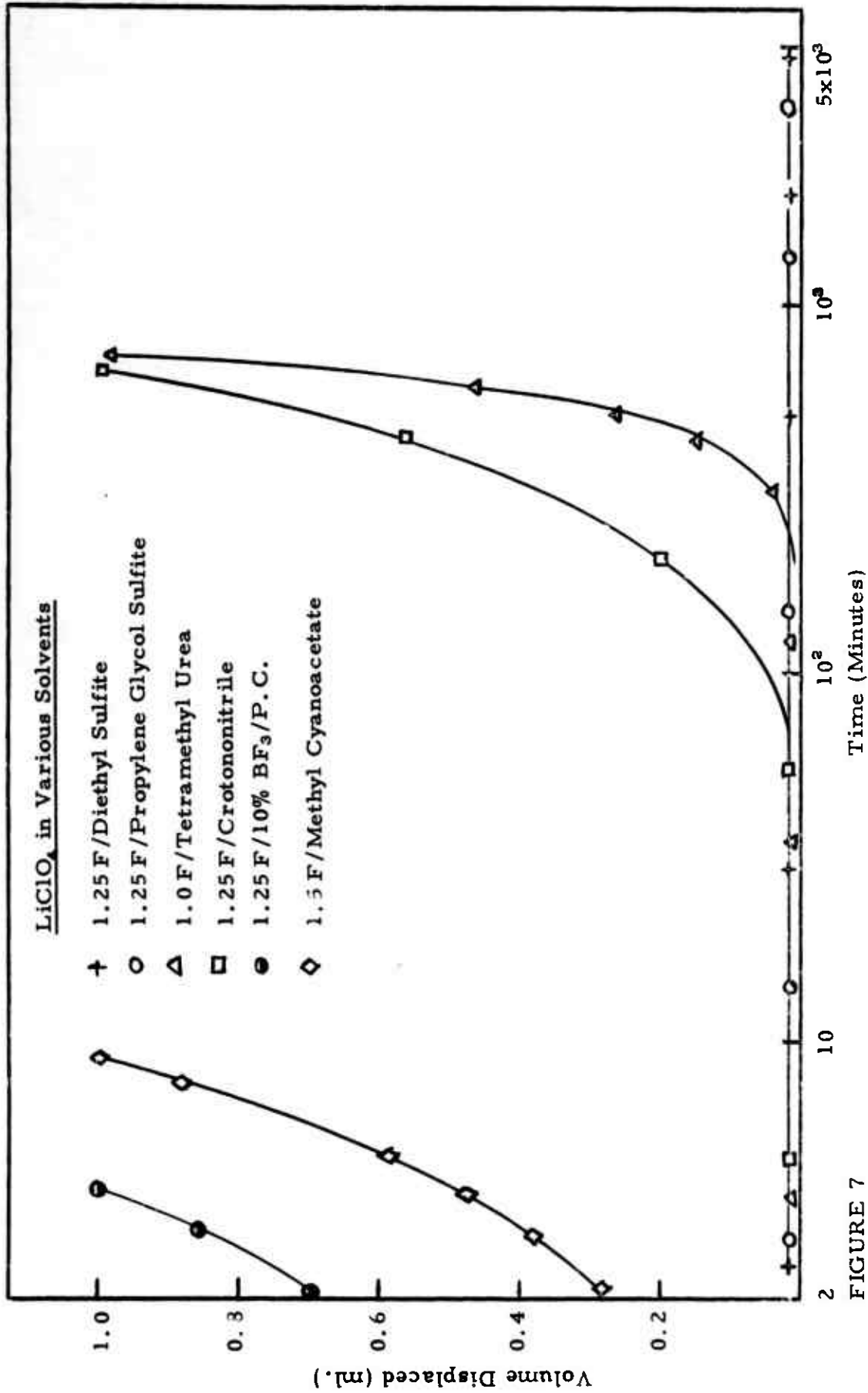


FIGURE 7

Corrosion of Lithium in Various Electrolytes
(LiClO₄ as Electrolyte Solute)

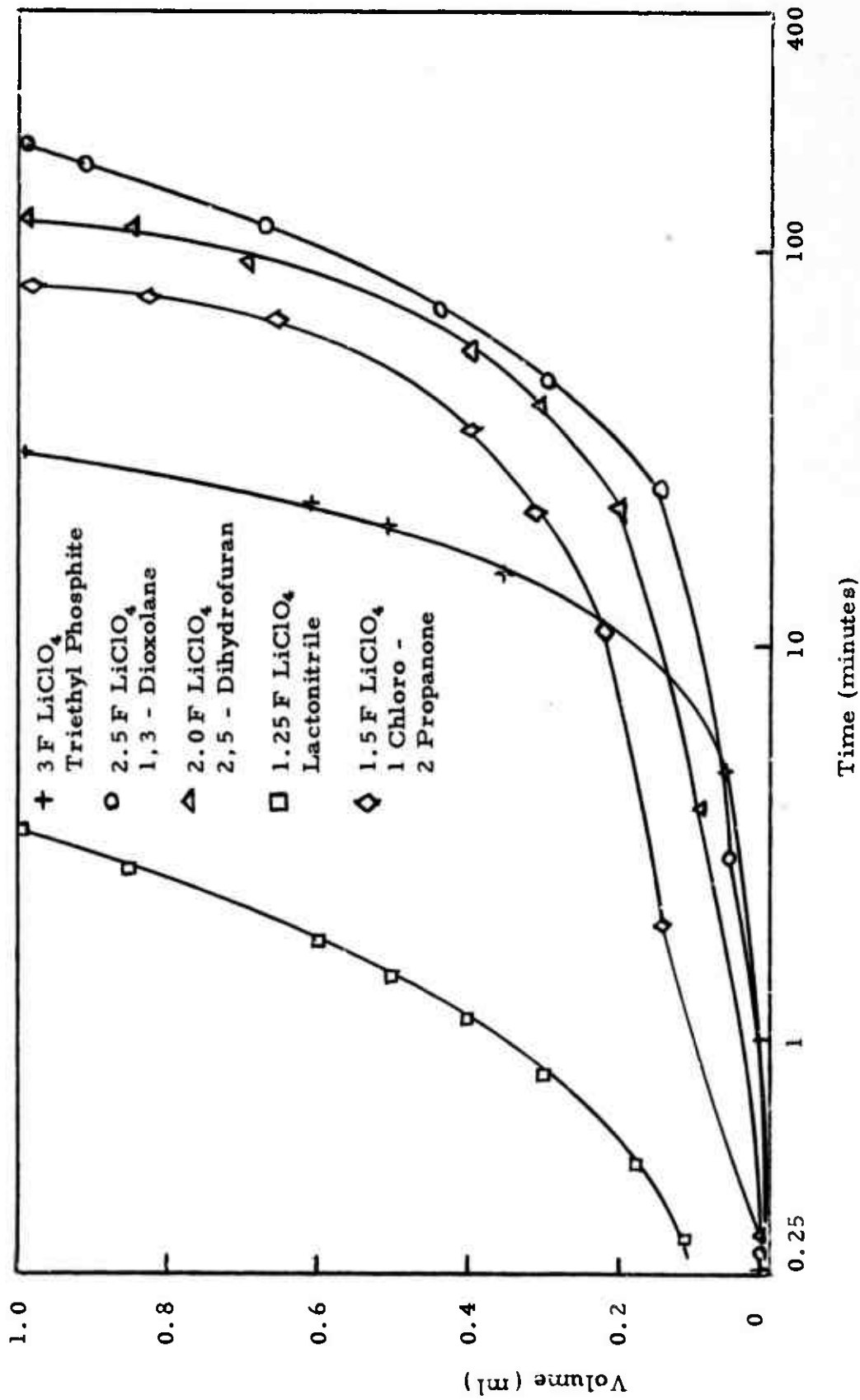


FIGURE 8

Corrosion of Lithium in Various Electrolytes

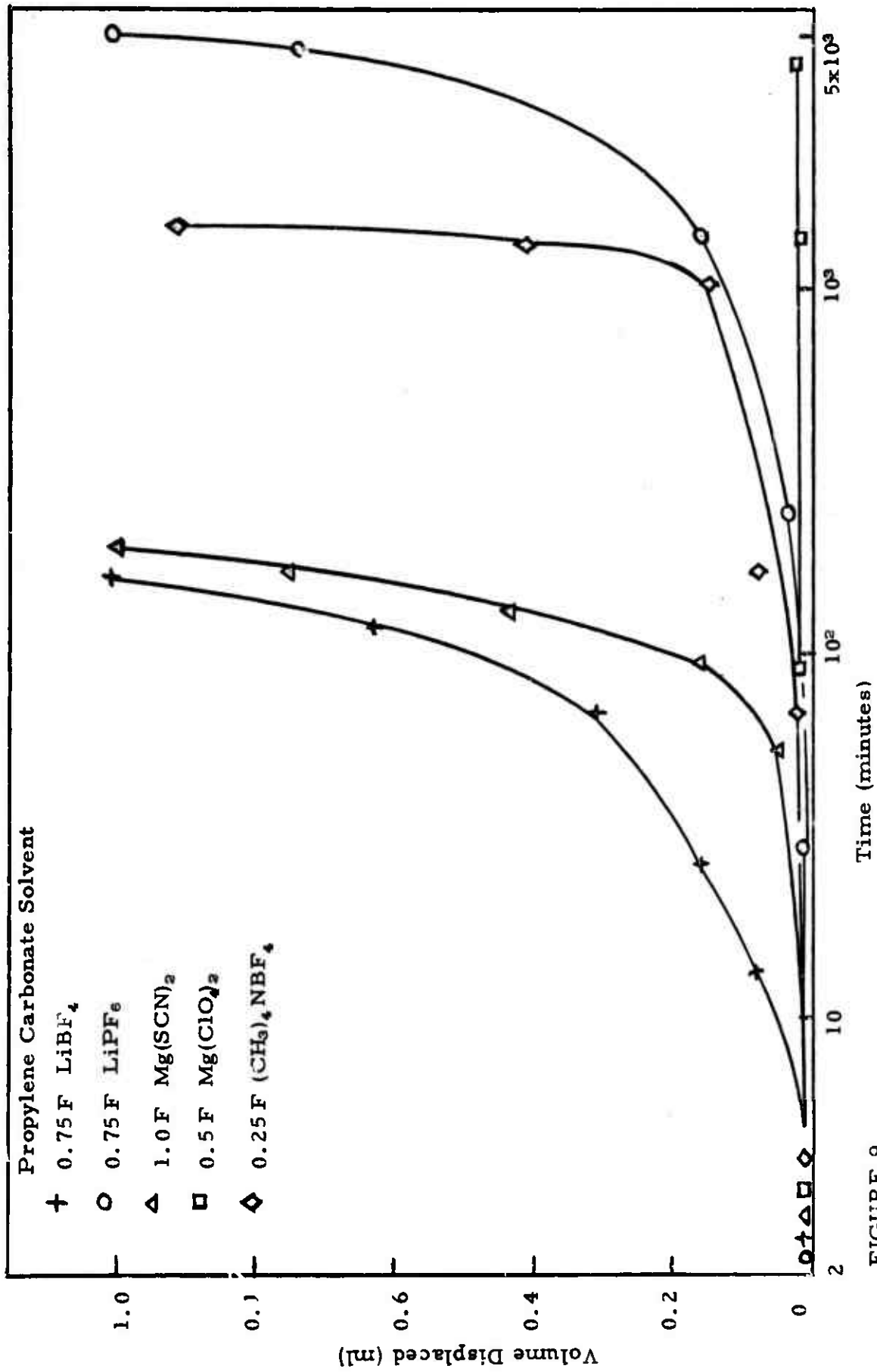


FIGURE 9

Cupric Fluoride Solubility vs. Time

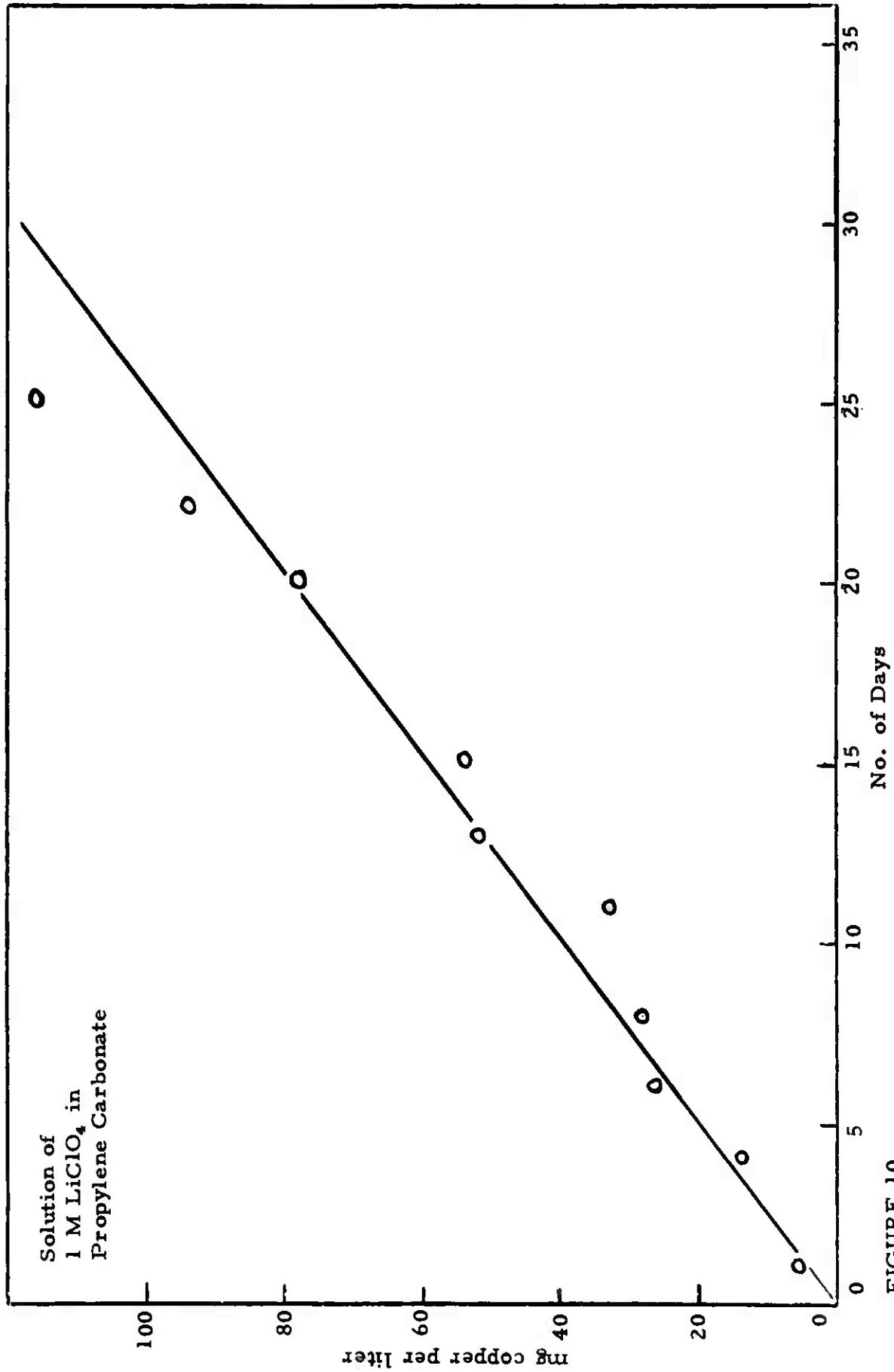


FIGURE 10

Rate of Dissolution of CuF_2 in 1 F LiClO_4 /Propylene Carbonate

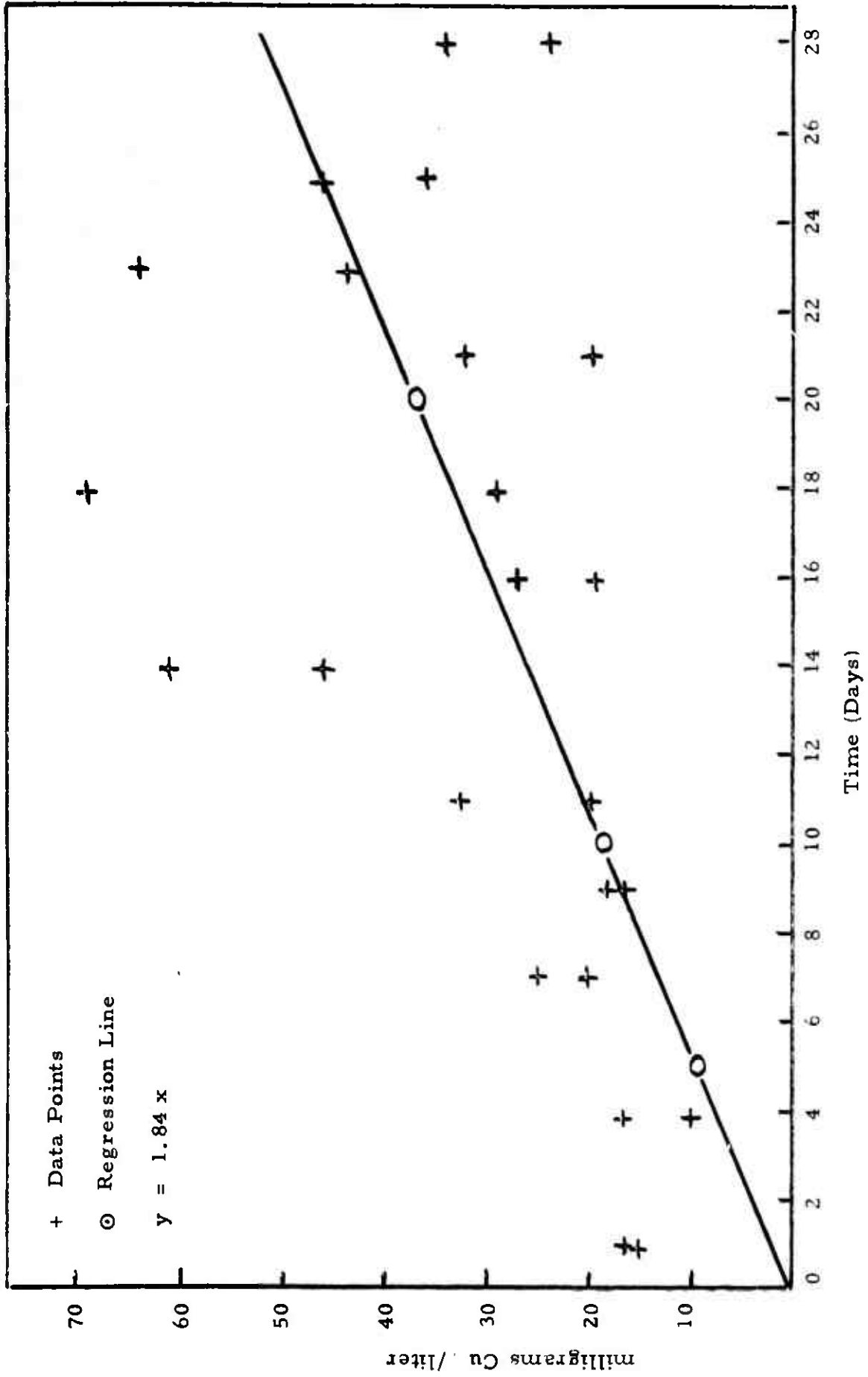


FIGURE 11

Performance of Various Cathode Materials in 1F LiClO₄ - PC

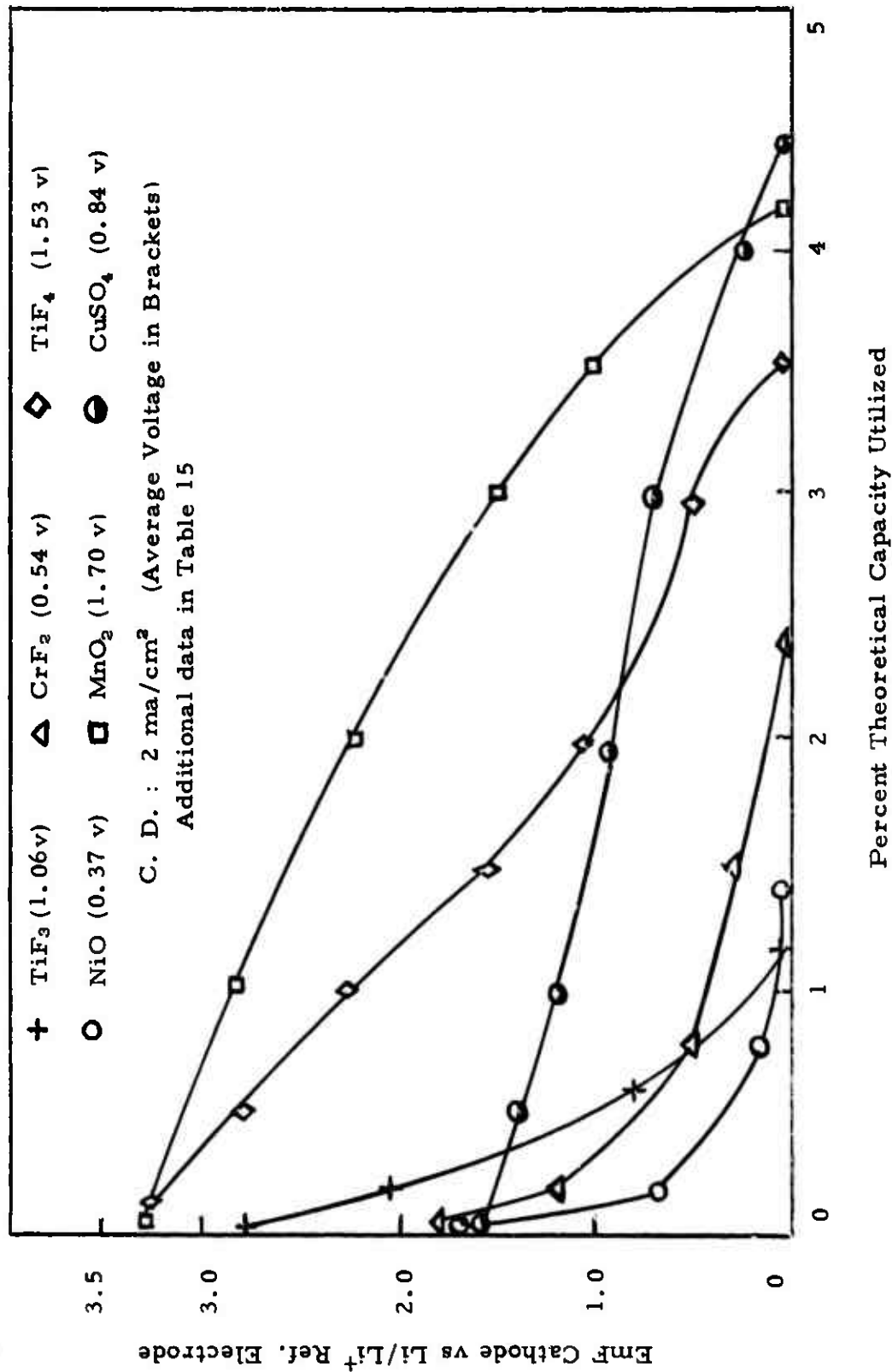


FIGURE 12

Performance of Various Cathode Materials in 1F LiClO₄ - PC

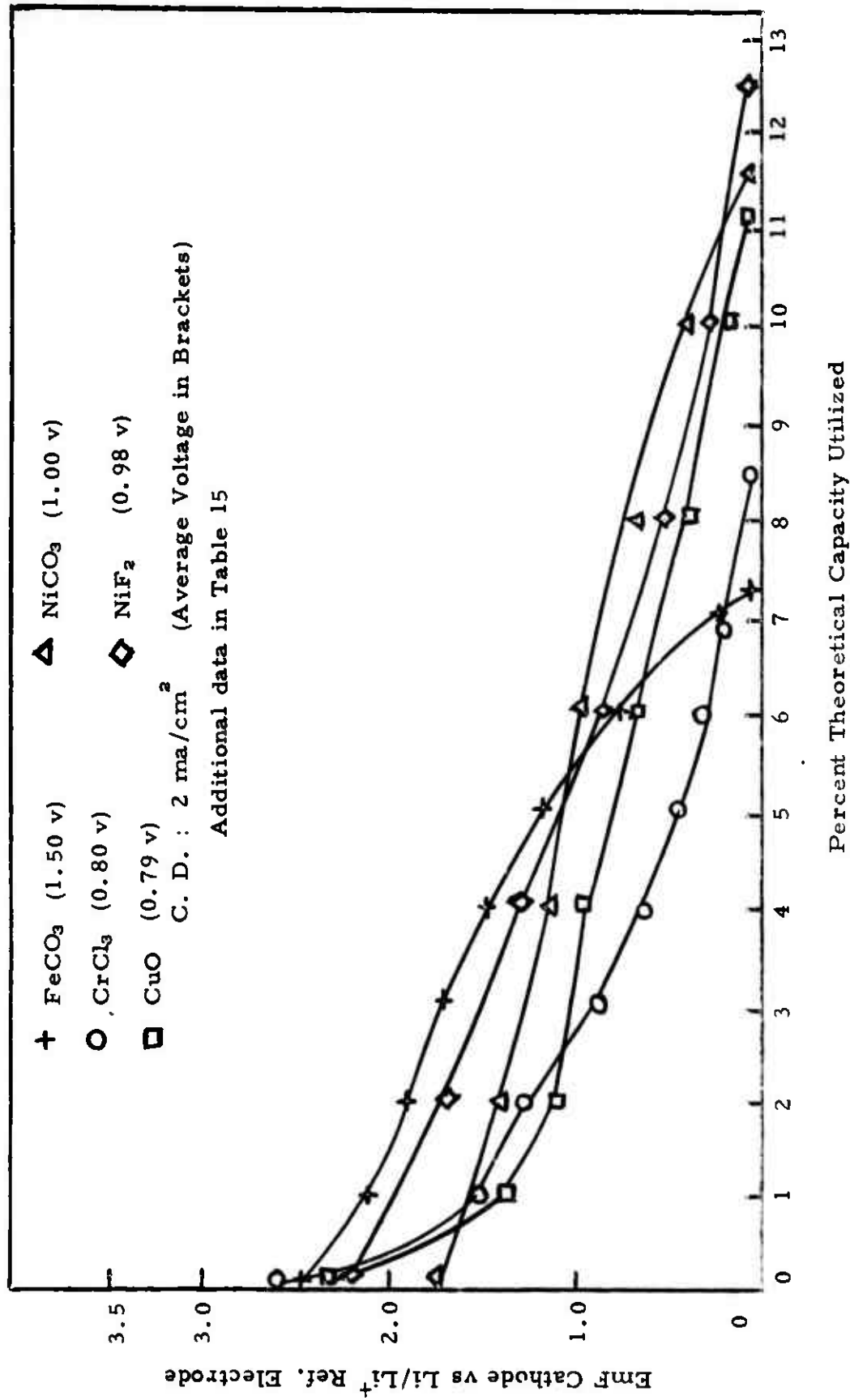


FIGURE 13

Performance of Various Cathode Materials in 1F LiClO₄ - PC

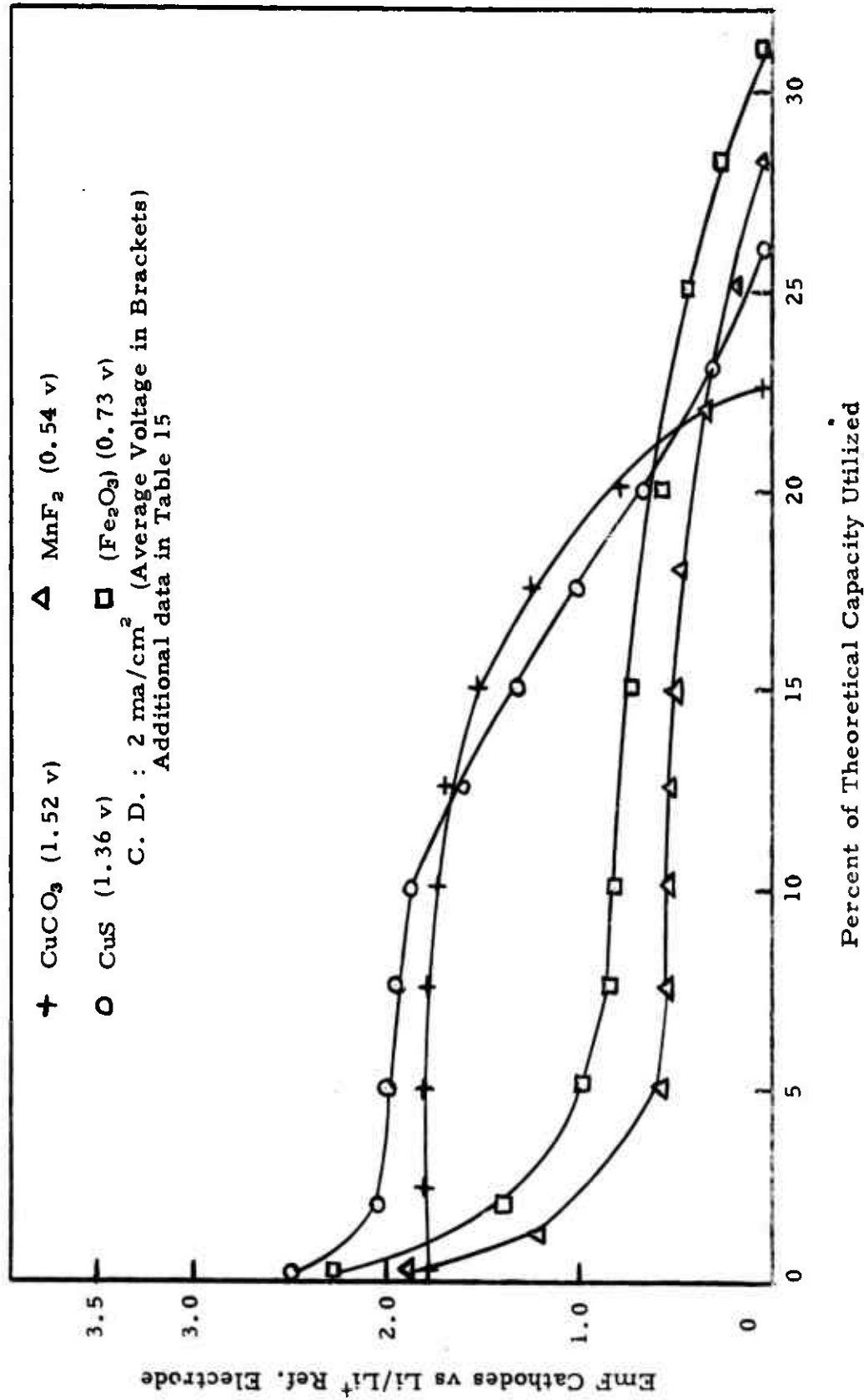


FIGURE 14

Performance of AgO as Cathode Material in 1F LiClO₄ - PC

C. D. : 2 ma/cm²
(1.74 Average Voltage)
Additional data Table 15

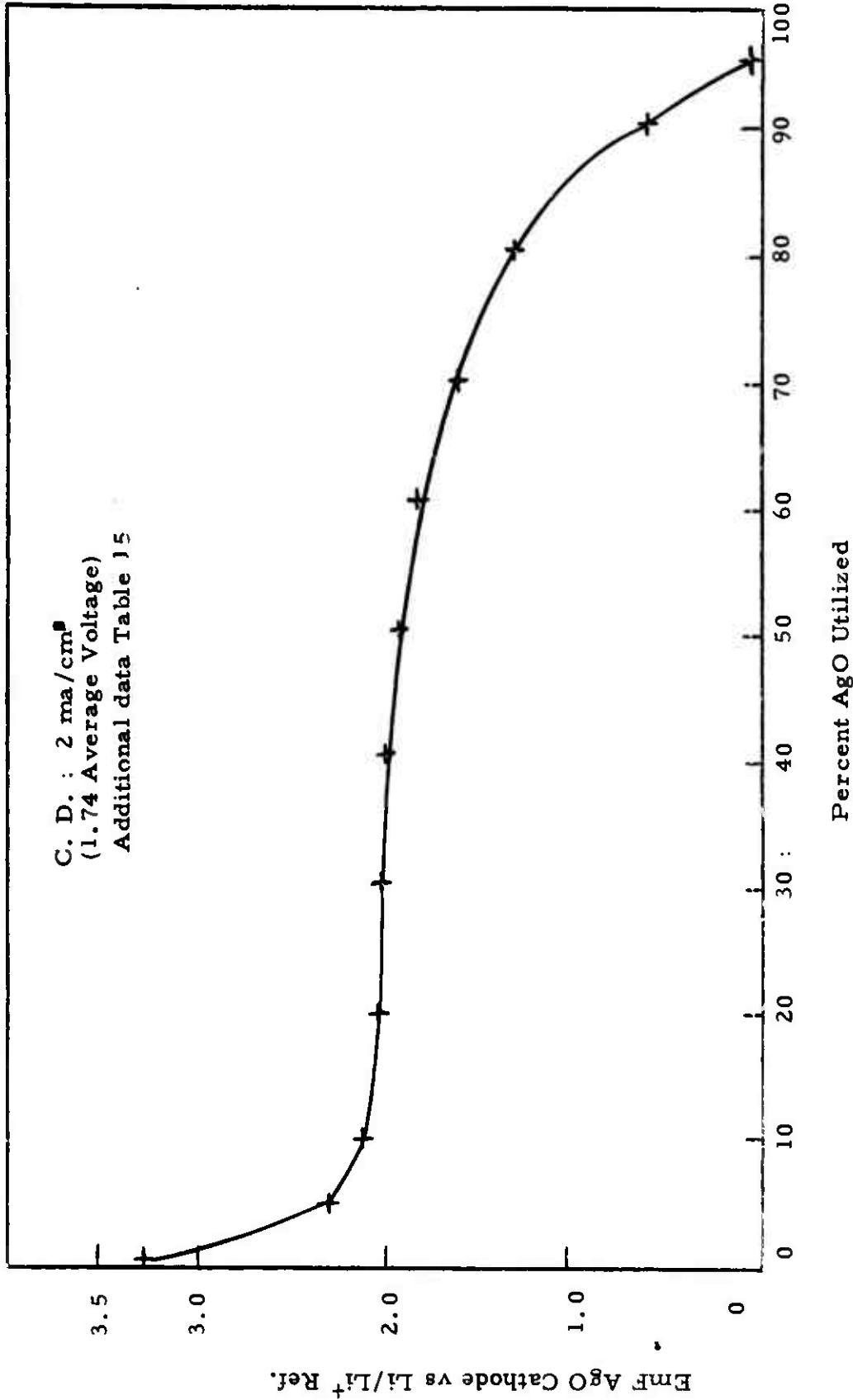


FIGURE 15

AgO Cathodes in 1F LiClO₄ - PC
 Effect of Current Density on Performance

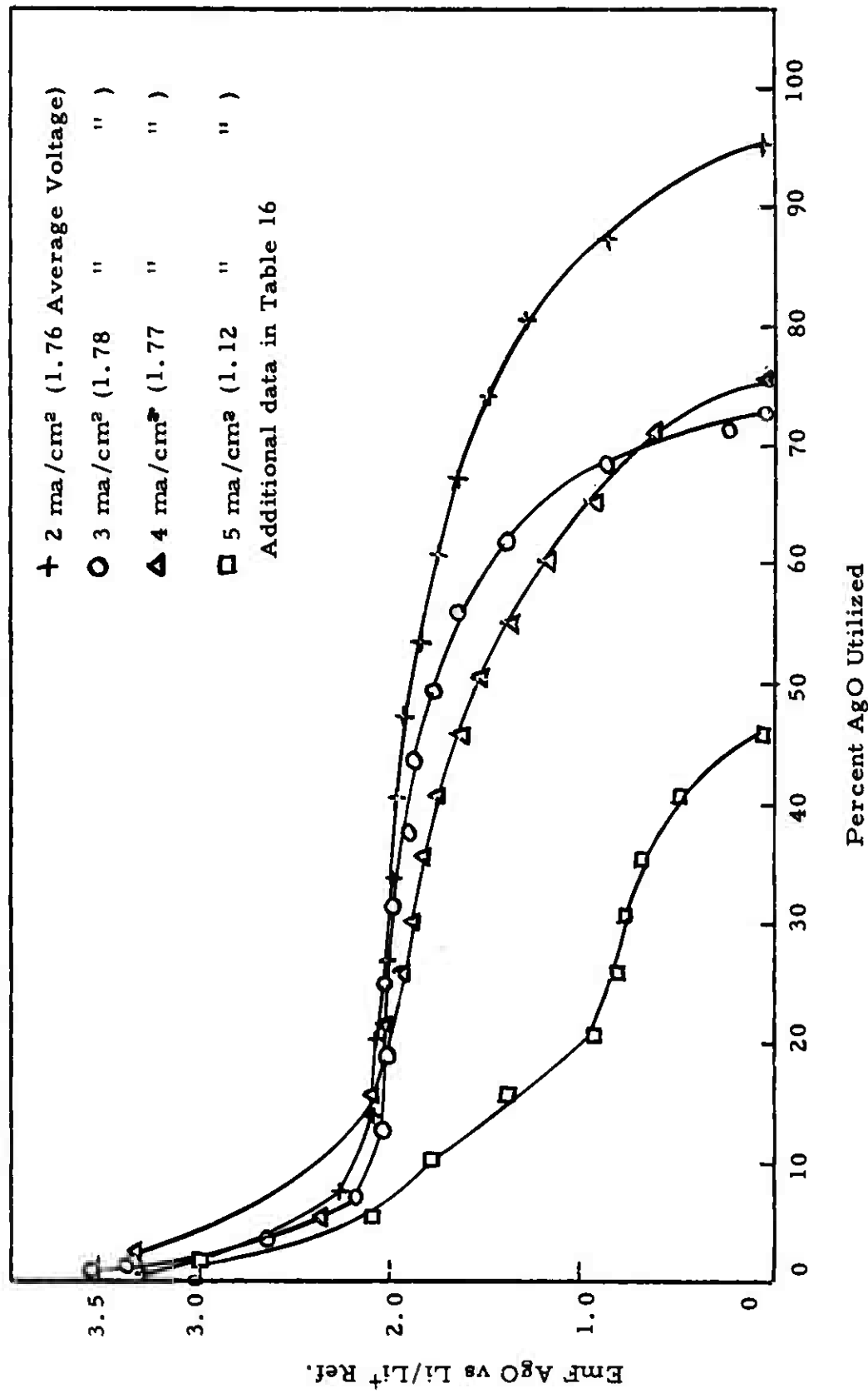


FIGURE 16

Performance of AgO Cathodes in Various Electrolytes

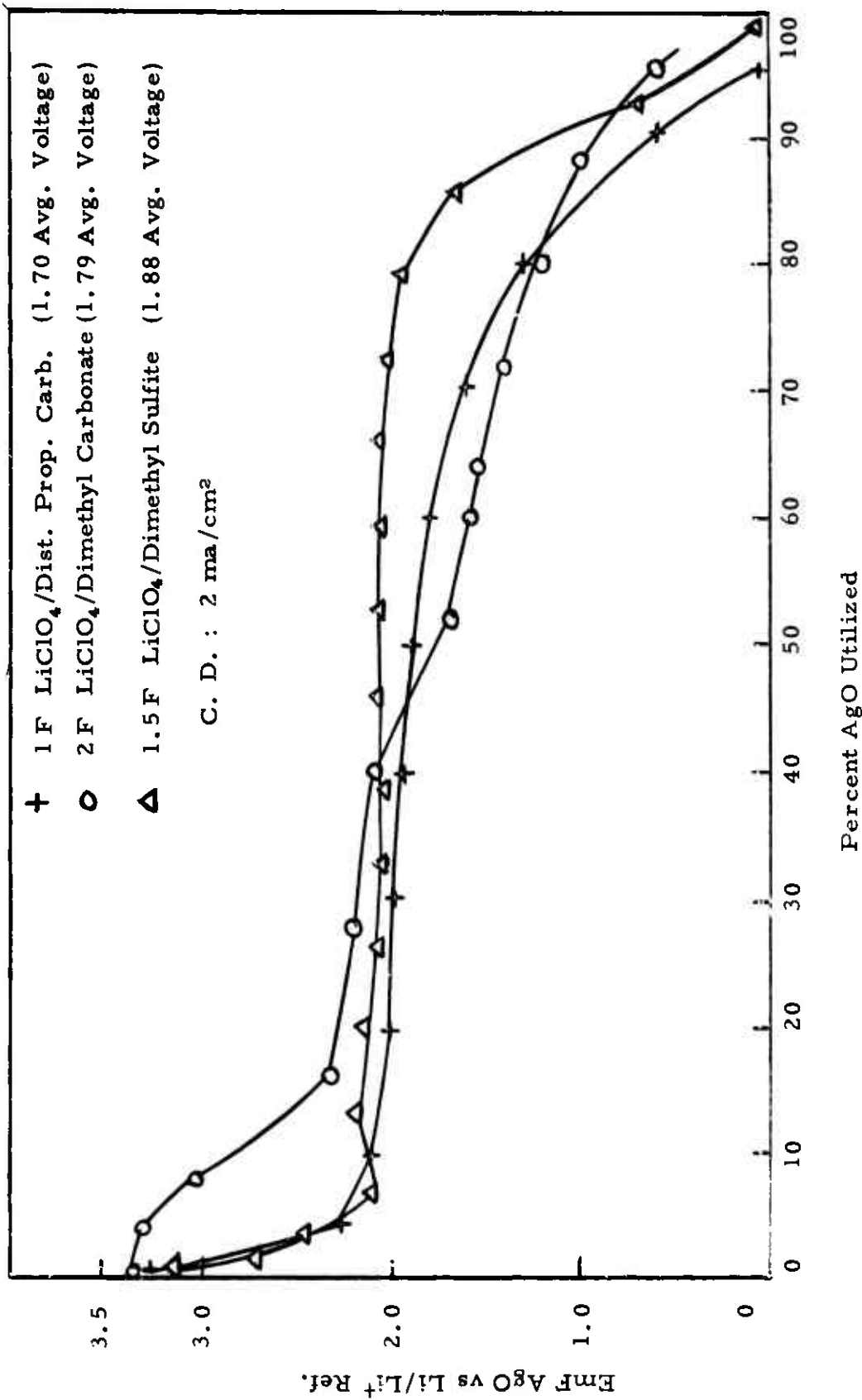


FIGURE 17

Effect of Activated Storage on Li/AgO Cell Performance in 1F LiClO₄ - PC

2 weeks activated storage

C. D. - 2 ma/cm²
(1.70 Average Voltage)

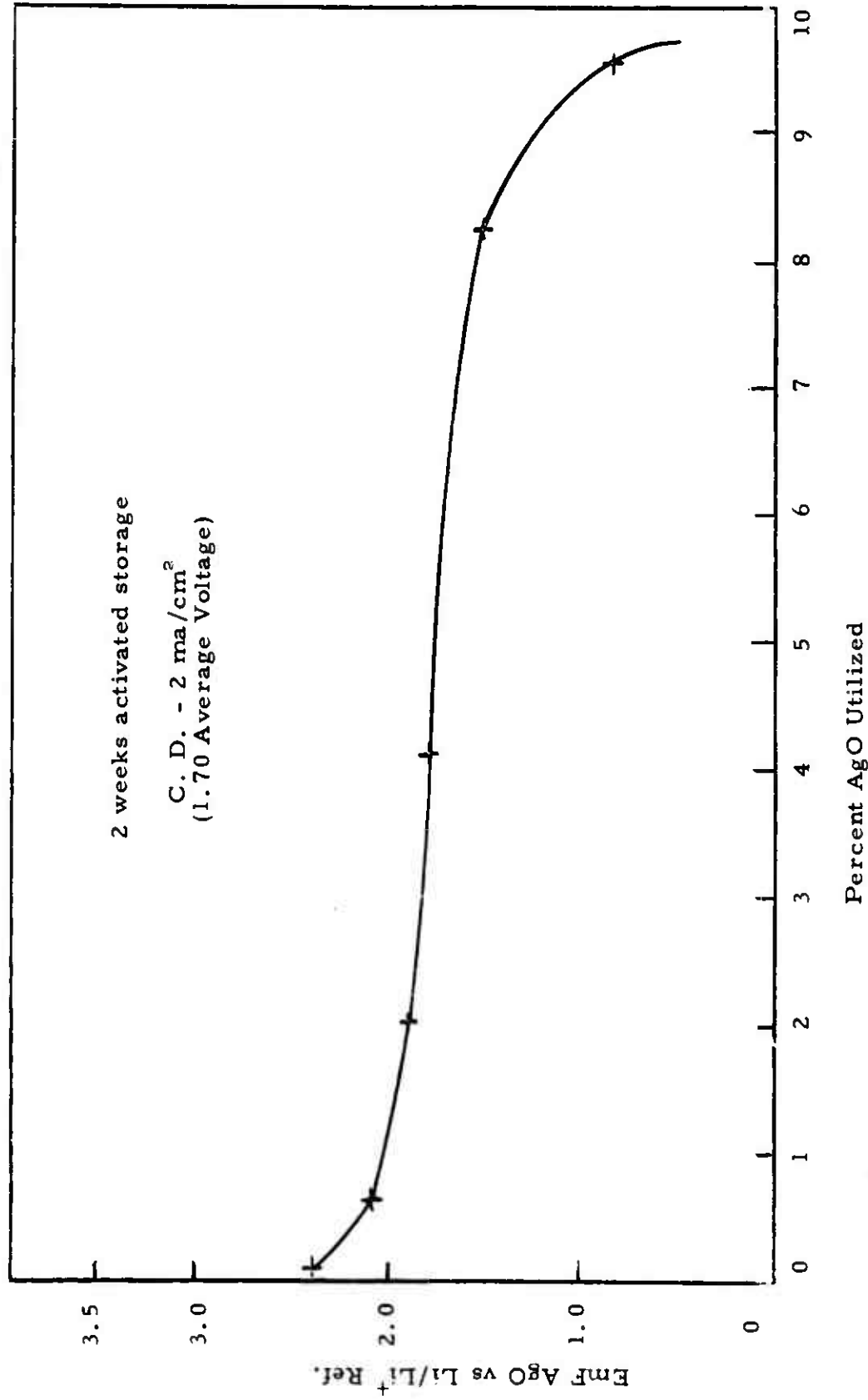
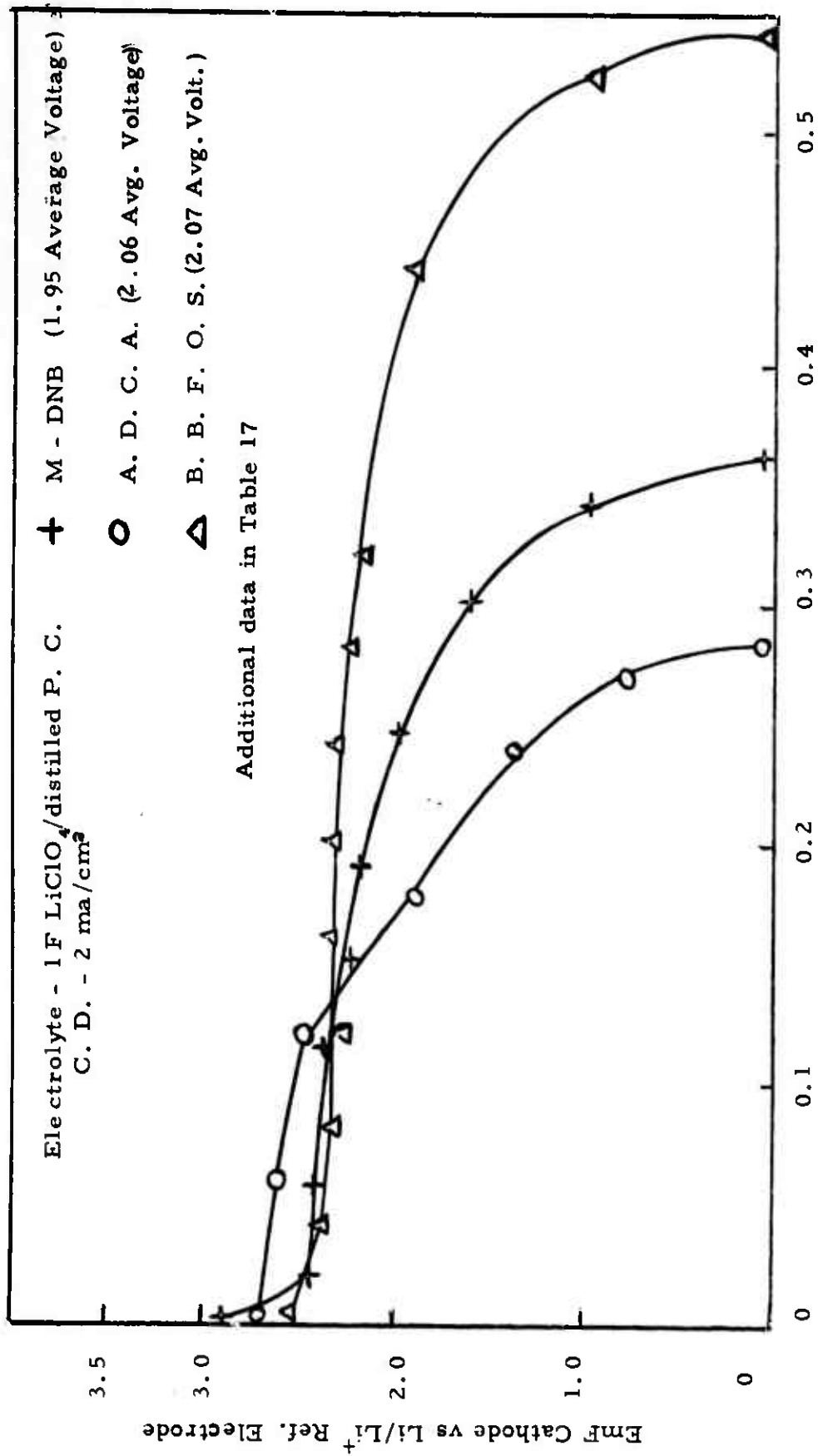


FIGURE 18

Evaluation of Various Organic Cathode Materials
 Pasted Type Cathodes



Ampere-Hrs./Gram Cathode Material

FIGURE 19

Evaluation of Various Organic Cathode Materials

Pasted Type Cathodes

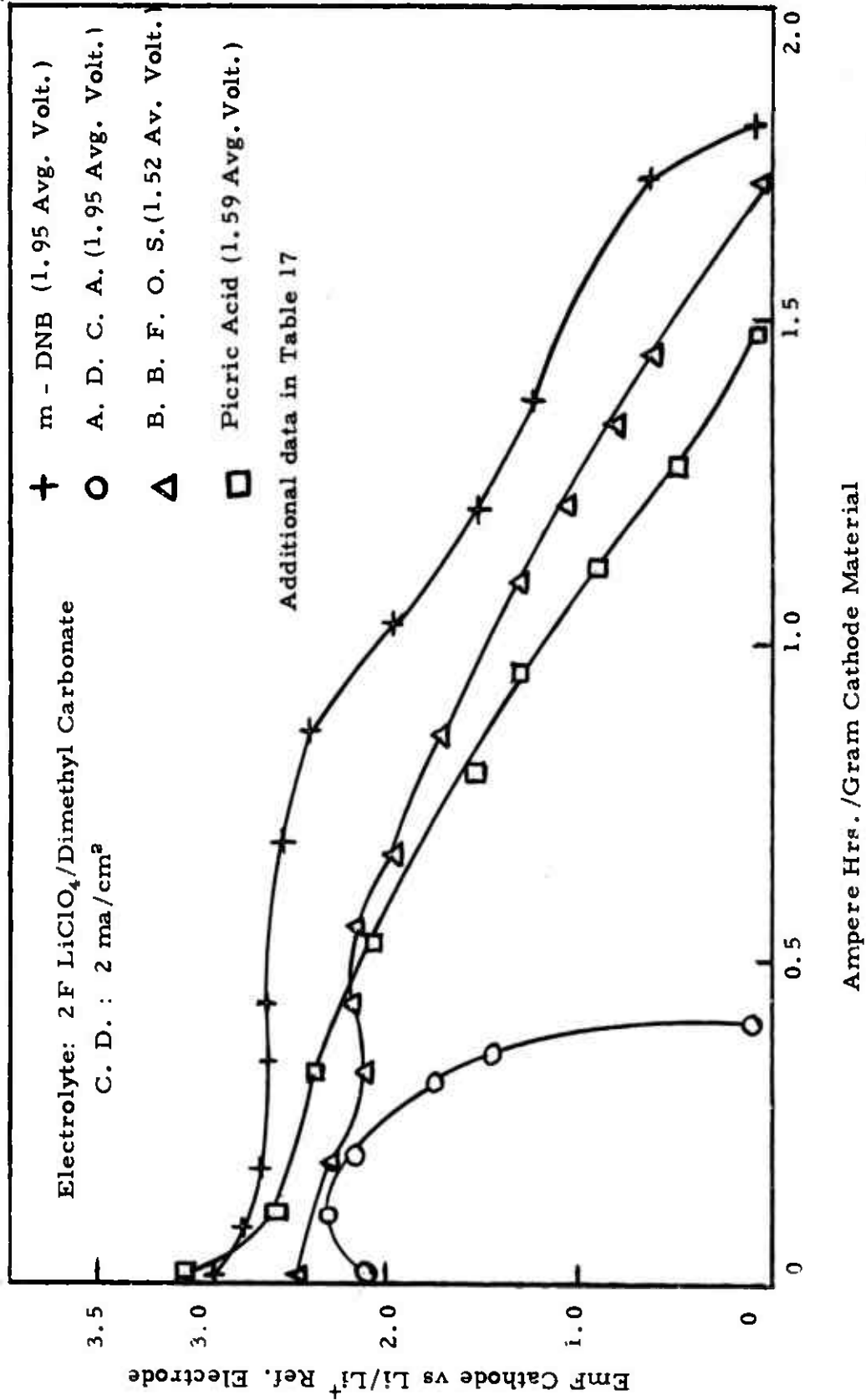


FIGURE 20

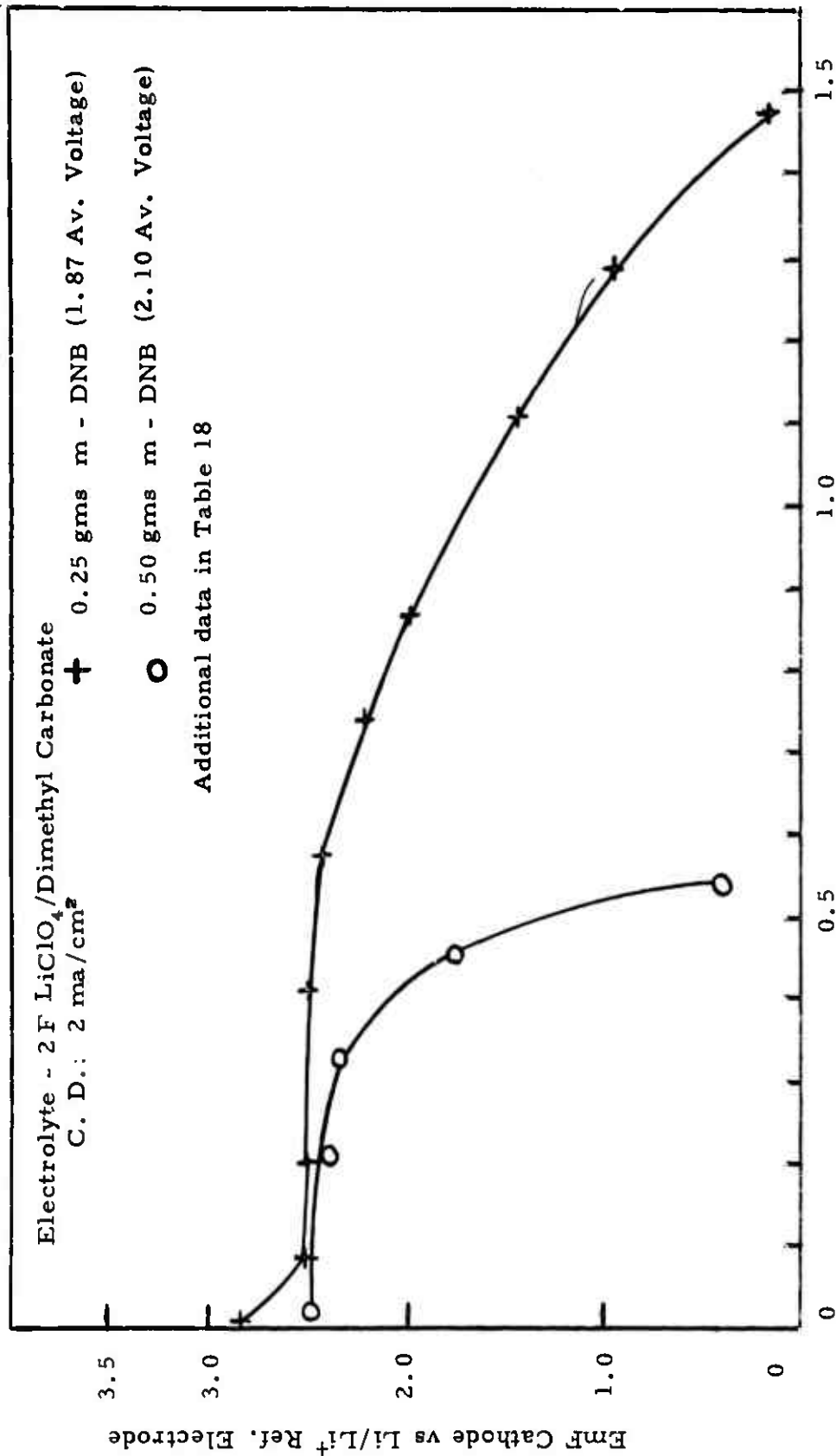
Evaluation of m - DNB Cathodes (Pasted)

Effect of Cathode Weight on Performance

Electrolyte - $2 F LiClO_4 / Dimethyl Carbonate$
C. D.: $2 ma/cm^2$

\dagger 0.25 gms m - DNB (1.87 Av. Voltage)
 \circ 0.50 gms m - DNB (2.10 Av. Voltage)

Additional data in Table 18



Ampere Hrs./Gram m - DNB

FIGURE 21

Effect of Compacting Pressure on m-DNB Cathodes

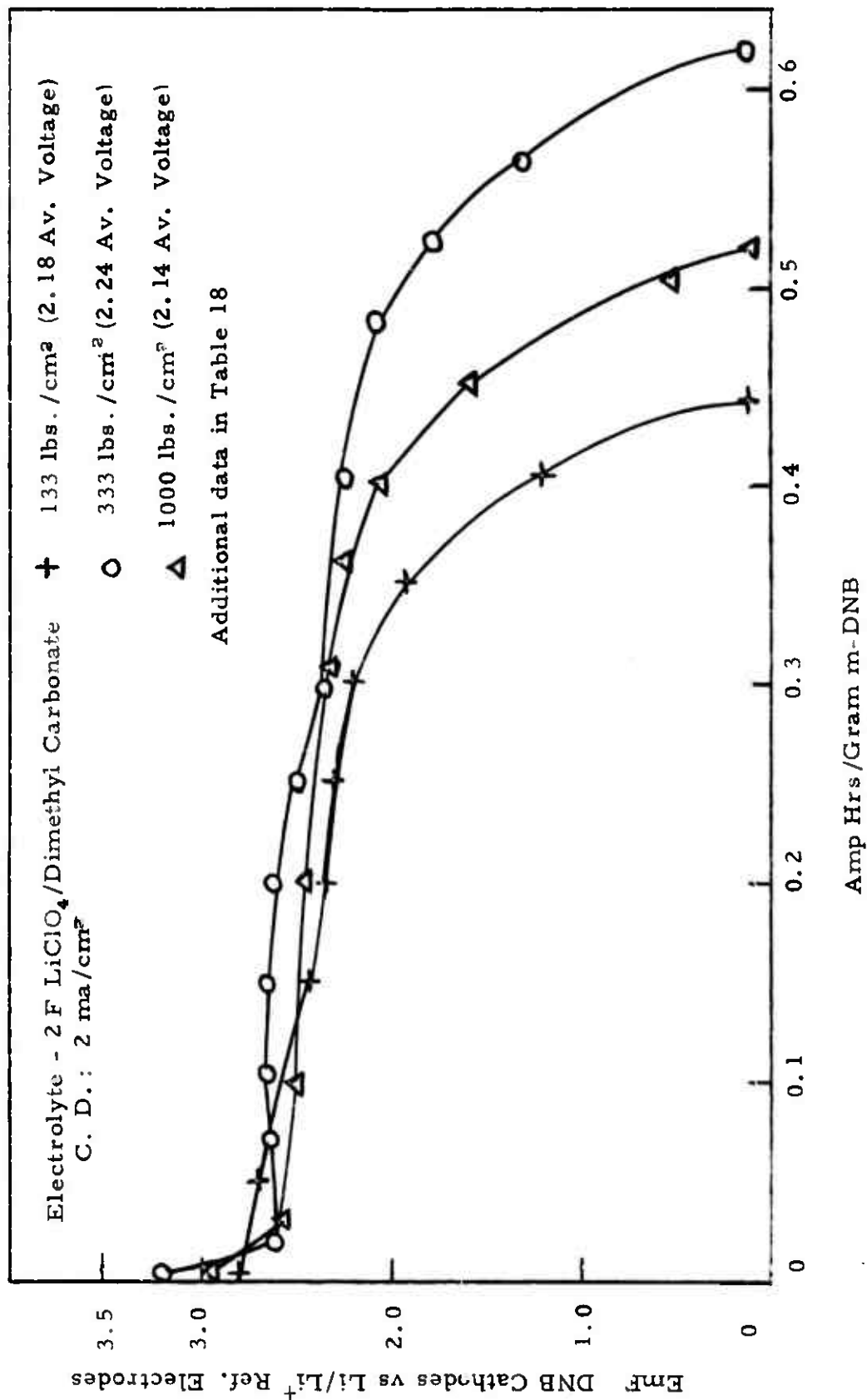


FIGURE 22

Regression Line for the Effect of the Percent Floc on the Average Percent Utilization of CuF_2

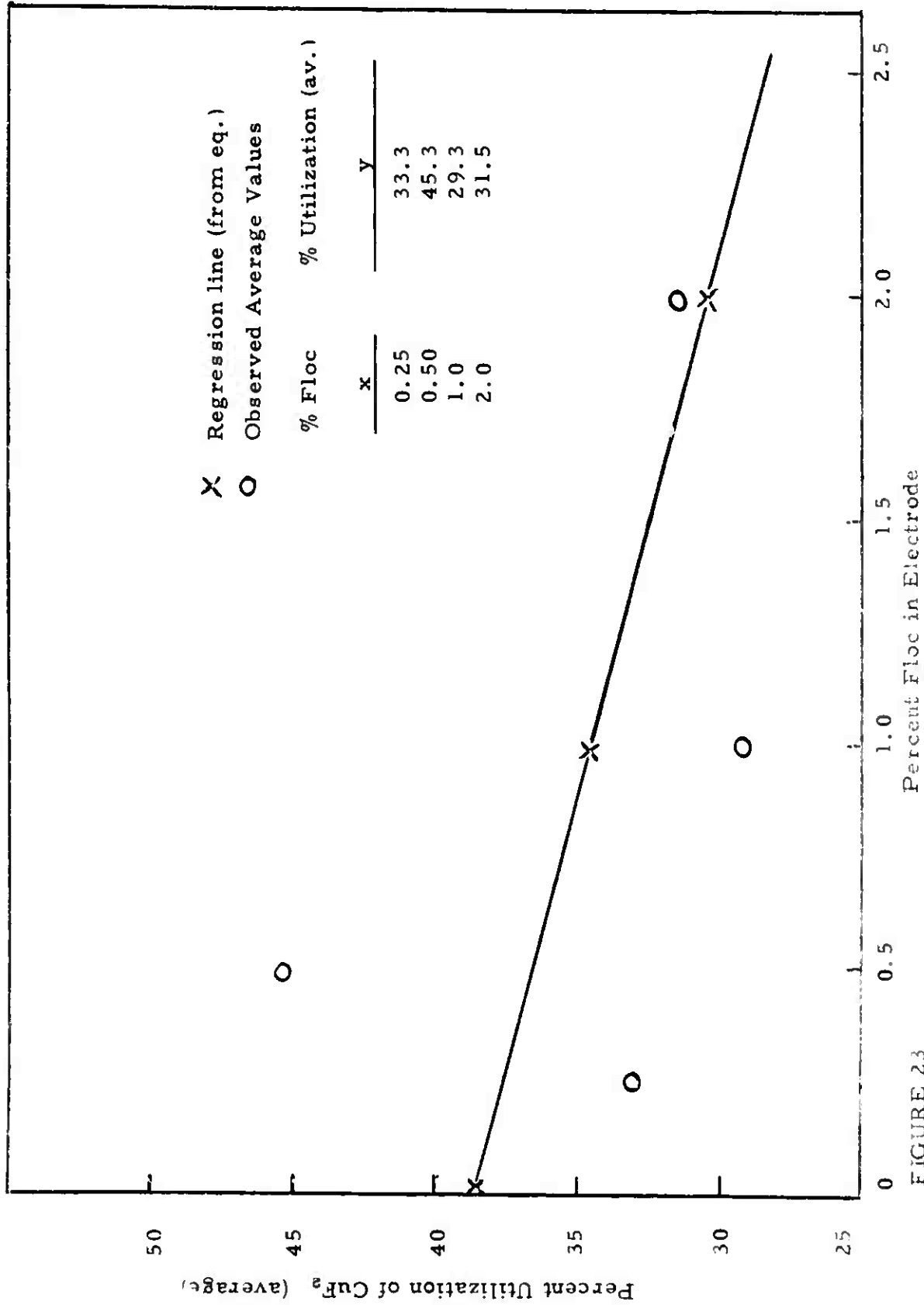


FIGURE 23

Regression Line for the Effect of the Compacting Pressure on the Average Percent Utilization of CuF_2

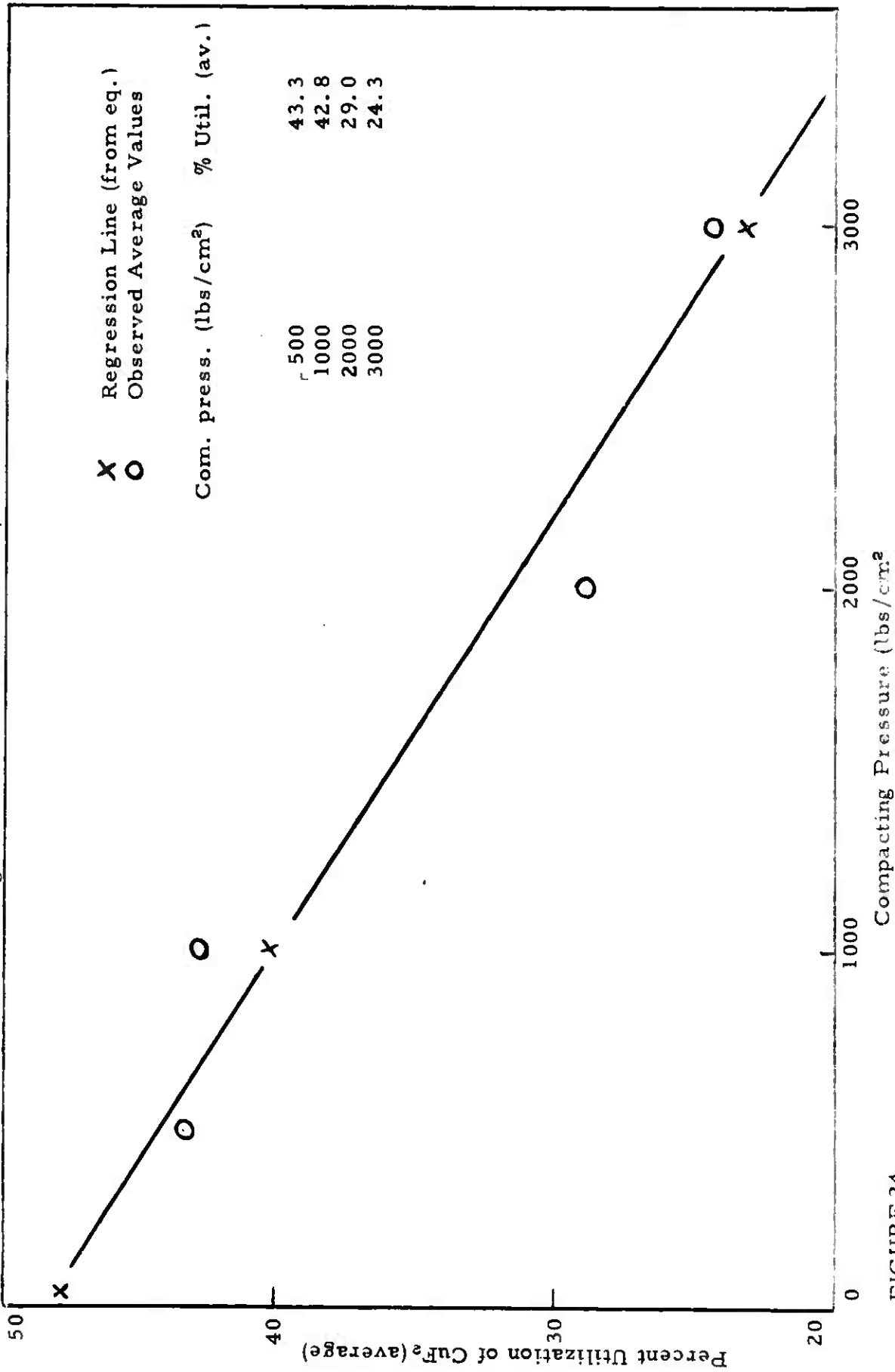


FIGURE 24

Effect of Current Density on Performance of CuF_2 Cathode in
2.0 F $\text{LiClO}_4/\text{DMC}$

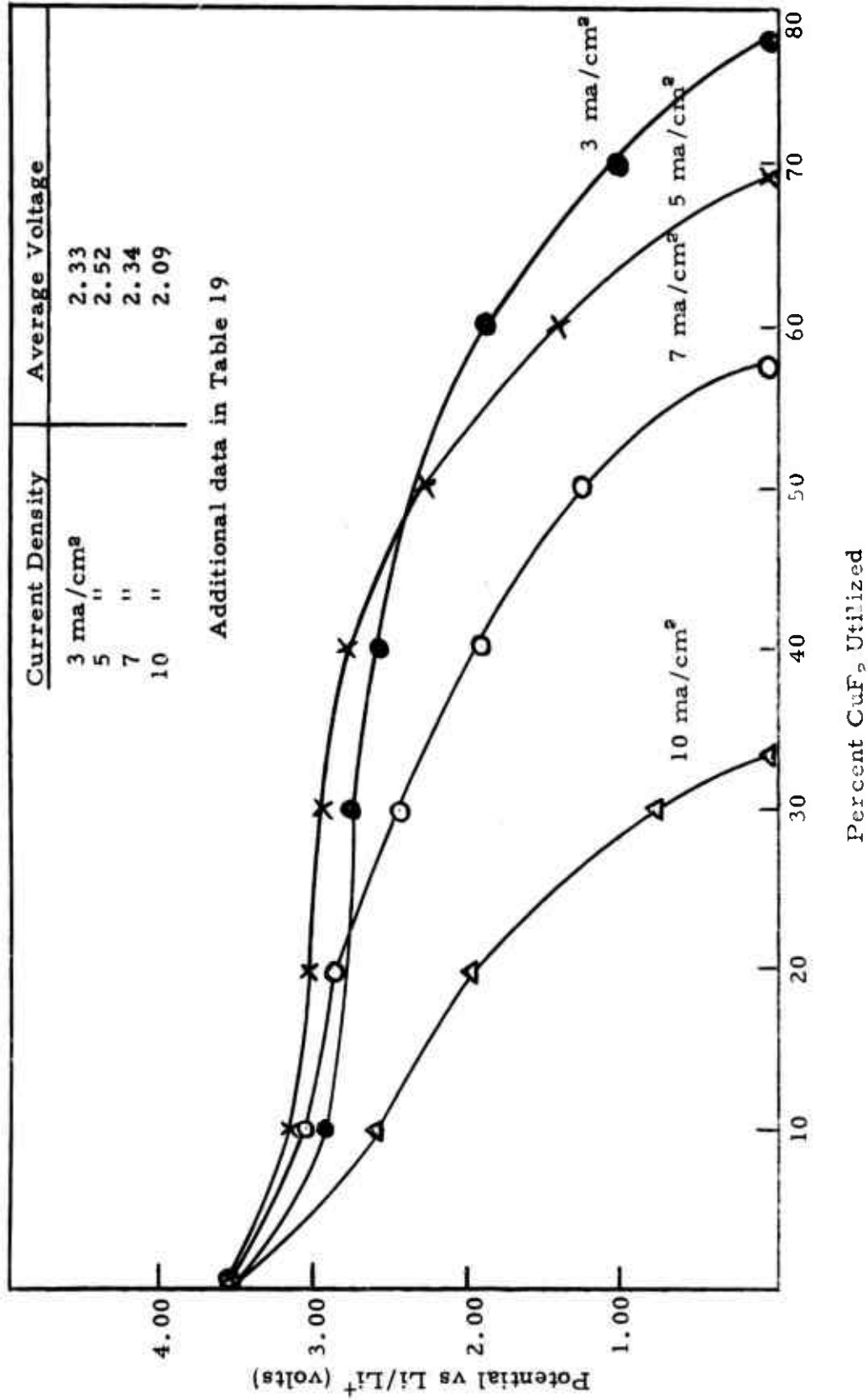


FIGURE 25

Performance of CuF_2 Cathodes in $\text{LiBF}_4/\text{P.C.}$ Electrolyte

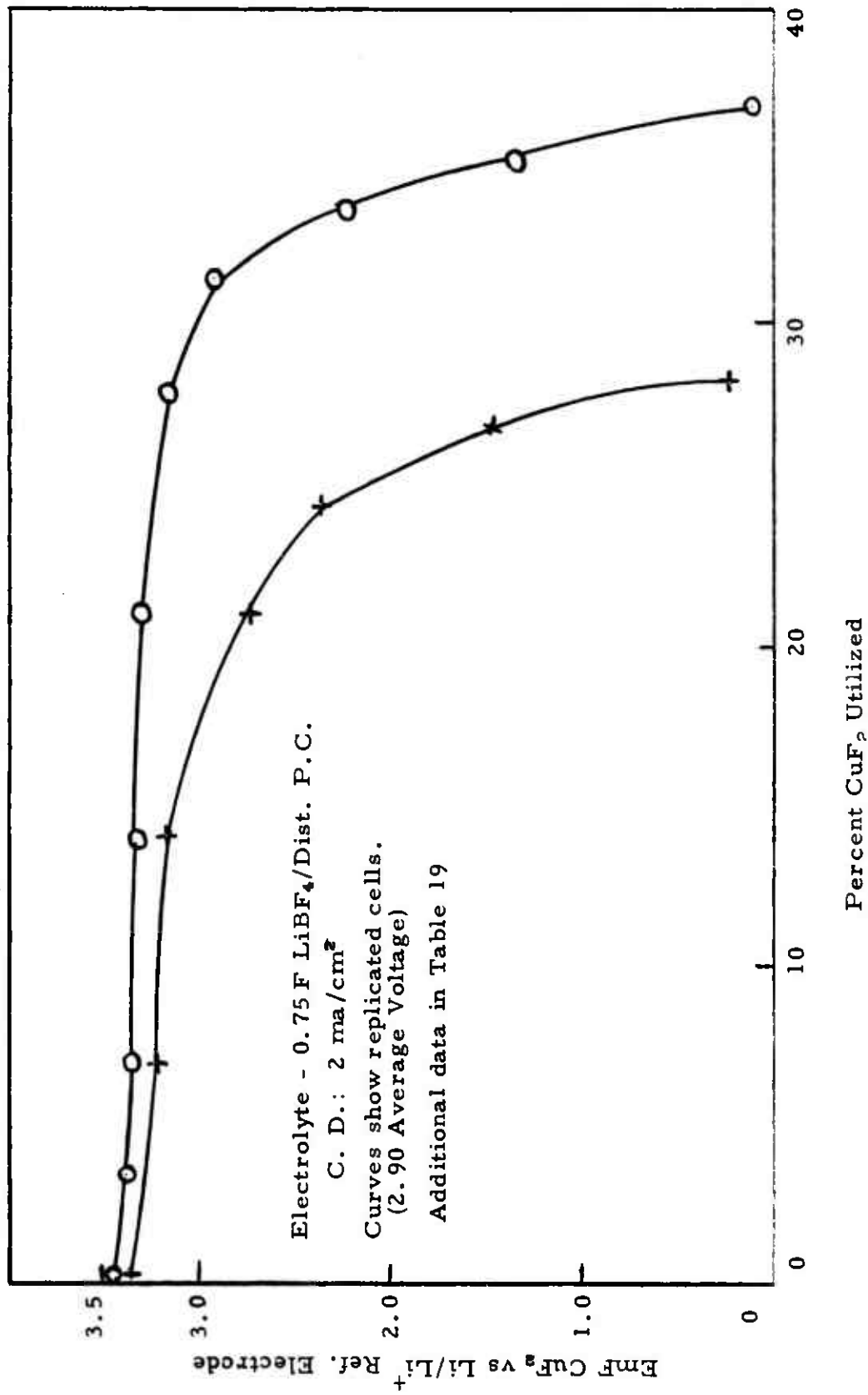


FIGURE 26

Performance of CuF_2 Cathodes in $\text{Mg}(\text{ClO}_4)_2/\text{P.C.}$ Electrolyte

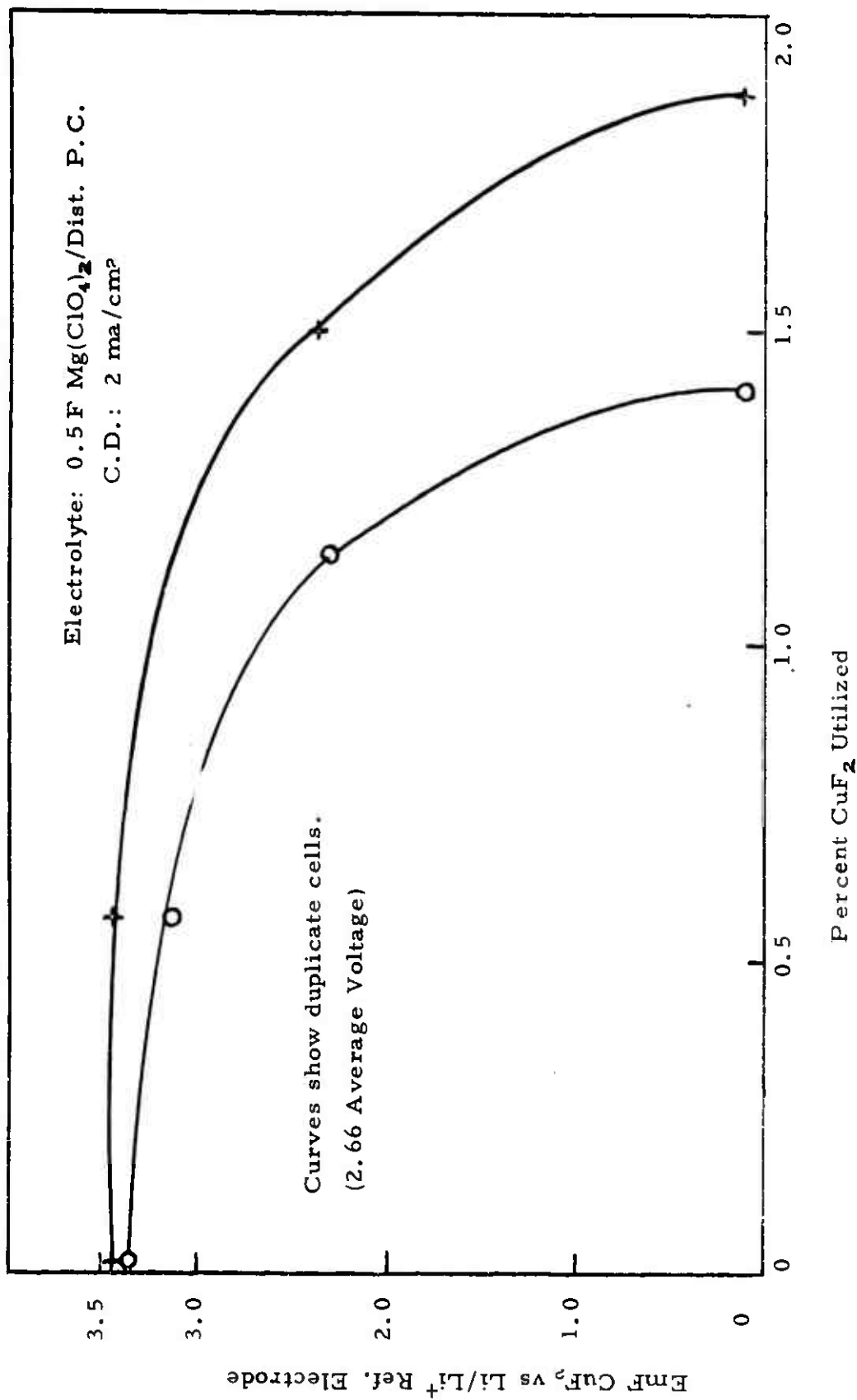


FIGURE 27

Performance of CuF_2 Cathodes in $\text{BF}_3/\text{THF}/\text{LiClO}_4/\text{P.C.}$ Electrolyte

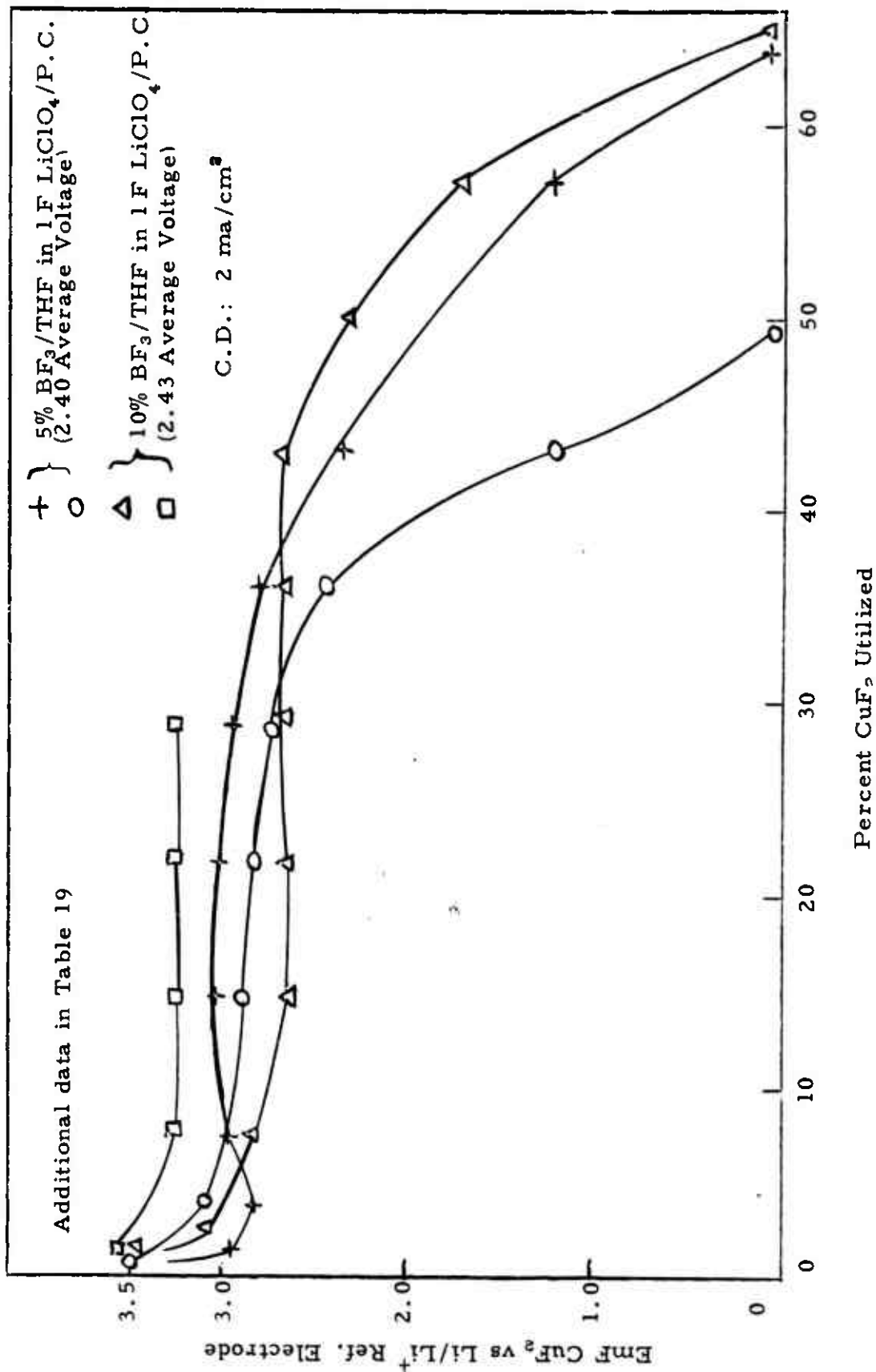


FIGURE 28

Effect of Current Density on Performance of CuF_2 Cathodes
 $\text{BF}_3/\text{THF}/\text{LiClO}_4/\text{P. C. Electrolyte}$

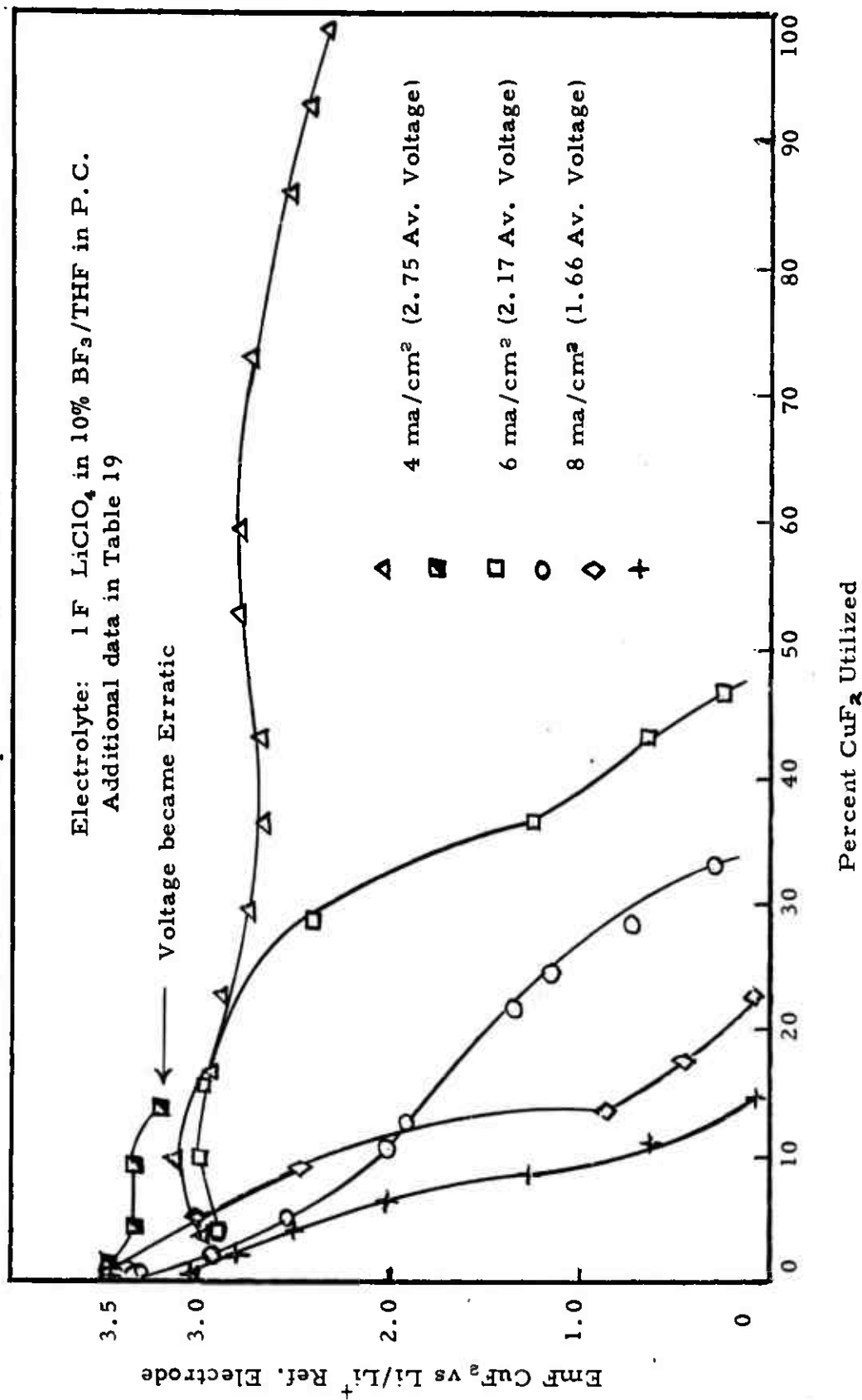
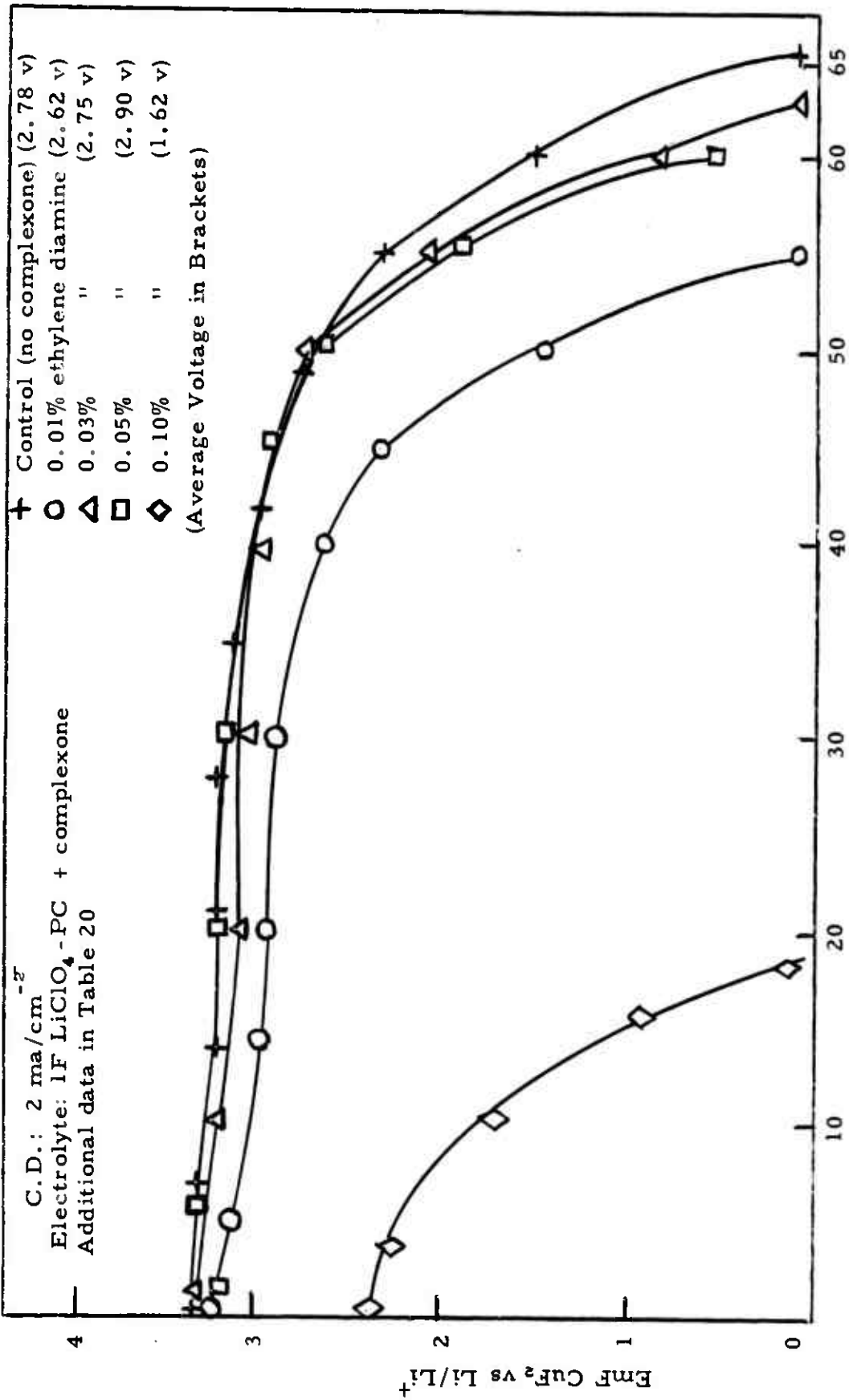


FIGURE 29

Effect of Ethylene Diamine Complexone on CuF_2 Cathode Performance



Percent Utilization of CuF_2

FIGURE 30

Effect of Diethylene Triamine Complexone on CuF₂ Cathode Performance

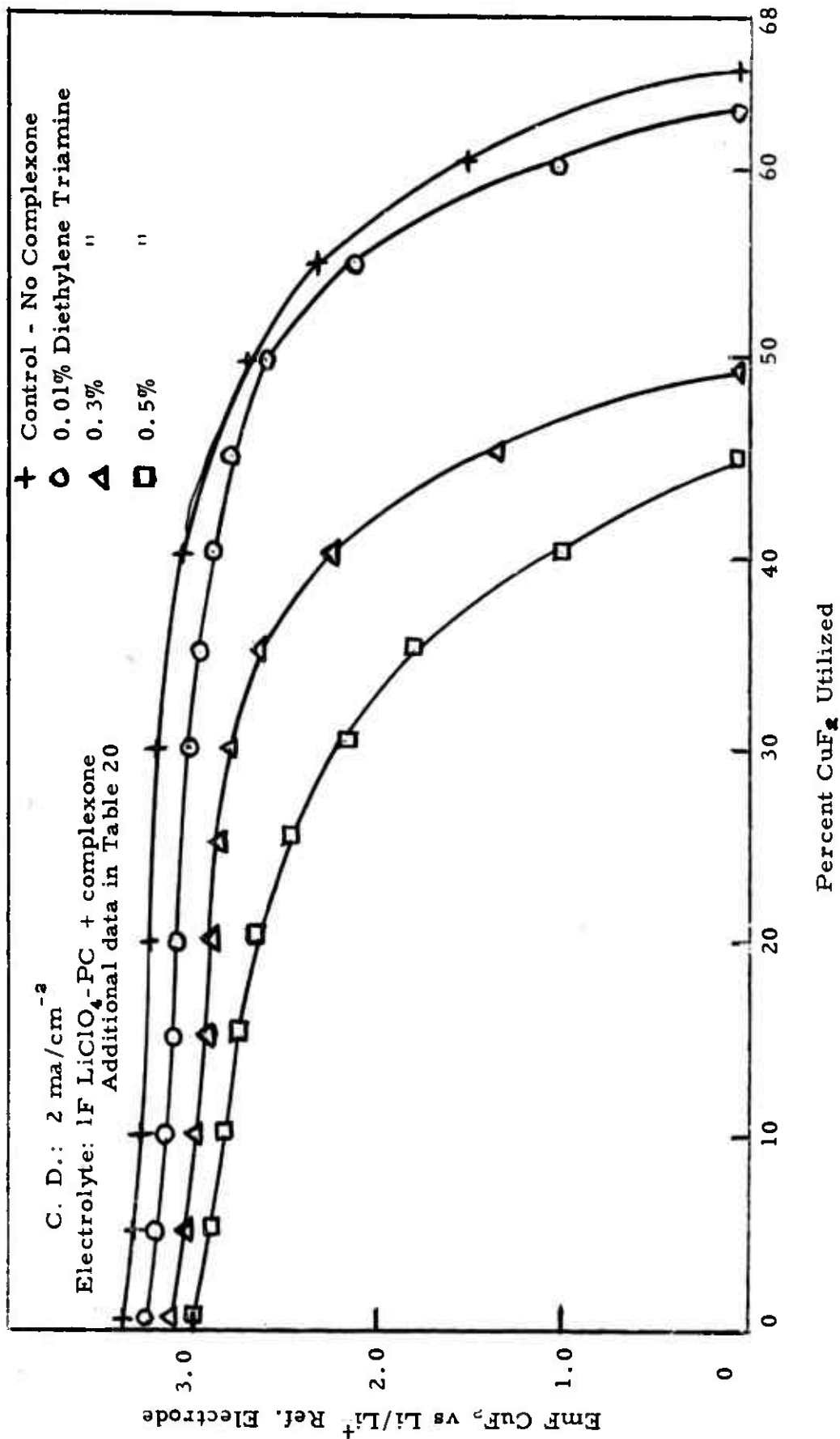


FIGURE 31

Effect of Complexones on Activated Storage of Li/CuF₂ Cells

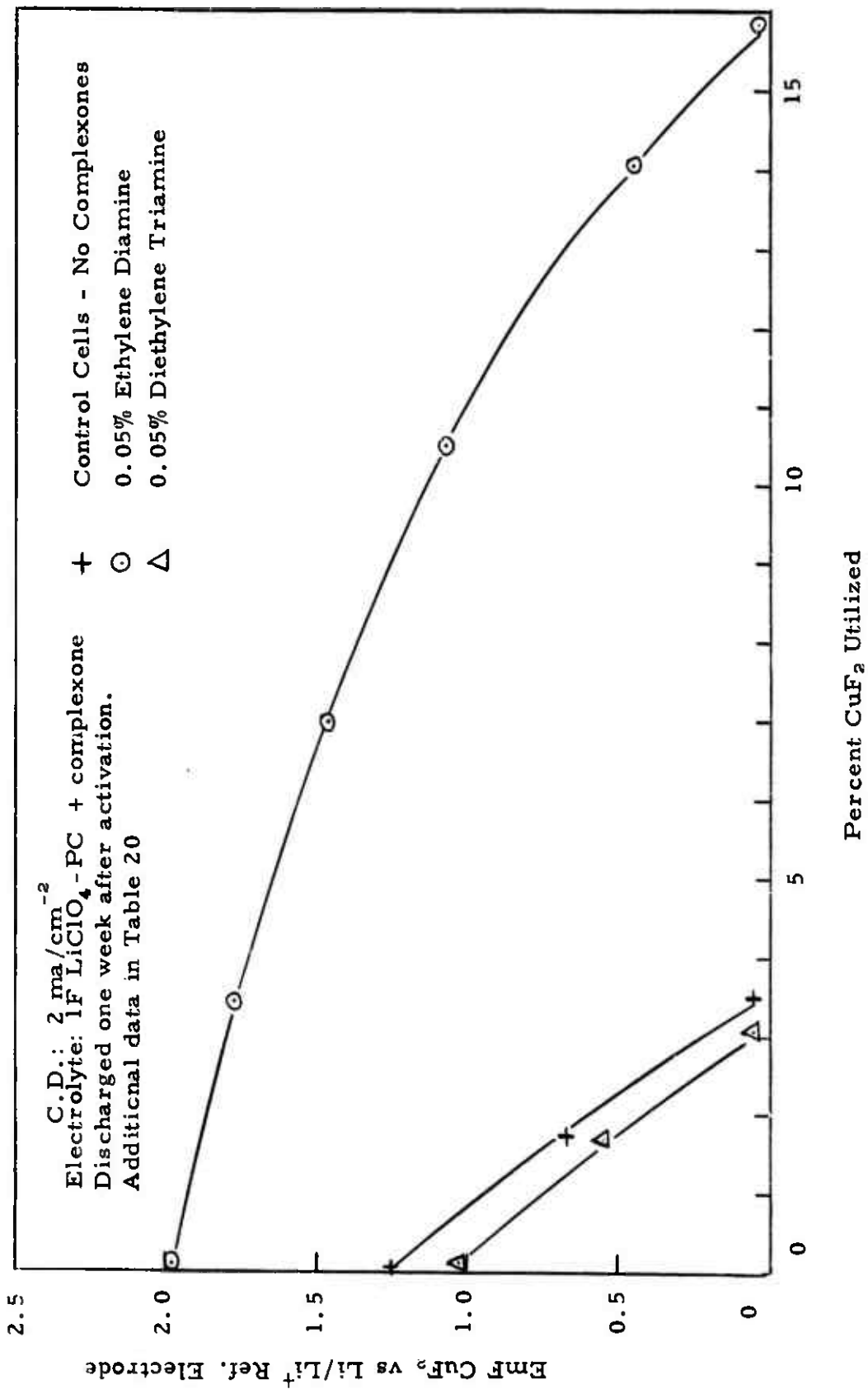


FIGURE 32

Effect of Water in CuF_2 on Performance

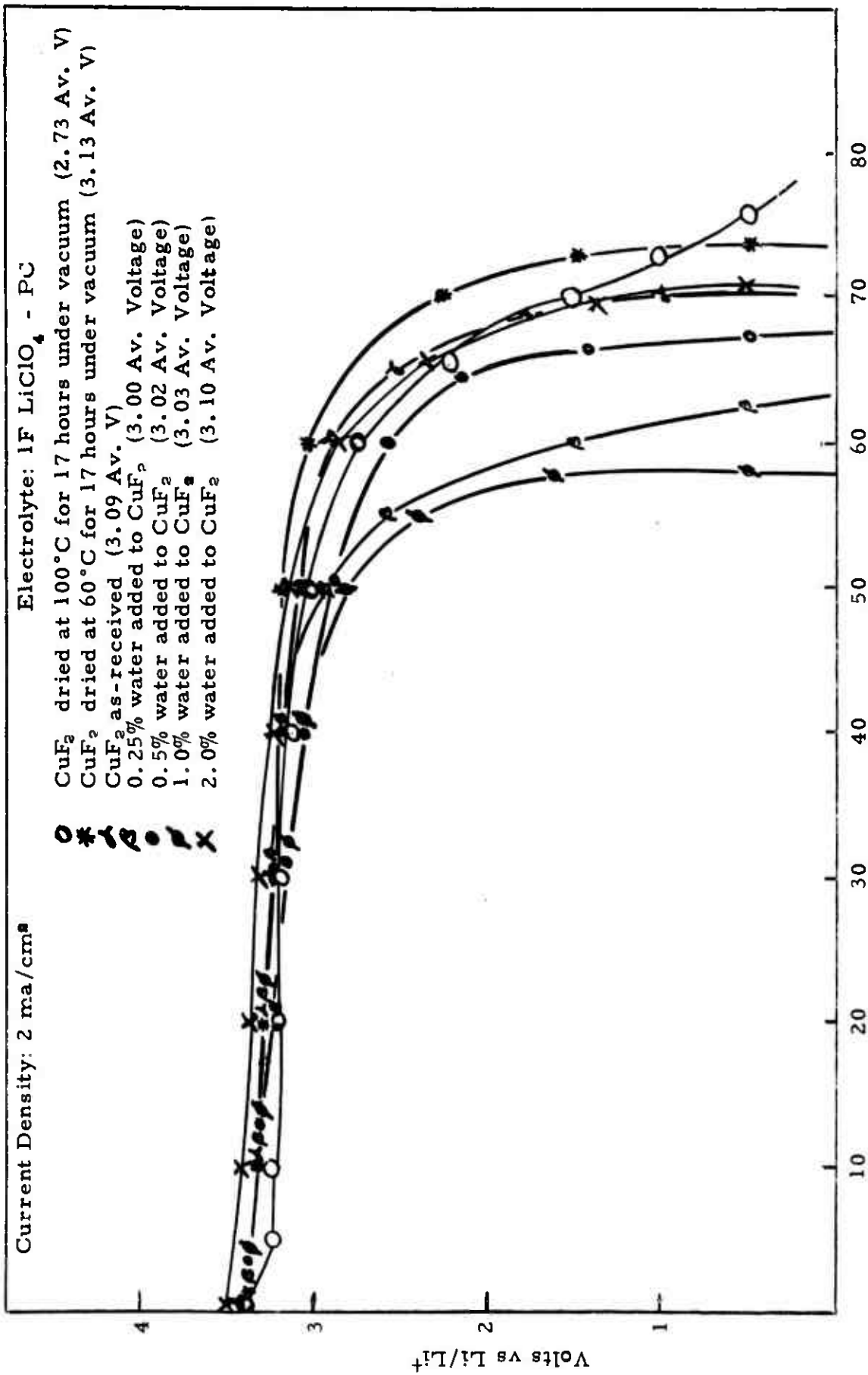


FIGURE 33

Effect of CuF_2 Particle Size on Performance

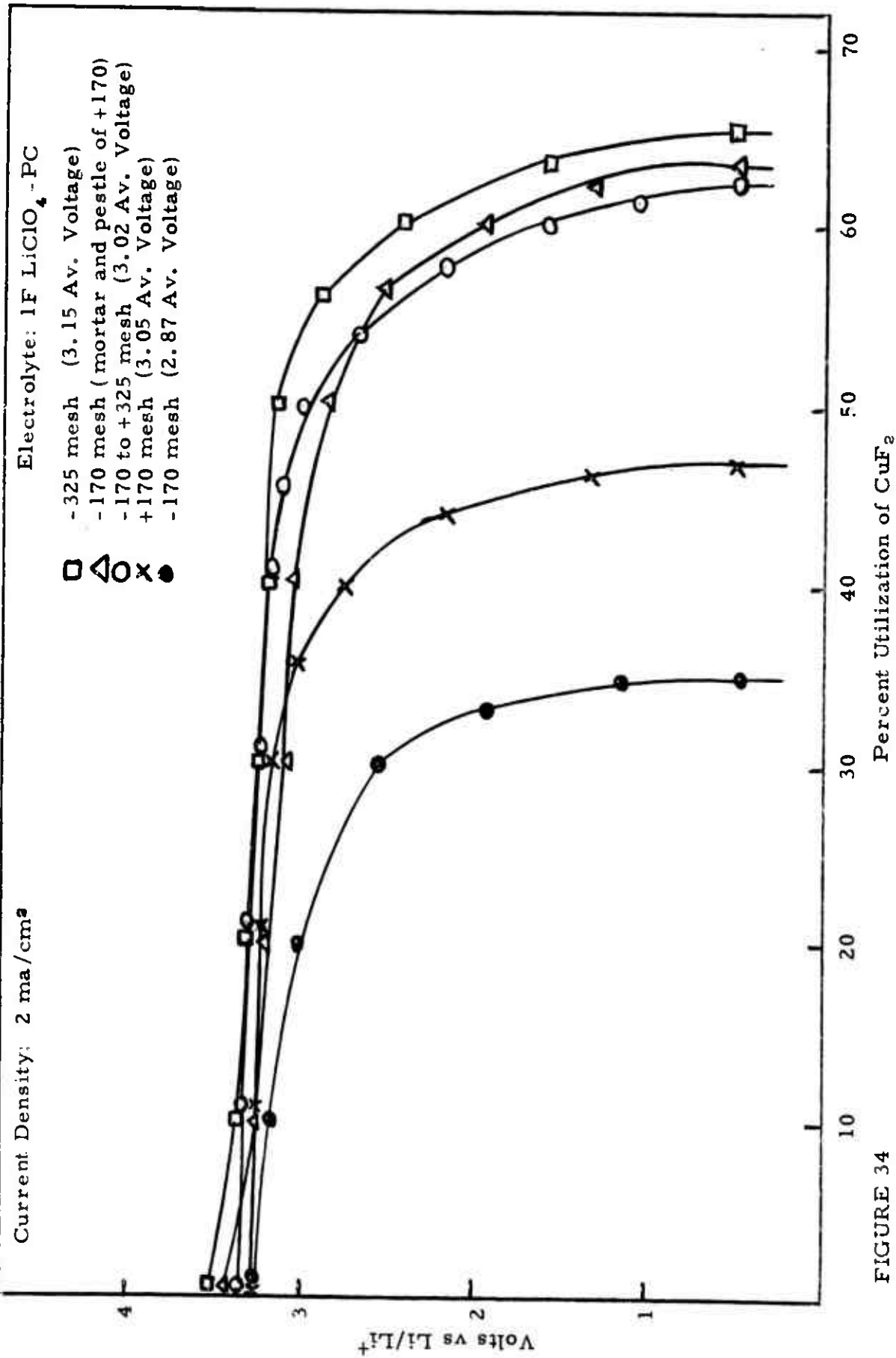


FIGURE 34

Effect of Cathode Wet Stand on Performance

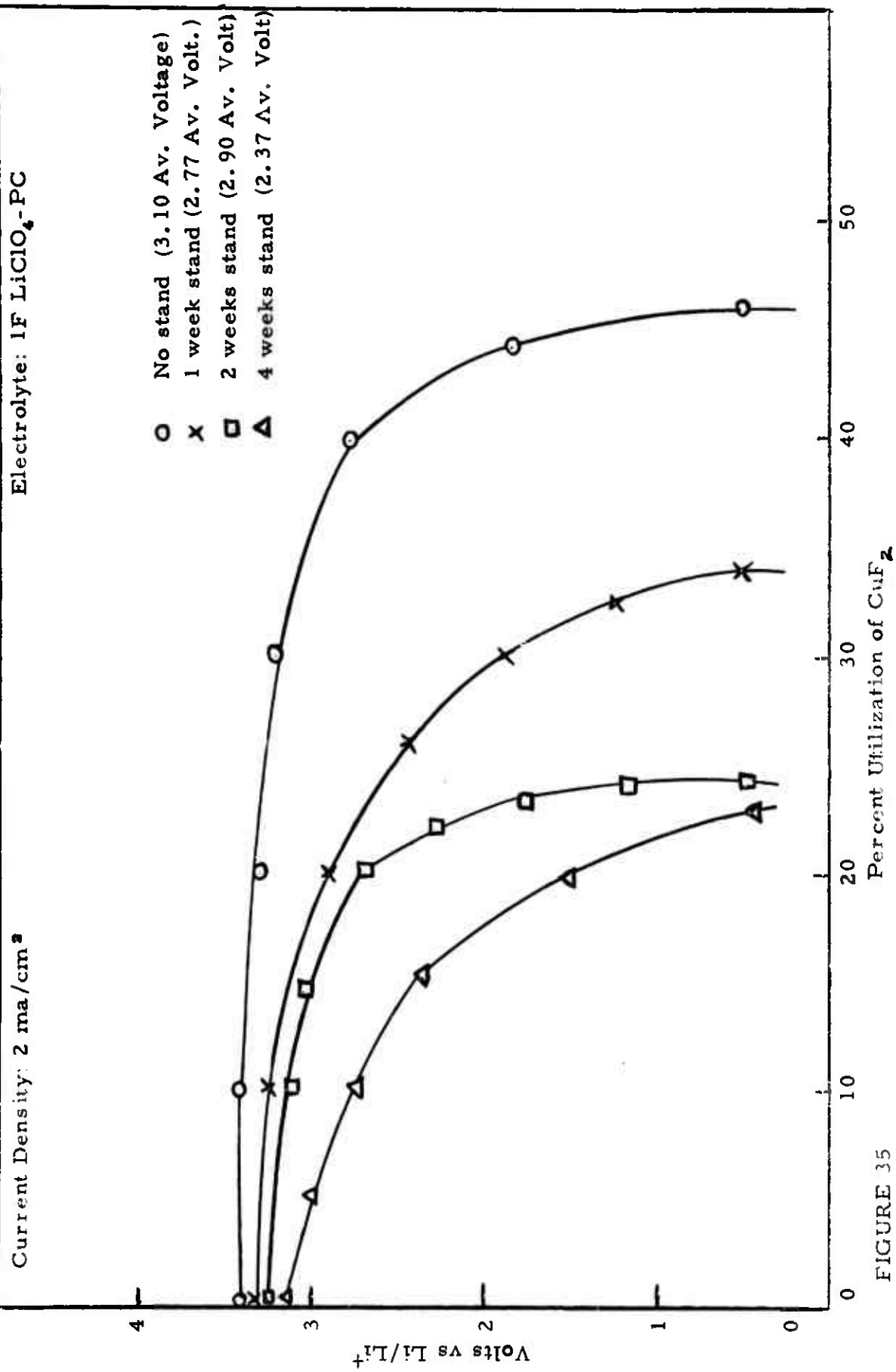


FIGURE 35

Effect of Cathode Activated Stand on Performance -
Electrodes Made with Unpurified SW 1651 Graphite

C.D.: 2 ma/cm²

Electrolyte: 1F LiClO₄-PC

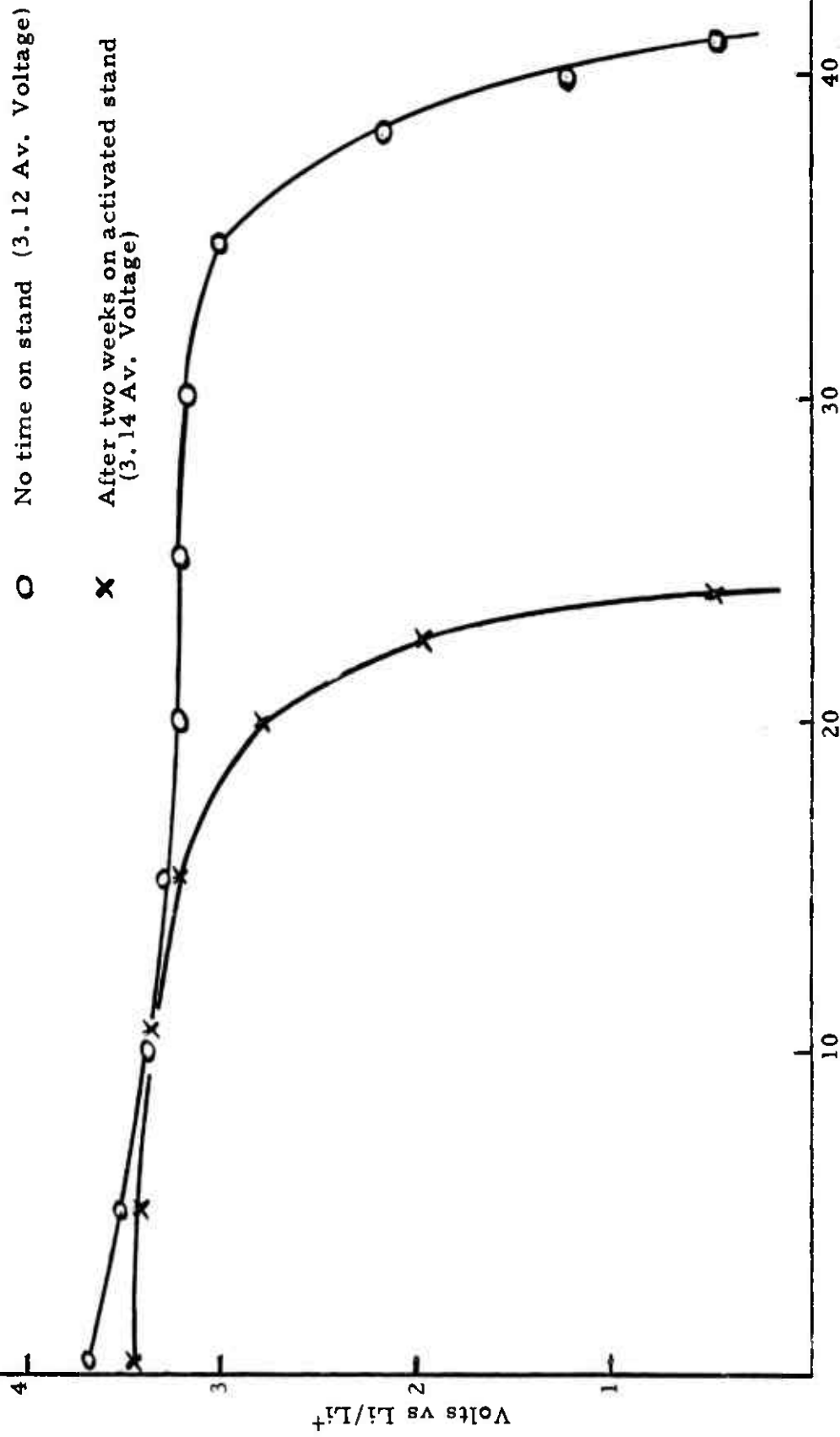


FIGURE 36

Percent Utilization of CuF₂

Volts vs Li/Li⁺

Effect of Cathode Activated Stand on Performance -
Electrodes Made with Nitric Acid Treated SW 1651 Graphite

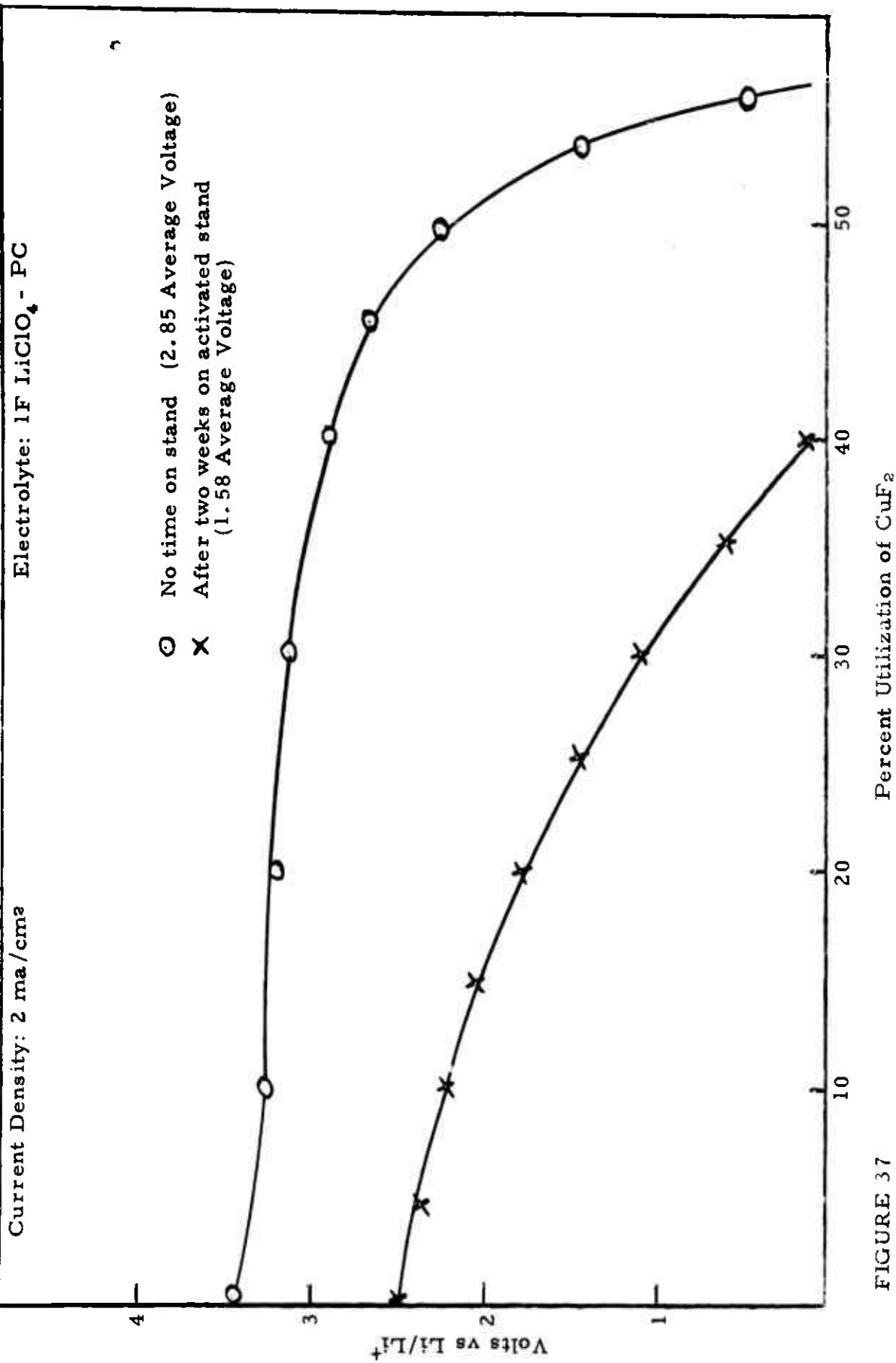


FIGURE 37

Effect of Cathode Activated Stand on Performance of
Electrodes Made With Hydrochloric Acid Treated SW 1651 Graphite

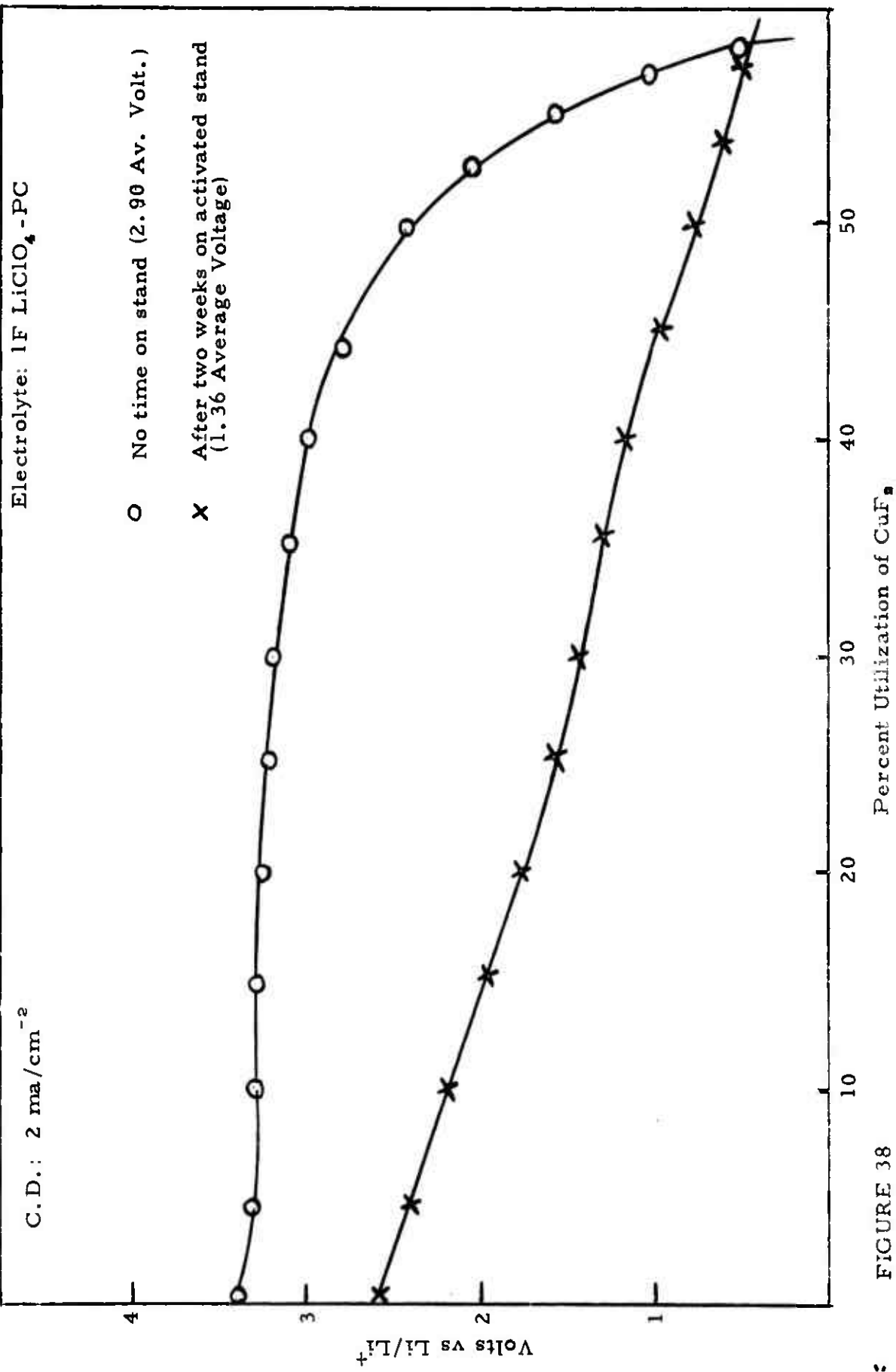


FIGURE 38

Effect of Cathode Activated Stand on Performance -
Electrodes Made With HCl-HNO₃ Treated SW 1651 Graphite

C.D.: 2 ma/cm²

Electrolyte: 1F LiClO₄-PC

- O No time on stand (1.54 Average Voltage)
- X After two weeks on activated stand (1.32 Average Voltage)

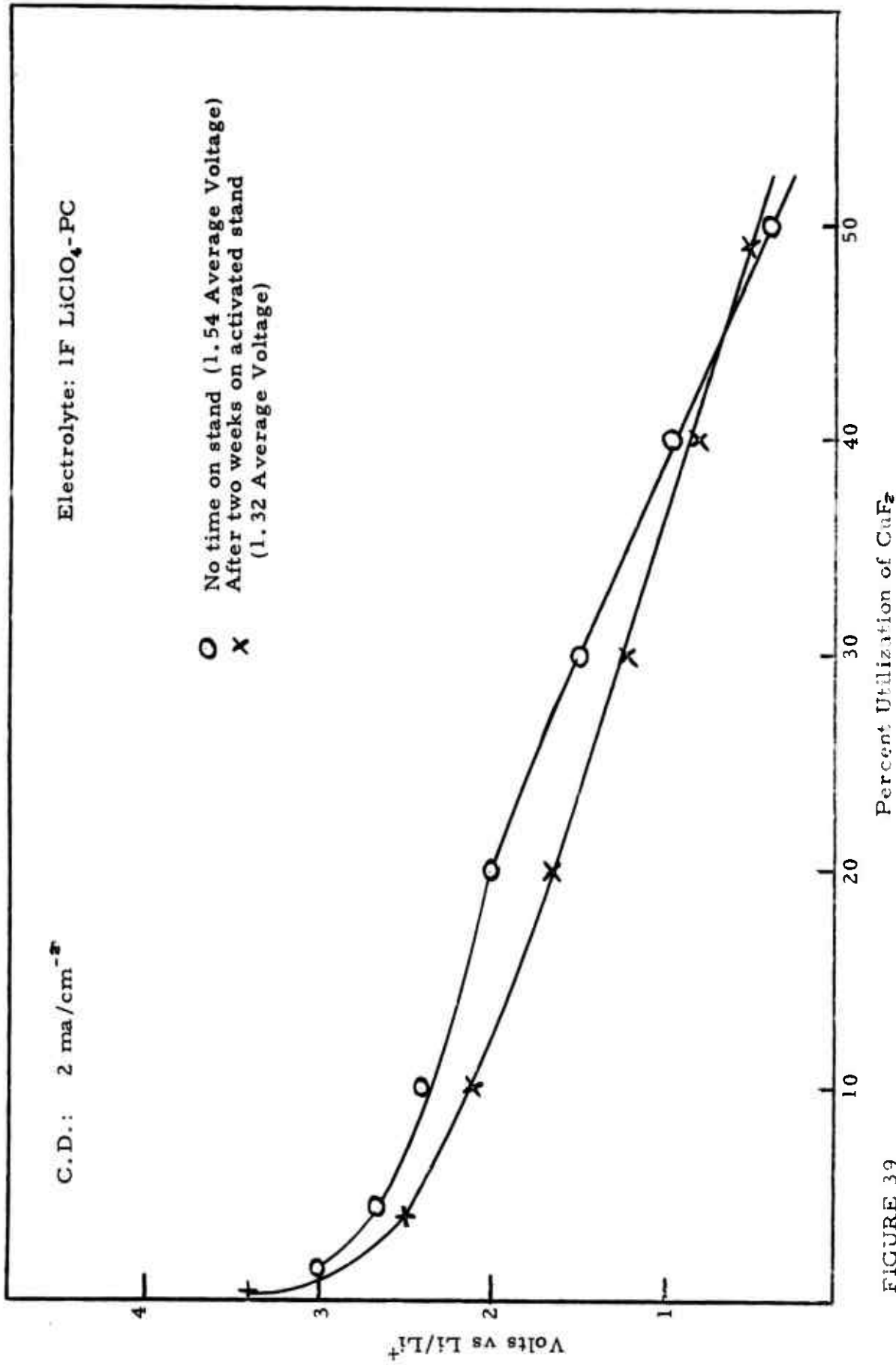


FIGURE 39

Effect of Purification of Graphite on Activated C. H. Stand Performance
 Electrolyte: 1F LiClO₄ PC
 Current Density: 2 ma/cm²
 Electrodes Pressed at 3000 lbs./cm²

- Untreated graphite with no stand (3.10 Average Voltage)
- × Untreated graphite with 1 week activated stand (0.40 Av. Voltage)
- ♣ HNO₃ purified graphite with no stand (1.73 Average Voltage)
- ⊖ HNO₃ purified graphite with 3 day activated stand (1.56 Av. Volt.)
- ⊕ HNO₃ purified graphite with 1 week activated stand (0.6 Av. Volt.)

Additional data in Table 21

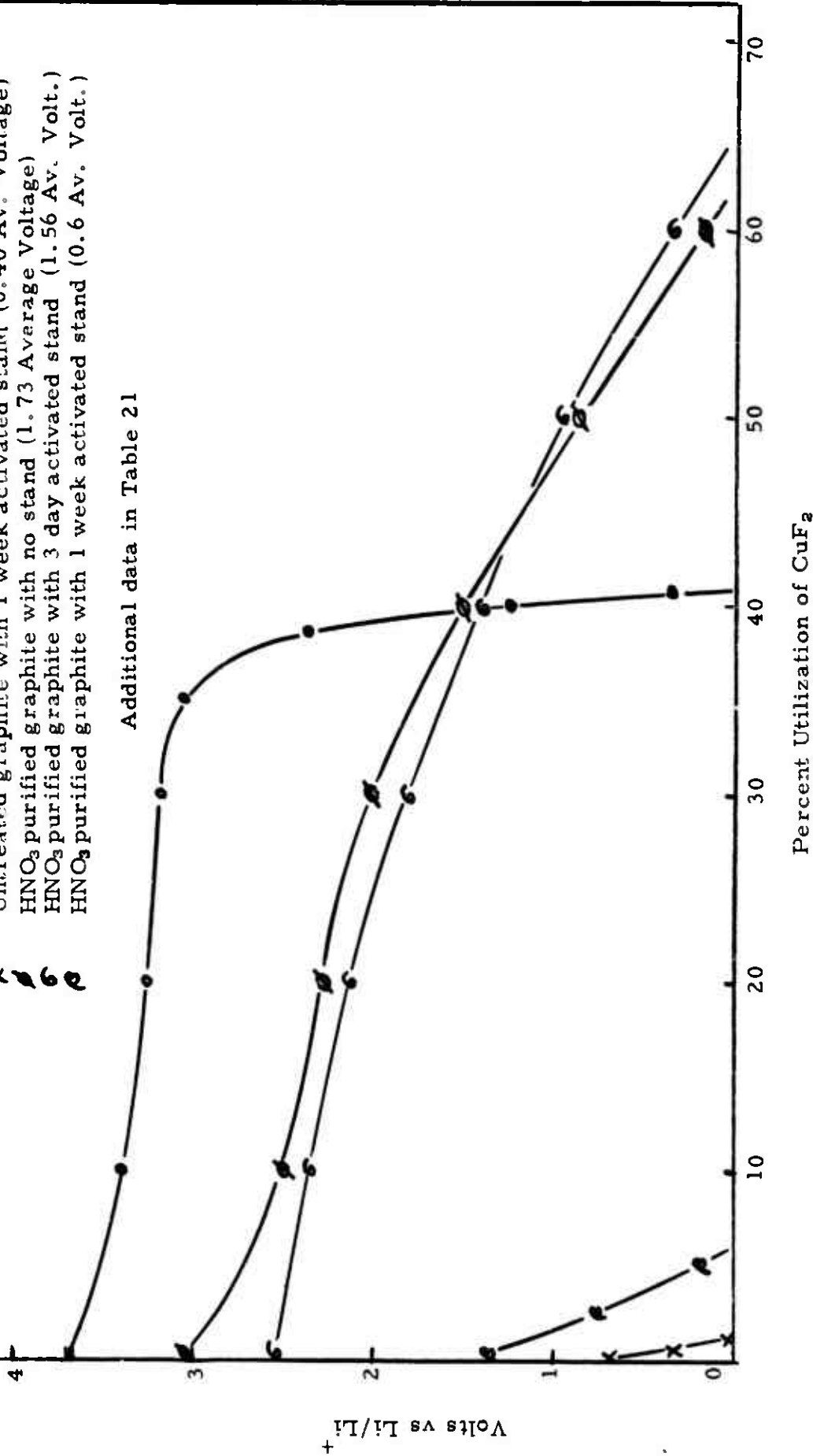


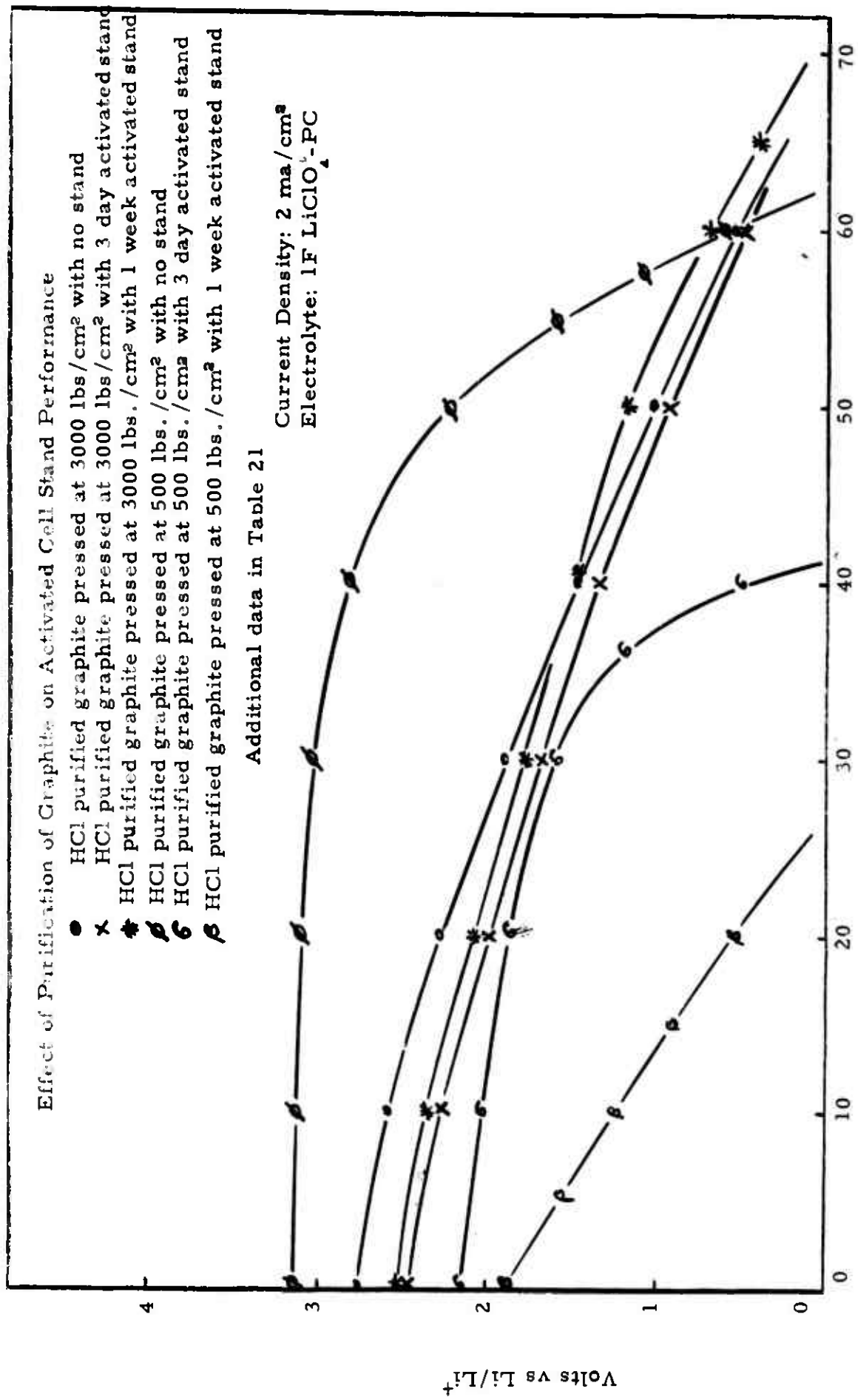
FIGURE 40

Effect of Purification of Graphite on Activated Cell Stand Performance

- HCl purified graphite pressed at 3000 lbs./cm² with no stand
- × HCl purified graphite pressed at 3000 lbs./cm² with 3 day activated stand
- ⬢ HCl purified graphite pressed at 3000 lbs./cm² with 1 week activated stand
- ♠ HCl purified graphite pressed at 500 lbs./cm² with no stand
- ⊖ HCl purified graphite pressed at 500 lbs./cm² with 3 day activated stand
- β HCl purified graphite pressed at 500 lbs./cm² with 1 week activated stand

Additional data in Table 21

Current Density: 2 ma./cm²
Electrolyte: 1F LiClO₄-PC



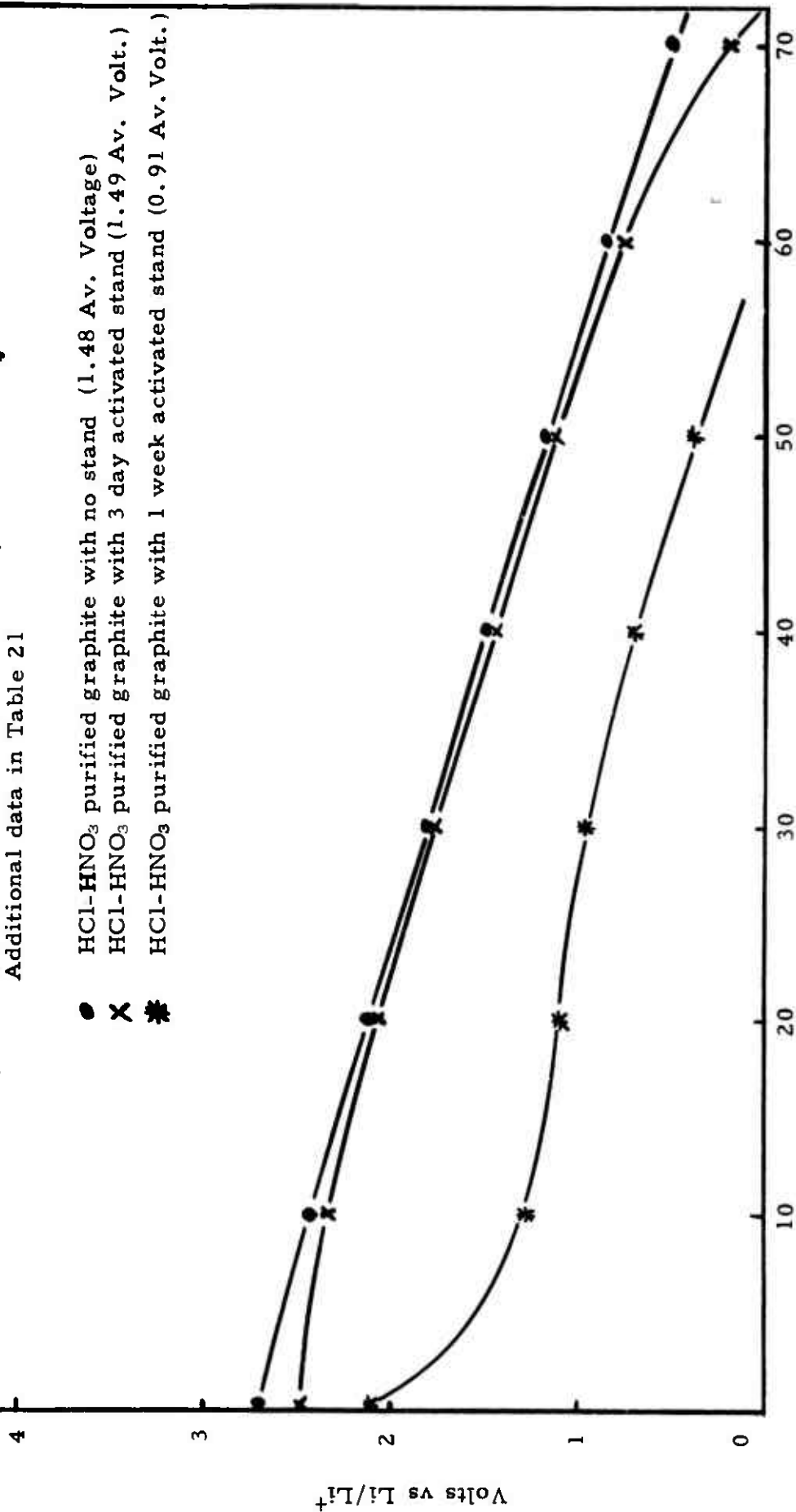
Percent Utilization of CuF₂

FIGURE 41

Effect of Purification of Graphite on Activated Cell Stand Performance -
Electrodes Pressed at 3000 lbs. / cm²

Current Density: 2 ma/cm² Electrolyte: 1F LiClO₄-PC
Additional data in Table 21

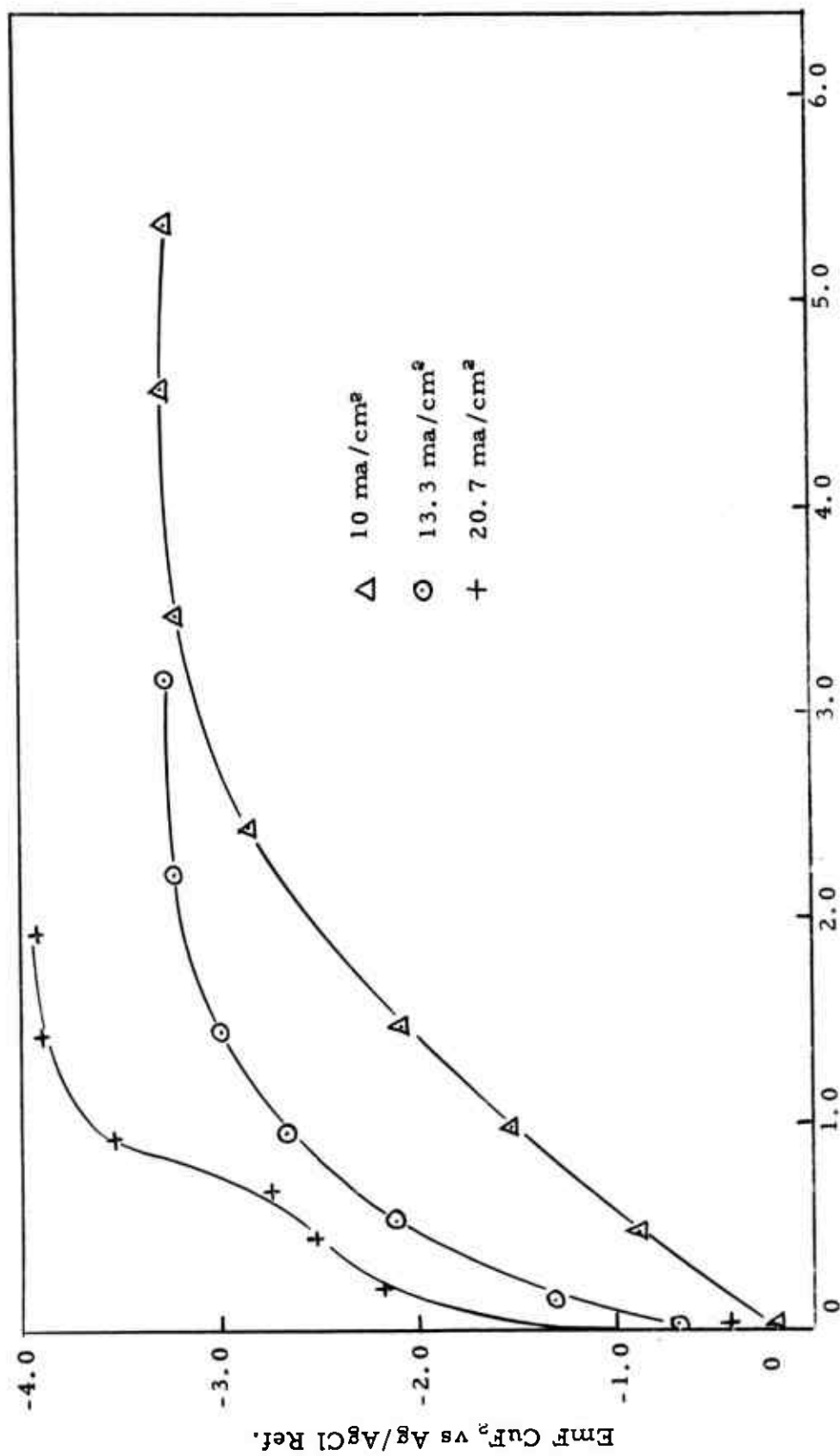
- HCl-HNO₃ purified graphite with no stand (1.48 Av. Voltage)
- × HCl-HNO₃ purified graphite with 3 day activated stand (1.49 Av. Volt.)
- * HCl-HNO₃ purified graphite with 1 week activated stand (0.91 Av. Volt.)



Percent Utilization of CuF₂

FIGURE 42

Chronopotentiograms of CuF_2 Cathode Discharge (0.25 F LiClO_4 /Propylene Carbonate)



Time (Minutes)

FIGURE 43

Chronopotentiograms of CuFe Cathode Discharge (0.5 F LiClO₄/Propylene Carbonate)

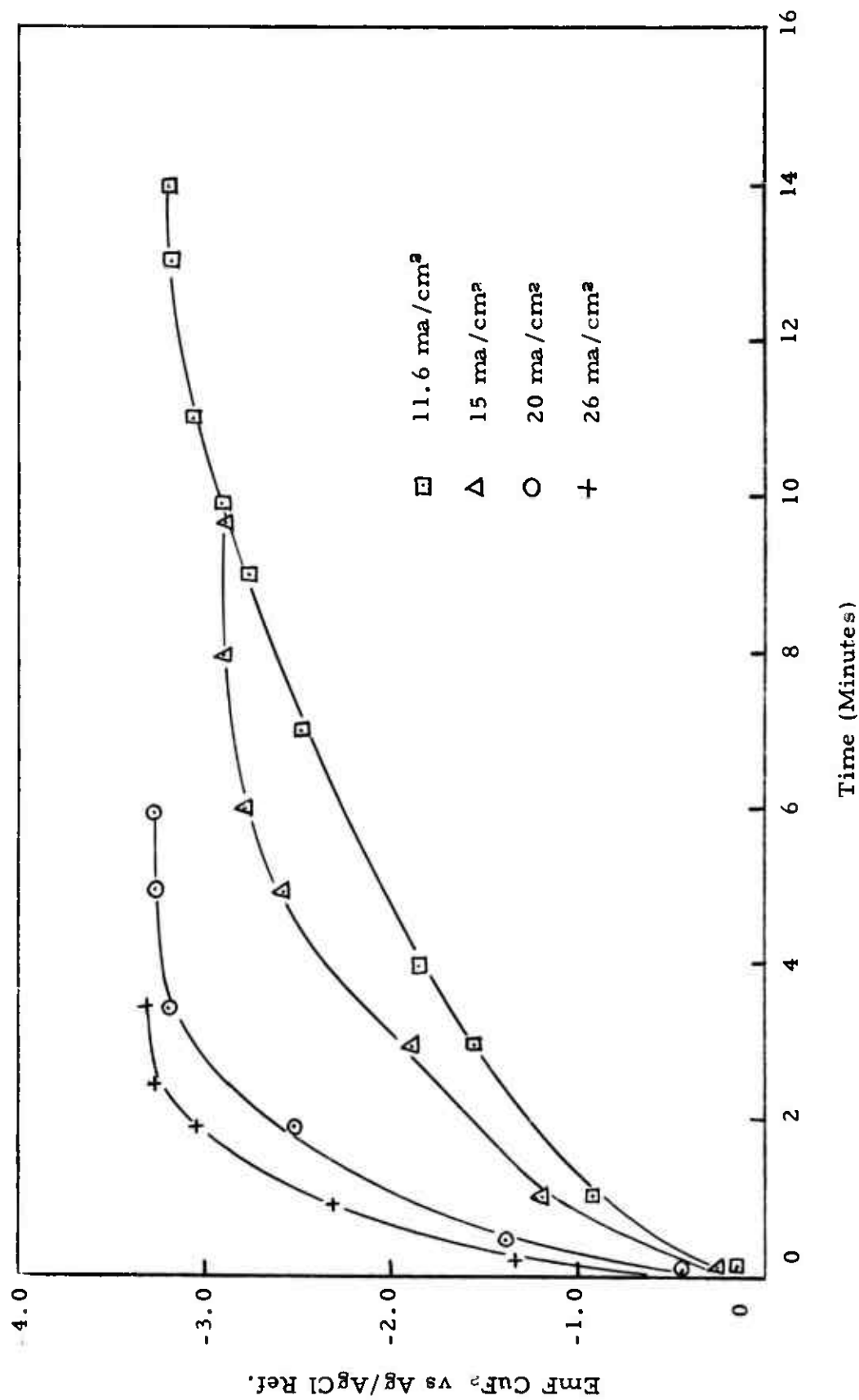


FIGURE 44

Chronopotentiograms - CuF_2 Cathode (1.0F LiClO_4 /Propylene Carbonate)

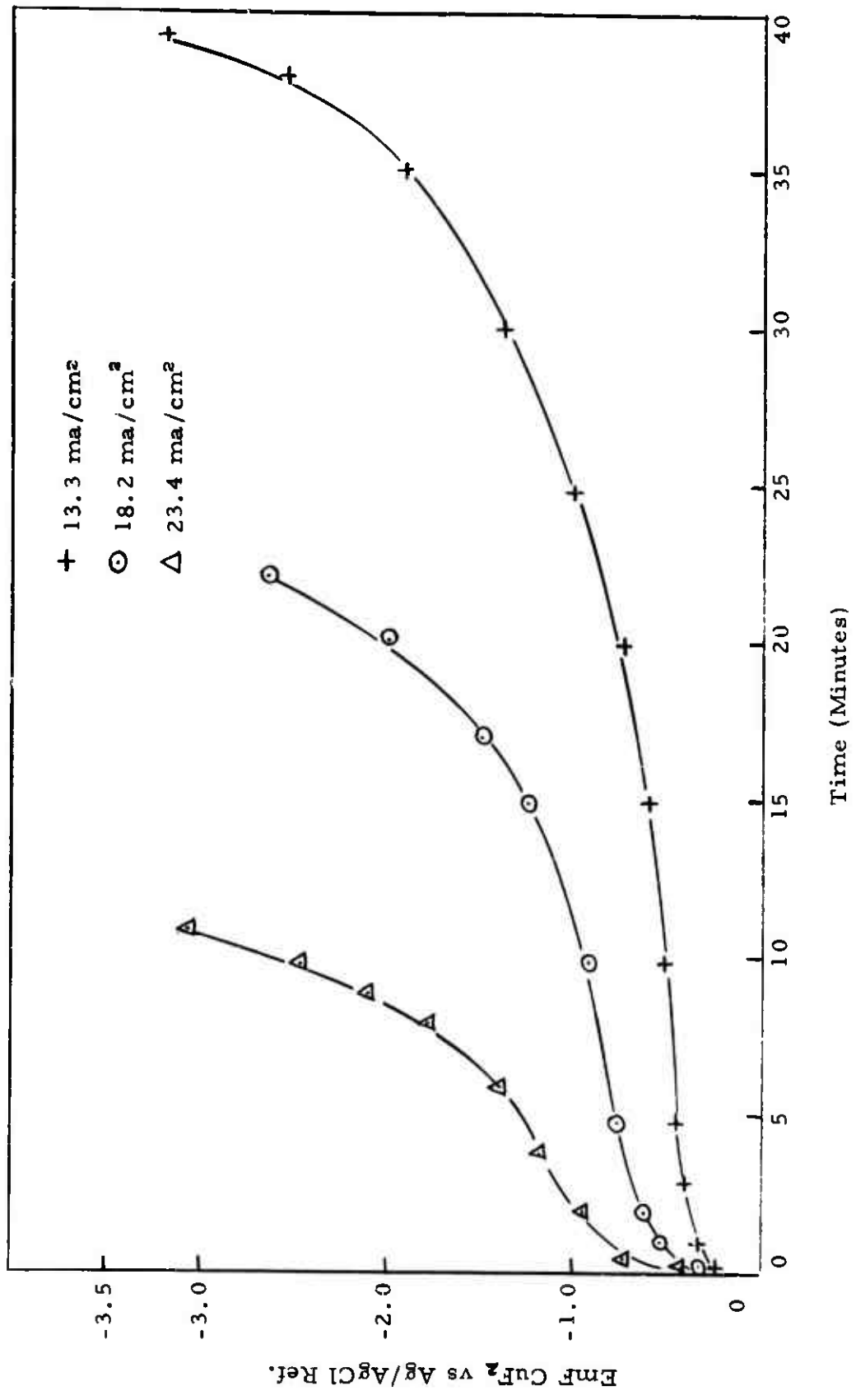


FIGURE 45

Potential-Time Transient

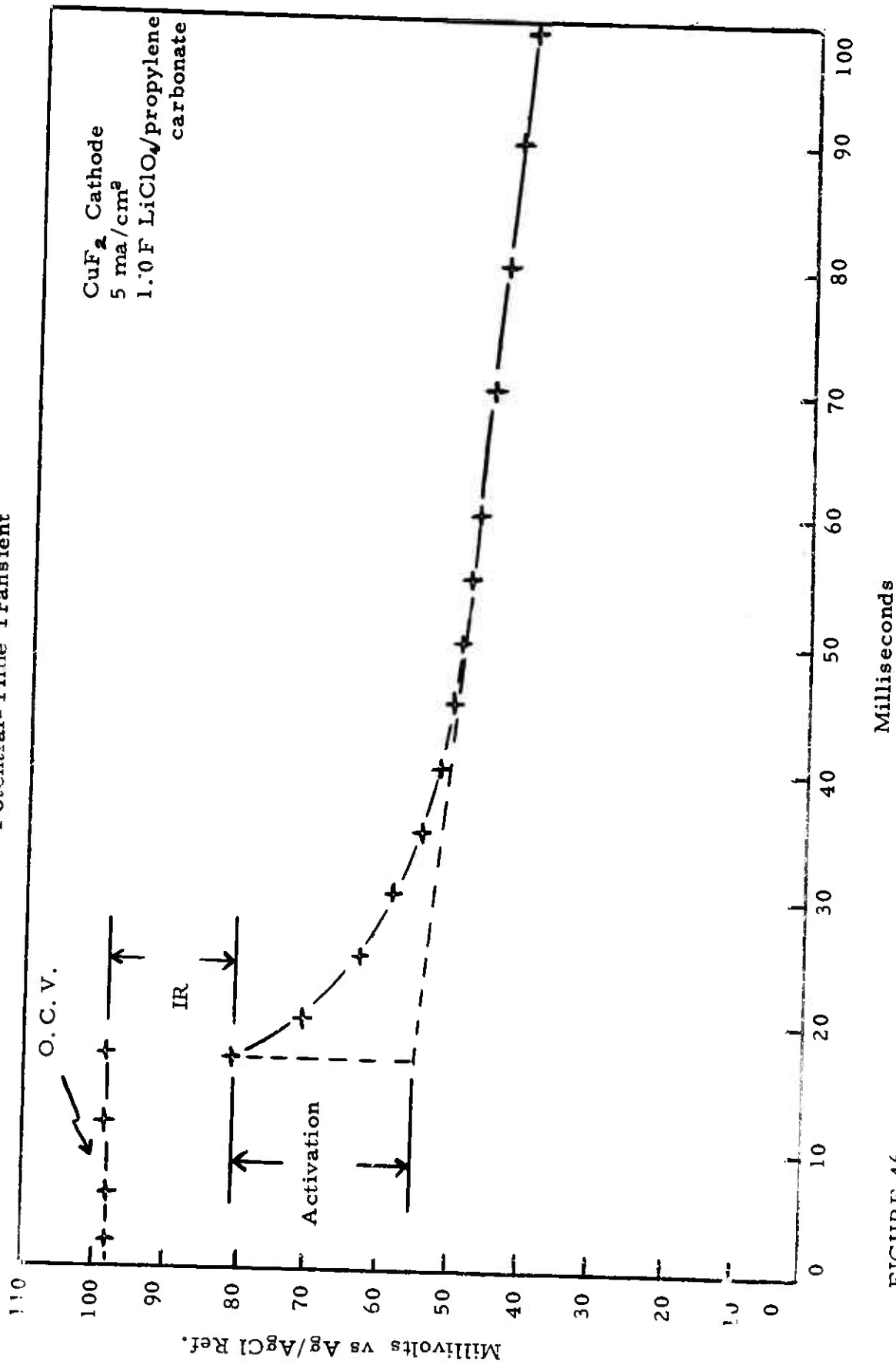


FIGURE 46

Current Sweep Voltammetry CuF_2 Cathodes (0.25F $\text{LiClO}_4/\text{P.C.}$)

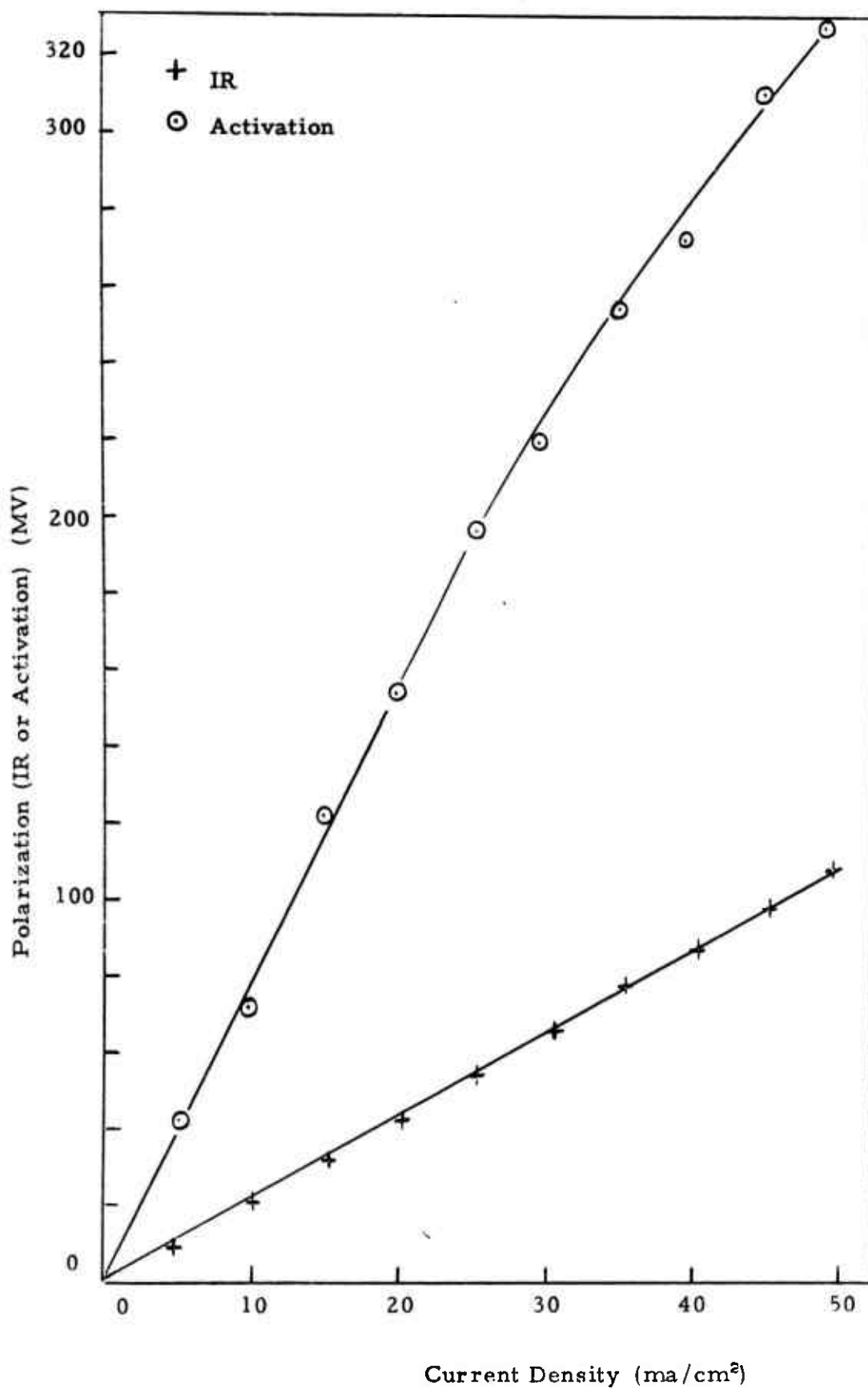


FIGURE 47

Current Sweep Voltammetry CuF_2 Cathodes
(0.5 F $\text{LiClO}_4/\text{Propylene Carbonate}$)

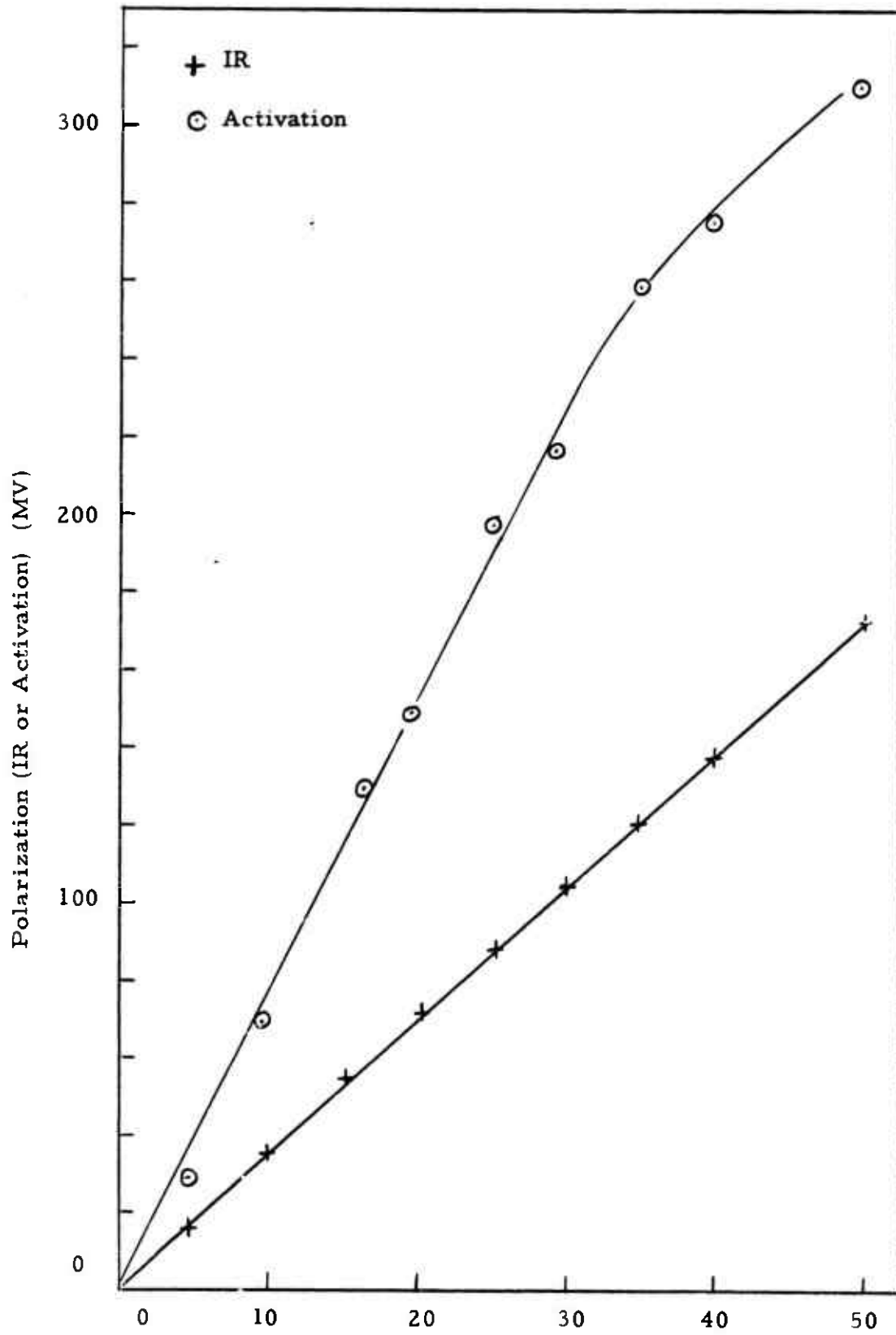


FIGURE 48 Current Density (ma/cm^2)

Current Sweep Voltammetry
CuF₂ Cathode in 1 F LiClO₄/P. C.

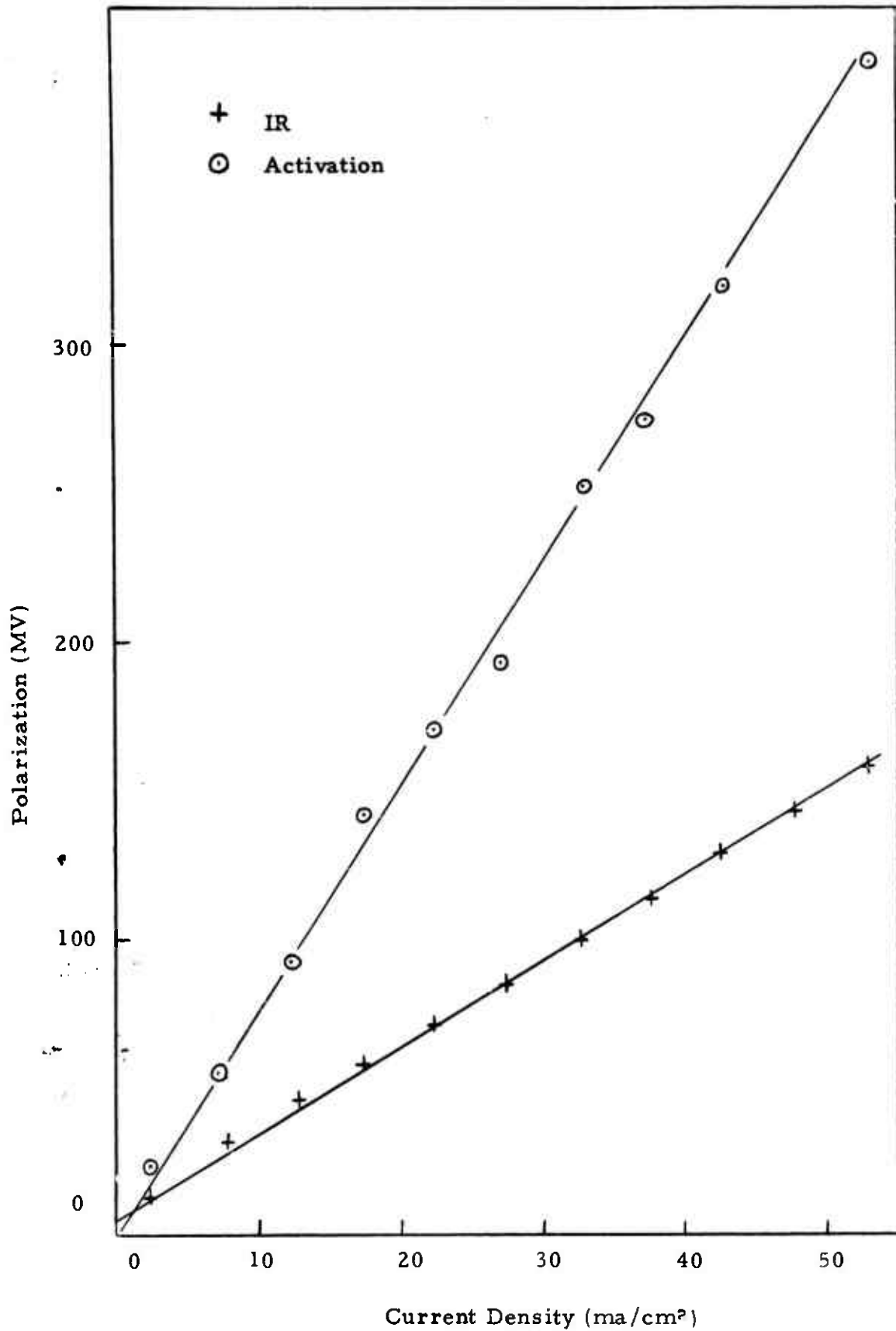


FIGURE 49

Current Sweep Voltammetry

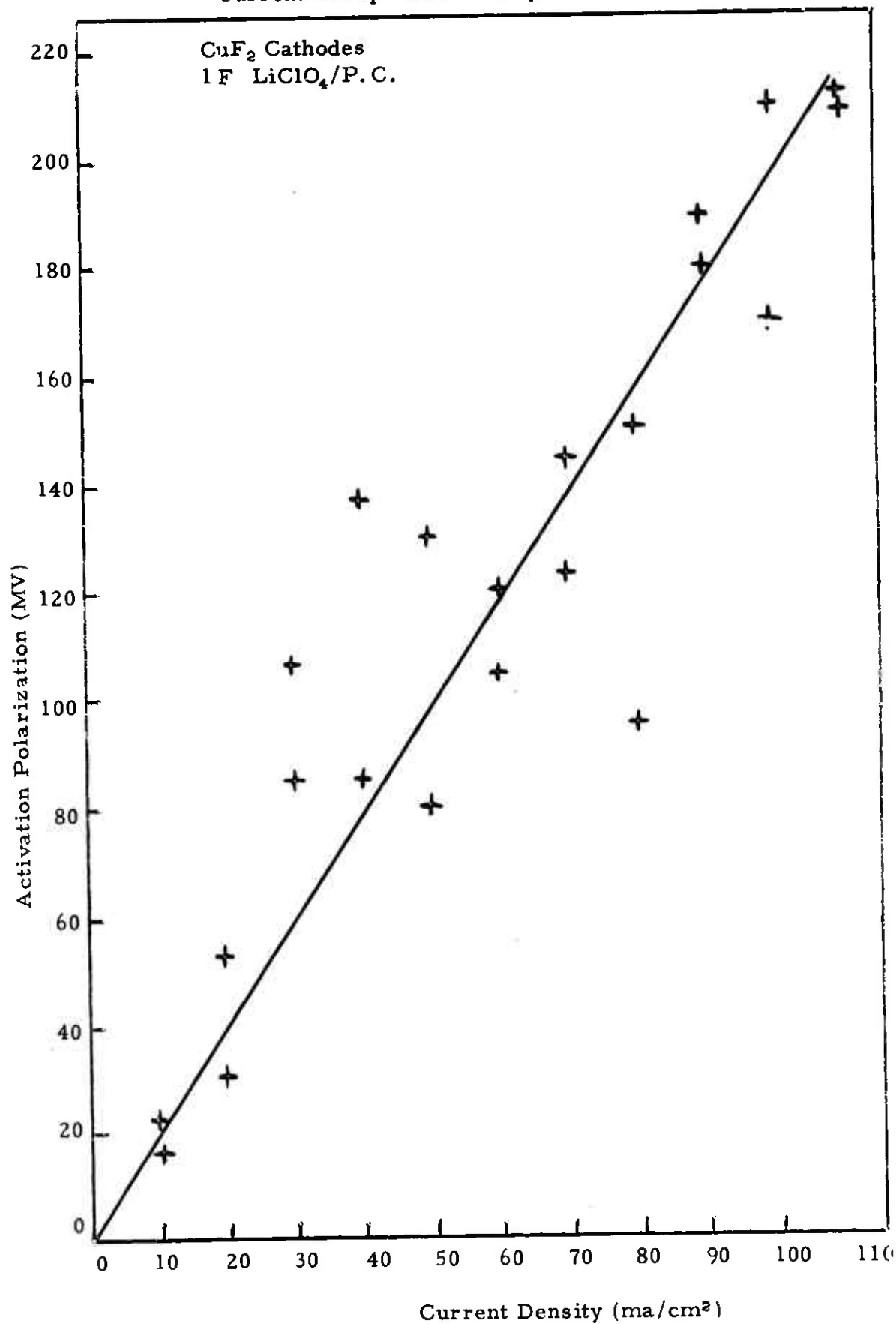


FIGURE 50

Mercury Pool Cell

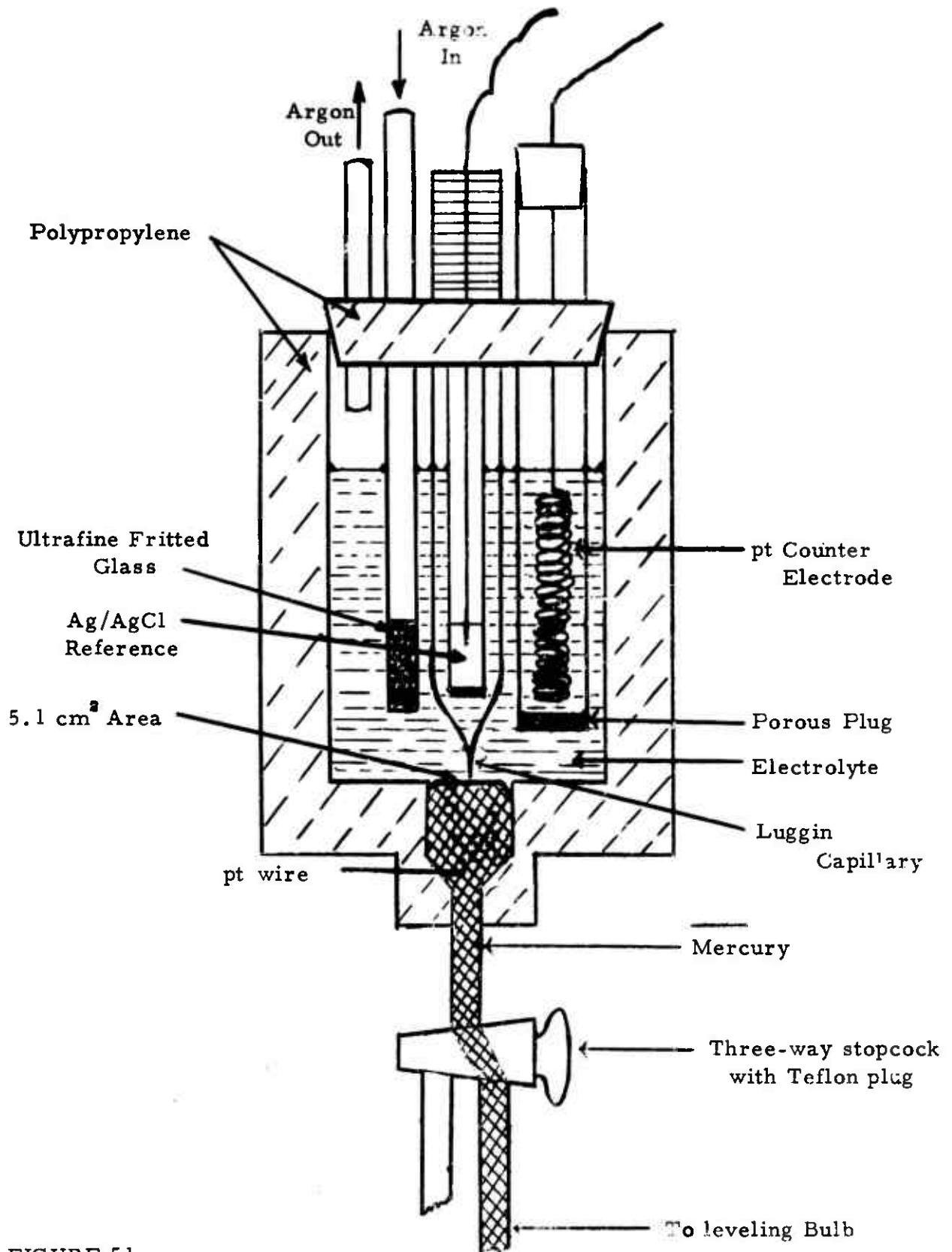


FIGURE 51

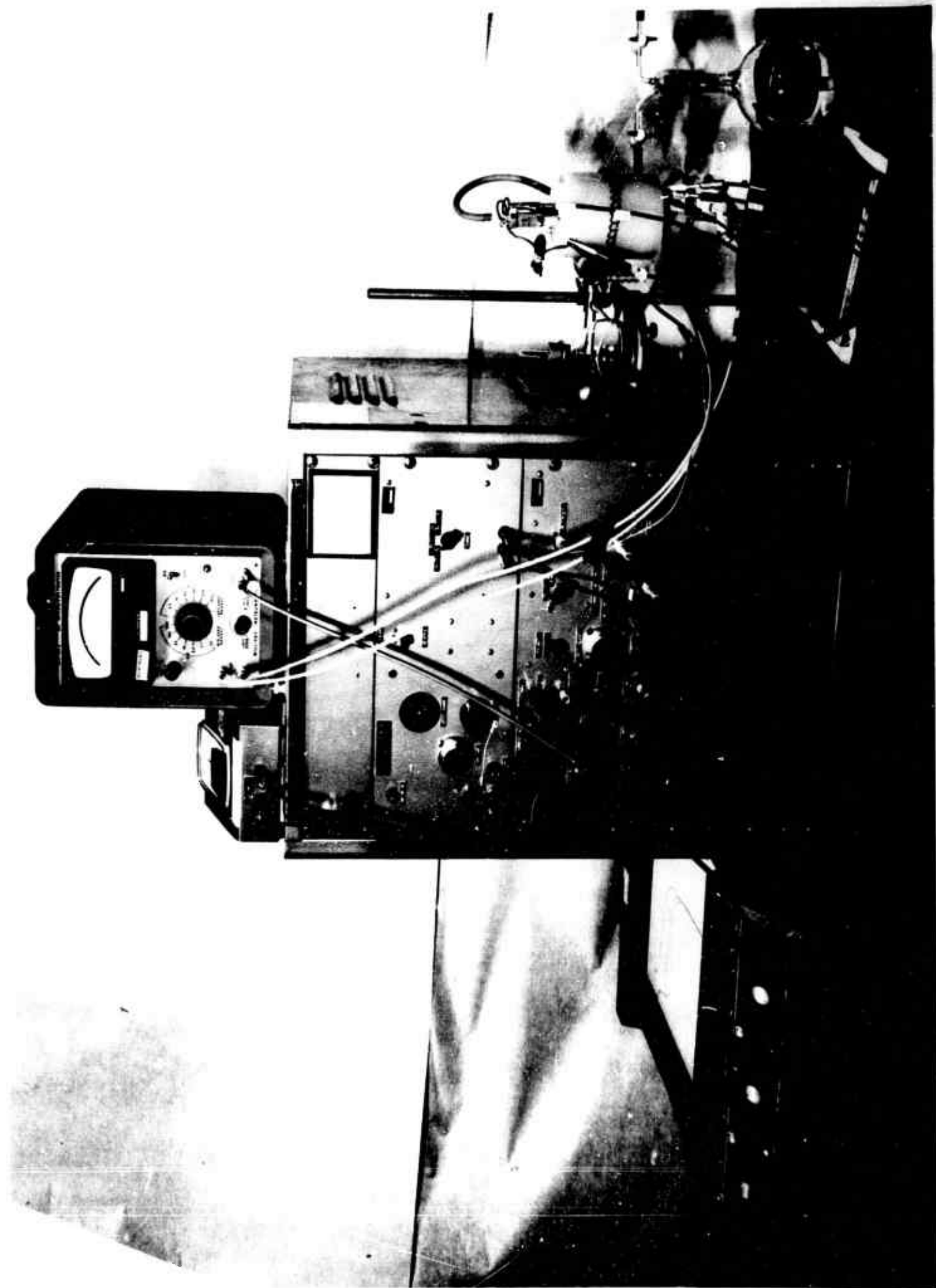
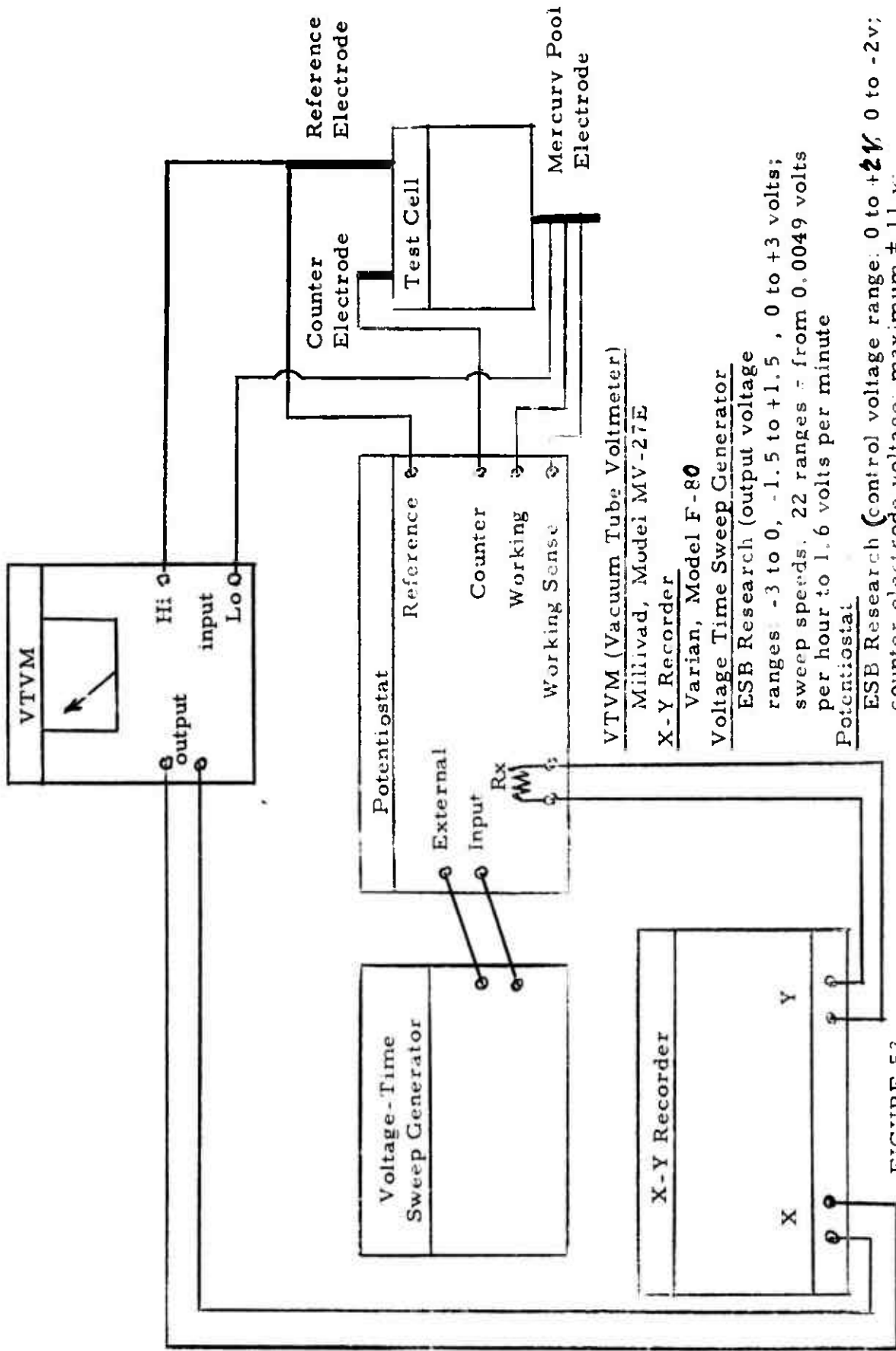


FIGURE 82

Block Diagram of Voltammetric Apparatus



VTVM (Vacuum Tube Voltmeter)

Milivivad, Model MV-27E

X-Y Recorder

Varian, Model F-80

Voltage Time Sweep Generator

ESB Research (output voltage

ranges: -3 to 0, -1.5 to +1.5, 0 to +3 volts;

sweep speeds: 22 ranges from 0.0049 volts

per hour to 1.6 volts per minute

Potentiostat

ESB Research (control voltage range: 0 to +2V, 0 to -2v;

counter electrode voltage: maximum ± 11 v;

current ranges: maximum ± 1 ampere)

FIGURE 53

Voltammetry - Residual Current Curves at Various Electrolyte Concentrations
 Scan Rate: 4.07 mv/sec.

- 1.0 F LiClO₄ in distilled propylene carbonate
- × 0.5 F LiClO₄ in distilled propylene carbonate
- 0.1 F LiClO₄ in distilled propylene carbonate
- β 1.0 F LiClO₄ in distilled propylene carbonate; electrolyzed for 1 hour at 1.50 v vs Ag/AgCl reference.

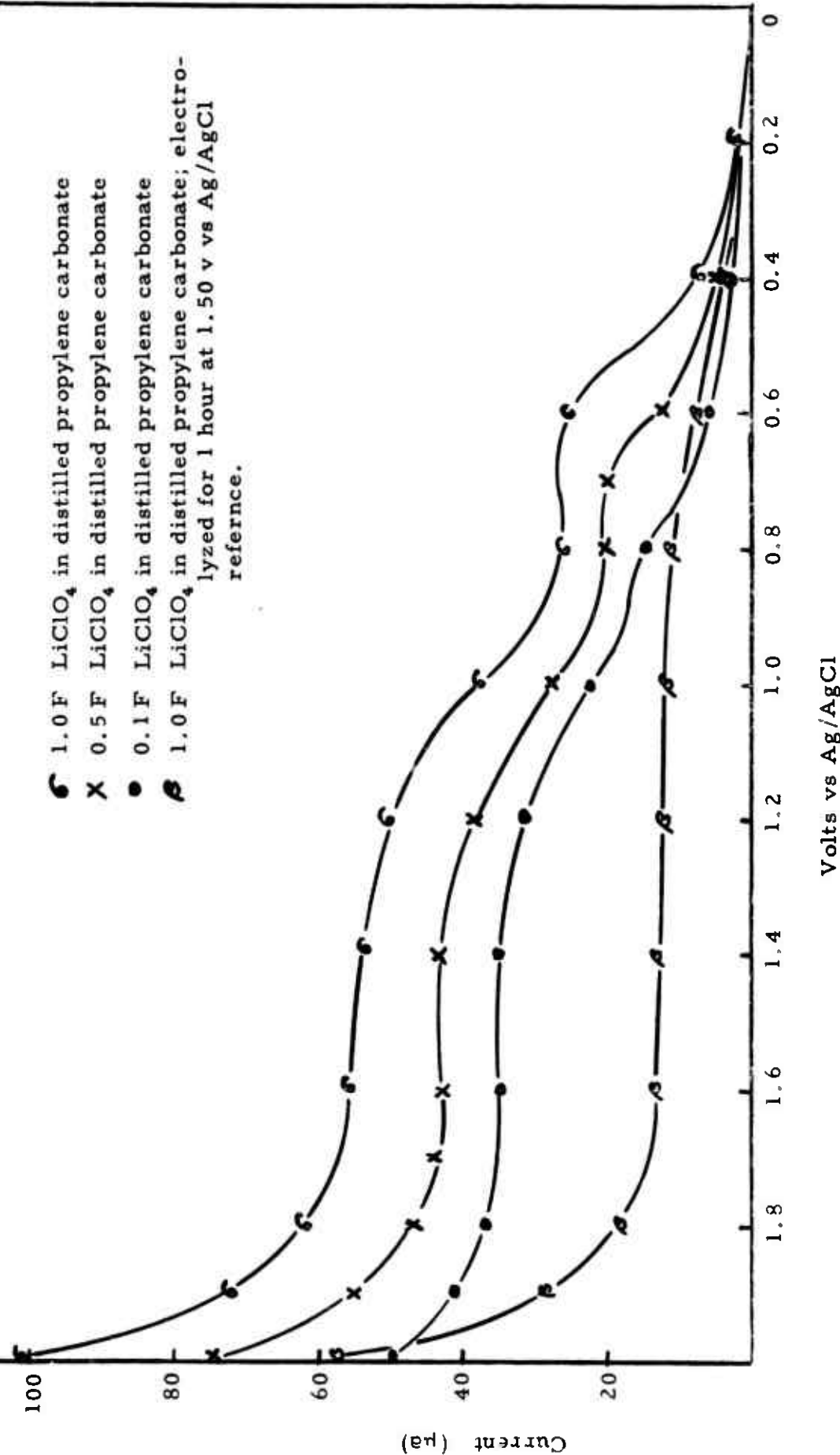


FIGURE 54

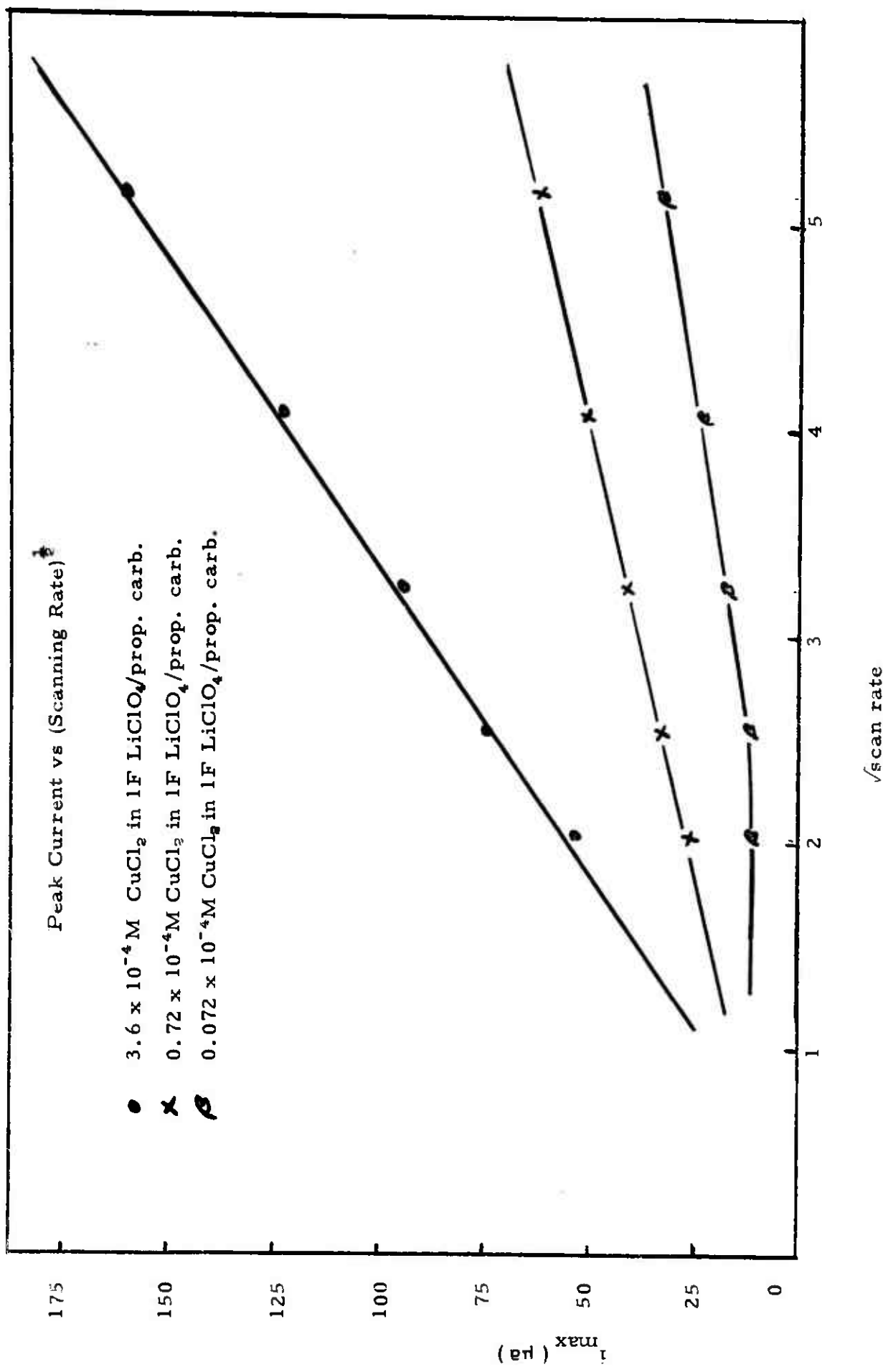
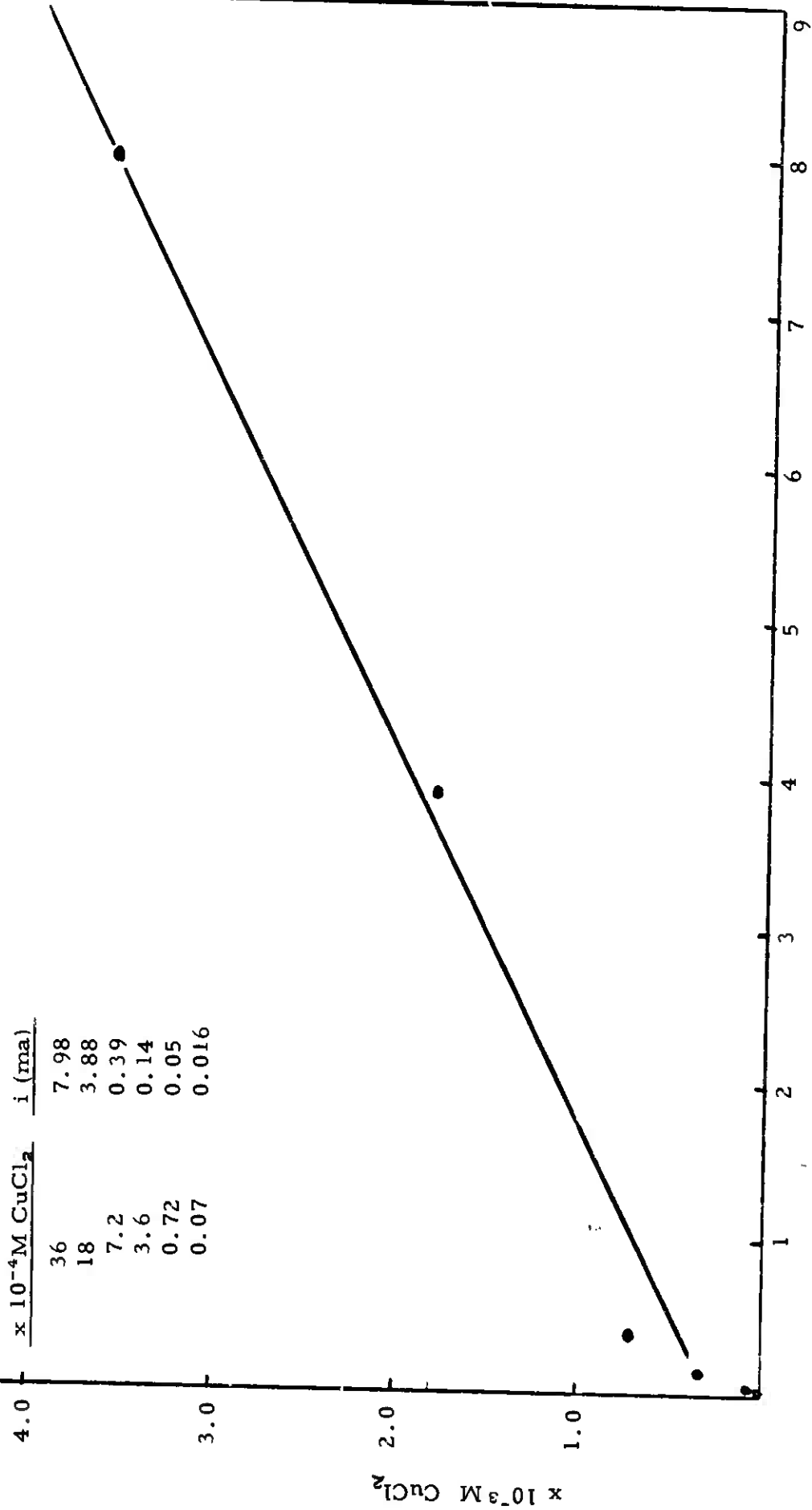


FIGURE 55

Copper Concentration vs Diffusion Current
 Supporting Electrolyte: 1 F LiClO₄ in Distilled Propylene Carbonate
 Scan Rate: 26.7 mv/sec.

$\times 10^{-4} \text{M CuCl}_2$	i (ma)
36	7.98
18	3.88
7.2	0.39
3.6	0.14
0.72	0.05
0.07	0.016



Diffusion Current (ma)

FIGURE 56

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

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		2b. GROUP	
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5. AUTHOR(S) (Last name, first name, initial) Boden, D.P.; Buhner, H. R.; Spera, V. J.			
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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Commanding General US Army Electronics Command Fort Monmouth, New Jersey ATTN: AMSEL-KL-PB	
13. ABSTRACT This report describes, in summary, the work conducted from June 15, 1966 to June 14, 1967 on Contract DA-28-043-AMC-02304(E) "High Energy System" (Organic Electrolyte). The major goal of this work was to improve the activated storage life and discharge rate capability of the Li/CuF ₂ cell developed under Contract DA-28-043-AMC-01394(E). In addition, the scope was extended to include investigation of new cathode material and electrolytes. Electrolyte studies indicated that very few of the many prospective organic solvents and solutes tested were suitable, either because of low electrolytic conductances or incompatibility with the cell components. The most promising new solvents appeared to be propylene glycol sulfite and diethyl sulfite. A reduction of more than an order of magnitude, in the solubility of CuF ₂ in LiClO ₄ /P. C. solution, was effected by purification of LiClO ₄ diethyl ether according to the method of Berglund and Sillen. Studies of the rate of dissolution of CuF ₂ in LiClO ₄ /P.C. electrolytes have not been conclusive, but it appears that the copper concentration increases with time over a period of one month, the longest interval thus far tested. It appears that a reaction between the electrolyte and the CuF ₂ , rather than a simple solubility function, may possibly be involved. Studies of the CuF ₂ cathode revealed that certain impurities in the graphite used as a conducting additive adversely affected performance on activated stand. This led to the purification of the graphite and the subsequent finding that (Continued on Attached Sheet)			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High Energy Density Batteries Organic Electrolyte Batteries Lithium Anode Cupric Fluoride Cathode Shelf Life Rate Capability Cathode Materials						

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TR P I

ABSTRACT (CONTD)

activated stand was improved. A study of Li/CuF₂ cells with cathodes containing purified graphite then revealed that activated storage of cells was improved, but at the expense of high cathode polarization.

A program of separator and ion exchange membrane evaluation revealed that conventional microporous separators were incapable of preventing the transfer of soluble copper species and subsequent galvanic deposition of copper on the Li anode and resultant cell failure on activated storage. Ion exchange membranes were found to have prohibitively high resistivities, apparently because of inability to swell and absorb organic electrolytes.

→ The results of kinetic studies of the CuF₂ cathode discharge mechanism appear to indicate that the reaction is diffusion controlled. The high viscosity of the organic electrolyte (LiClO₄/P. C.) apparently adversely affects ionic mass transport of the species required to sustain the electrode reaction.

Voltammetric studies involving the use of a mercury pool cell were initiated to determine the copper species present in solution of CuF₂ in LiClO₄/P.C. electrolyte. Preliminary results appear to indicate that the equations developed for aqueous system may be applied to organic systems. (Author)

III