AD

AD648920

TECHNICAL REPORT ECOM - 02304-2

HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

SECOND QUARTERLY REPORT

By

H. R. BUHNER, V. J. SPERA

FEBRUARY, 1967

ARCHIVE COPY

ECOM

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTRACT DA-28-043-AMC-02304(E)

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

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government indorsement or approval of commercial products or services referenced herein.

DISTRIBUTION/AVAILABILITY CODES
DIST. AVAIL. and/or SPECIAL
A

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

TECHNICAL REPORT ECOM-02304-2 FEBRUARY 1967

HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

SECOND QUARTERLY REPORT

15 SEPTEMBER 1966 TO 15 DECEMBER 1966

Report No. 6

CONTRACT NO. DA-28-043-AMC-02304(E)

Prepared by

H. R. BUHNER, V. J. SPERA

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

For

ELECTRONIC COMPONENTS LABORATORY

U. S. ARMY ELECTRONICS COMMAND, FORT MONMOUTH, N. J.

Distribution of this Document is Unlimited

ABSTRACT

This report describes the work carried out during the second quarter of contract No. DA-28-043-AMC-02304(E), High Energy System (Organic Electrolyte).

Several new electrolyte solvents were evaluated in an attempt to obtain a solution with properties superior to those of $LiClO_4$/propylene carbonate. Although high specific conductivities, greater than 1×10^{-2} ohm^{-1} cm^{-1}, were obtained in a few instances, $LiClO_4$/lactonitrile and $LiClO_4$/1, 3, Dioxolane, these electrolytes were very corrosive toward lithium.

A new technique was used to prepare highly purified and anhydrous $LiClO_4$, by recrystallization from water and refluxing in ether. This process is based on the highly preferential solubility of anhydrous, as compared to hydrated, $LiClO_4$ in diethyl ether.

The effect of electrolyte ($LiClO_4$/propylene carbonate) concentration on CuF_2 solubility was re-evaluated, and contrary to previous findings, where solubility was found to be constant over the electrolyte concentration range studied, it was found to increase as concentration increased. This might have been caused by inadvertent use of electrolyte which was found to contain impurities.

Storage of CuF_2 cathodes in electrolyte was found to result in more than a 50% loss in discharge efficiency after only two weeks storage. There was an indication that certain impurities, especially iron, in the graphite, might have been responsible for this behavior, although reaction between electrode and electrolyte is also a possibility.

Complexones were re-evaluated, at low concentrations, in highly purified electrolyte, to determine the effect on CuF_2 cathode performance. They were found to adversely affect the efficiency causing a 30-50% loss in performance with as little as 0.15% complexone.

Water was added, in amounts up to 2%, to anhydrous CuF_2 and found to have no appreciable effect on cathode performance.

Silver II oxide cathodes were discharged at current densities between 2 and 8 ma/cm^2 in $LiClO_4$/dimethyl sulfite and $LiClO_4$/dimethyl carbonate solutions. Energy density was found to decrease about 50% as current density increased over the range tested.

A study of the effect of CuF_2 particle size on cathode performance revealed a generally increasing electrode efficiency with decrease in particle size.

Separator studies involving evaluations of microporous, ion exchange membrane, and polymer film materials revealed none that were satisfactory, with resistivities

between 10^4 and 10^5 ohm-cm. Activated storage of Li/CuF_2 cells with microporous polyethylene (Porothene) separators was very poor, with short circuiting due to extensive copper dendrite penetration after only one week.

LIST OF TABLES

1. Properties of Non-aqueous Solvents

2. Solubility of CuF_2 in Solutions of $LiClO_4$ in Propylene Carbonate

3. Effect of Partially Hydrated CuF_2 on Cathode Performance

4. Effect of Current Density and Type of Electrolyte on Ag O Cathode Performance

5. Physical Characteristics of Various Ion Exchange Membranes

6. Characteristics of Various Polymers in 1 F $LiClO_4$/Propylene Carbonate

7. Characteristics of Polymer Films in 1 F $LiClO_4$/Propylene Carbonate

LIST OF FIGURES

Figure No.	
1.	Conductance of Solutions of $LiClO_4$ in Various Solvents
2.	Corrosion of Lithium in Various Electrolytes
3.	Effect of Storage in Electrolyte on Cathode Performance
4.	Effect of Ethylene Diamine Complexone on CuF_2 Cathode Performance
5.	Effect of Diethylene Triamine Complexone on CuF_2 Cathode Performance
6.	Effect of Water in CuF_2 on Cathode Performance
7.	Effect of Current Density on AgO Cathode Performance in 1.5F $LiClO_4$/Dimethyl Sulfite
8.	Effect of Current Density on AgO Cathode Performance in 2.0F $LiClO_4$/Dimethyl Carbonate
9.	Effect of CuF_2 Particle Size on Cathode Performance
10 & 11	Effect of Porothene Separator Thickness on Cathode Performance

TABLE OF CONTENTS

Abstract i

List of Tables iii

List of Figures iv

Introduction 1

1. Electrolyte Studies 1

1.1 Investigation of Organic Solvents 2

1.2 Determination of Conductance 2

1.3 Lithium Corrosion Studies 2

1.4 Investigation of Electrolyte Solutes 3

1.5 Preparation of Purified $LiClO_4$/Propylene Carbonate 3

1.5.1 Purification of Propylene Carbonate 3

1.5.2 Purification of Lithium Perchlorate 3

1.6 Determination of Cupric Fluoride Solubility in $LiClO_4$/Propylene Carbonate Solutions 4

1.6.1 Preparation of Solutions 4

1.6.2 Analysis of Solutions 5

2. Cathode Studies 5

2.1 Storage of CuF_2 Cathodes in Electrolyte 5

2.2 Effect of Complexones on CuF_2 Cathode Performance 7

2.2.1 Preparation and Testing of Electrolyte Containing Complexones 7

2.3 Effect of Water in CuF_2 on Cathode Performance 8

TABLE OF CONTENTS (cont'd)

2.4 Effect of Discharge Current Density and Electrolyte on Ag O Cathode Performance 9

2.4.1 Electrode Preparation and Testing 9

2.5 Particle Size Evaluation of CuF_2 9

3. Separator Studies 10

3.1 Evaluation of Porothene Separators in Li/CuF_2 Cells 10

3.1.1 Effect of Separator Thickness on Performance of CuF_2 Cathodes 11

3.1.2 Effect of Porothene Separators on Activated Storage of Li/CuF_2 Cells 11

3.2 Evaluation of Ion Exchange Membranes 12

3.2.1 Preparation of Macroreticular Ion Exchange Membranes 12

3.2.2 Evaluation of Various Ion Exchange Membranes 13

3.3 Evaluation of Various Polymeric Materials as Membranes in Organic Electrolyte 13

List of Materials and Suppliers 15

References 17

INTRODUCTION

This report describes the work performed during the second quarter of Contract DA-28-043-AMC-02304(E), High Energy System (Organic Electrolyte). The goal of this work is to improve the activated storage life and to increase the current density capability of the Li/CuF_2 cell, characteristics which have been shown to be limited to storage of less than one week and current density of about 2 ma/cm^2.

A continuing search was made for new solvents and electrolytes in order to obtain an electrolyte with properties superior to those obtained with the $LiClO_4$/propylene carbonate system. This solution has been the best thus far evaluated, but its high viscosity and low electrolytic conductance place severe limitations on its use at high current densities.

A new technique was used to obtain high purity $LiClO_4$, by double recrystallization from water and refluxing in ether.

Earlier investigations of activated storage have involved complete Li/CuF_2 cells. It was decided to determine separately the effect on performance of storage of CuF_2 cathodes in electrolyte for various intervals. It was found that performance decreased greatly after only two weeks storage.

Efforts to improve the activated storage life of Li/CuF_2 cells were made. The use of complexones and membrane type separator materials was investigated in an attempt to reduce or eliminate the migration of dissolved copper.

The performance of AgO cathodes was determined at various current densities and in different electrolytes.

1. ELECTROLYTE STUDIES

In a continuing effort to obtain an electrolyte with all of the desirable characteristics of the $LiClO_4$/propylene carbonate system, but with additionally a lower viscosity and higher conductivity, a number of new solvents were evaluated. The goal of this work is to develop an electrolyte that will allow high discharge efficiency of both the lithium and the CuF_2 electrodes at higher current densities than have been obtained previously (2 ma/cm^2). The high viscosity of the $LiClO_4$/propylene carbonate system is believed to limit discharge at higher current densities because of mass transport limitations. Another desirable characteristic of an electrolyte for the Li/CuF_2 system would be a capability of dissolving the LiF reaction product at the cathode, which appears to aggravate the mass transport problem.

1.1 Investigation of Organic Solvents

The major efforts in the search for a new electrolyte have been directed toward investigation of the electrolyte solvents, and especially those with low viscosities. The ideal solvent would have a low viscosity and high dielectric constant and these are the characteristics used as basis of selection. The solvents selected, together with some of their physico chemical properties are shown in Table 1.

It was found that D-Xylitol and Succinonitrile were solid materials at room temperature and it was decided to discontinue use of these compounds, since it would appear to be impractical for applications under normal ambient temperatures.

1.2 Determination of Conductance

In evaluating the various solvents chosen for study, only $LiClO_4$ was used as a solute. The solvents were the purest commercially available and were not further purified before use.

The $LiClO_4$ used in this work was the highly purified material described in section 1.5.2 of this report. Solutions were prepared, over a wide concentration range, with all procedures conducted in a dry argon atmosphere. It was found that methyl nitrate and 1, 4-Dioxane were poor solvents, dissolving less than 0.1 F $LiClO_4$, and their use was discontinued.

The conductance of the various electrolytes was determined using a Kraus and Bray type cell in conjunction with a 1000 cycle A.C. Bridge (E.S.I. Universal Impedance Bridge, Model 290 R).

The results of this experiment are shown in Figure 1. The highest specific conductance was obtained with lactonitrile and 1, 3-Dioxolane as solvents, with conductance maxima over 1×10^{-2} ohm^{-1} cm^{-1}. Although triethyl phosphite was a very good solvent for $LiClO_4$, the conductance of these solutions was relatively poor, with a maximum conductance of only 3×10^{-4} ohm^{-1} cm^{-1}.

1.3 Lithium Corrosion Studies

The compatibility of lithium with the organic electrolyte is an important factor in the selection of an electrolyte for applications where there is a requirement for long activated storage. The criterion of compatibility was taken as the rate of corrosion of lithium in the electrolytes investigated.

The rate of corrosion was determined using the micro-gassing technique previously described (1). The length of time required for one ml of gas to be evolved was used as a relative measure of the rate of corrosion.

The results of this experiment are shown in Figure 2. The lowest corrosion rate was obtained in 2.5F $LiClO_4$/1, 3 Dioxolane and 2.0F $LiClO_4$/2, 5-Dihydrofuran. However, these rates are still more than an order of magnitude greater than in $LiClO_4$/propylene carbonate solutions.

No further work is planned with these electrolytes since the extremely high rate of corrosion of lithium in these solutions would preclude their uses in a practical Li/CuF_2 cell, especially for an activated storage application.

1.4 Investigation of Electrolyte Solutes

Only one new electrolyte solute was evaluated this quarter as a part of the search for new electrolyte systems. Anhydrous AlF_3 was investigated and its solubility was determined in propylene carbonate, dimethyl carbonate and dimethyl sulfite. It was found to be practically insoluble in all the solvents chosen. No further work is planned with this material.

1.5 Preparation of Highly Purified $LiClO_4$/Propylene Carbonate Electrolyte

A highly purified $LiClO_4$/propylene carbonate electrolyte can now be made by the use of special techniques in the purification of propylene carbonate and lithium perchlorate. The use of this electrolyte in further investigations of the Li/CuF_2 system should allow the gathering of more reliable physico-chemical data, especially in those areas where electrolyte impurity may have significant effects. One example is the reduced solubility of CuF_2 in purified as compared to impure electrolyte.

1.5.1 Purification of Propylene Carbonate

Propylene carbonate was purified as previously described (2) by distilling twice from dried CaO. The first and last quarter of the distillate were discarded each time. Examination of the final distillate by gas chromatography indicated that the product was very pure.

1.5.2 Purification of Lithium Perchlorate

Lithium perchlorate (G.F. Smith Chem. Co.) was recrystallized twice from doubly distilled water and then dried under vacuum for 16 hours at room temperature. The temperature was then increased in increments of about 20°C until examination of the dry ice/methanol water trap indicated that no more water was being evolved. The final temperature was about 120°C, at which the salt was held for 8 hours. This material was then recrystallized from anhydrous diethyl ether using a technique described by Berglund and Sillen (3).

A weight of 80 grams of the $LiClO_4$ was added to 250 ml of anhydrous diethyl ether, and the solution refluxed at 45°C for 10 hours. A trap containing $Mg(ClO_4)_2$ as drying agent was connected to the top of the reflux column to prevent water from entering the system. After refluxing, the undissolved solid was discarded and the ether evaporated from solution under vacuum at 40-45°C. The product was then dried, under vacuum, by increasing the temperature slowly from room temperature to 100°C, holding at this temperature for 20 hrs, and cooling to room temperature under vacuum.

This technique is effective in removing $LiClO_4(H_2O)_3$ from incompletely anhydrous $LiClO_4$. Willard and Smith (4) have shown that the solubility of anhydrous $LiClO_4$ is as high as 53.21% by weight in anhydrous diethyl ether at 25°C, but that of $LiClO_4(H_2O)_3$ is only 0.196%.

Spectrographic analysis of the product revealed that impurities, essentially silicon, calcium and silver, were at very low levels: less than 1 ppm. In the initial preparation stop-cock grease was used on the glass joints but this was found to introduce impurities into the product. Therefore the use of grease was discontinued and the $LiClO_4$ can now be made with a very high purity.

1.6 Determination of Cupric Fluoride Solubility in $LiClO_4$/Propylene Carbonate Solutions

This study was conducted to determine the effect of electrolyte concentration on CuF_2 solubility. An earlier experiment (5) was done in electrolyte containing $LiClO_4$ which had been purified by recrystallization from water and dried under heat and vacuum. This technique produced a highly pure $LiClO_4$ but one which might have contained some hydrate, since it is very difficult to make completely anhydrous $LiClO_4$ simply by the use of heat and vacuum. Therefore a certain amount of water could have been carried into solution. During the second quarter, a search of the literature revealed a method for producing anhydrous $LiClO_4$, and it was decided to repeat the CuF_2 solubility test using $LiClO_4$, purified, and then made anhydrous using the new technique.

1.6.1 Preparation of Solutions

Solutions of purified, anhydrous $LiClO_4$ (Section 1.5.2 of this report) in twice distilled propylene carbonate were made over a wide concentration range: 2.5×10^{-3} to 1.0 Formal.

Cupric fluoride (-170 mesh) was treated at 60°C for 17 hours under vacuum to remove unreacted HF. A weight of 150 mg of this material was added to 50 ml of each of the electrolyte solutions. The solutions were prepared in a dry argon atmosphere, and stored under argon for two weeks. The flasks were shaken daily during this period. The solutions were then centrifuged, under argon, to separate any suspended CuF_2. The solutions were submitted for analysis to

determine the copper concentration.

1.6.2 Analysis of Solutions

The solutions were analyzed photometrically, using a neocuproine indicator, by the method described in the First Quarterly Report.

The results of this experiment are shown in Table 2. The solubility of CuF_2 was found to increase generally as the electrolyte concentration increased; from about 9.4×10^{-5} to 3.9×10^{-4} gm ions Cu/liter in going from 2.5×10^{-3} to 1.0 Formal electrolyte. This is contrary to results obtained in the previous experiment (5) where CuF_2 solubility was nearly constant over the same electrolyte concentration range. Also, in this latest experiment the CuF_2 solubility was generally higher than observed previously. However the maximum CuF_2 solubility, in 1.0 Formal electrolyte, was still about an order of magnitude less than that obtained in impure electrolyte, i.e., solutions prepared with $LiClO_4$ as received from vendor. It was shown in Section 1.5.2 of this report that the use of lubricant on the glass joints of the reflux apparatus for purifying $LiClO_4$ introduced high silicon impurity into the salt. This $LiClO_4$ was used inadvertently in preparation of electrolyte for this study before analysis was obtained. This might have affected CuF_2 solubility either directly or by interferring in the method used in determination of copper. Another experiment to determine CuF_2 solubility is in progress, using purified $LiClO_4$, of known purity, and much more reliable results should be obtained.

2. CATHODE STUDIES

In the second quarter, most of the experimental investigations with cathodes were concerned with the CuF_2 electrode.

The effect on cathode performance of storage in electrolyte, addition of complexones, addition of water to CuF_2, and CuF_2 particle size were determined. These studies are related to the activated storage capability of the Li/CuF_2 cell as affected by interaction of the cathode with the electrolyte.

Experiments were also conducted with AgO cathodes to determine the effect of discharge current density and type of electrolyte on performance.

2.1 Effect of Activated Storage on Cathode Performance

This study was undertaken to determine the effect on performance of standing cathodes in electrolyte for various lengths of time. Cupric fluoride (-170 mesh) was mixed for 2 hours with 5% polyethylene (-100 mesh) and 10% graphite

(SW 1651), and pressed at 3,000 lbs per cm^2 onto 5-Cu-14-2/0 expanded copper screens (1½ in. x 1⅝ in.) at 90°C for 3 minutes. All work was done in a dry box under argon. The electrodes were soaked for a specified time in purified electrolyte which was 1 M $LiClO_4$ in twice distilled propylene carbonate. The lithium perchlorate was prepared by twice recrystallizing from water, drying, and then recrystallizing from diethyl ether (Section 1.5.2). The electrodes were discharged in the purified electrolyte against two lithium anodes at 2 ma per cm^2 (60 ma) with a separator of two layers of 15 mil glass filter paper. Discharge was terminated when the potential of the cathode was 0.5 v vs Li reference. The average percent utilization of two electrodes was used as the criterion of performance. The results are shown in Figure 3.

The longer time the cathode stood in electrolyte, the lower the performance. To account for the loss in 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 graphite, 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 possibly, 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. More electrodes will be analyzed by x-ray to further study reactions and products formed.

Electrodes soaked in purified electrolyte for several days caused a noticeable green color in solution due to CuF_2 solubility. When cupric fluoride alone was put in purified electrolyte, the solution was colorless. Since all materials in the electrode except the graphite were purified, the increased solubility was attributed to the presence of impurities in the SW 1651 graphite. A sample of SW 1651 powder was analyzed with the spectrograph; the results were:

Minor Elements (1-10%) - Fe, Mg, Al, Si

Trace Elements (less than 1%) - Mn, V, Ca, Mo, Ti

Faint Trace (much less than 1%) - Ni, Cr, Cu, Ag, Ba, Na, Pb

These impurities might have caused increased CuF_2 solubility, low performance and short stand life.

Spectroscopic graphite powder from Union Carbide, National (Grade SPE) with total impurities less than 6 ppm was made into a mix as described above and pressed into electrodes at 500 lbs per cm^2 at 90°C for three minutes. They were given no stand and discharged (as above) in purified electrolyte at 2 ma per cm^2. Only 2% utilization of the CuF_2 was found to a 0.5 volt cut-off vs the Li reference electrode. This behavior has been attributed to the graphite, which may have a higher resistance than the SW 1651 type. Conductivity measurements will be made on both types to determine if this is the cause. Other types of graphite have been ordered and their electrochemical and physical properties will be determined. Electrodes will be made and analyzed by x-ray to determine the products formed on stand and discharge.

Since SW 1651 graphite gave much better performance than the spectroscopic type, attempts were made to purify the SW 1651 rather than activate the spectroscopic grade. The purification procedure was as follows: 30 gm of SW 6151 graphite was slurried with 600 ml of nitric acid (1:1, conc. HNO_3: water). The slurry was stirred continuously at 60°C for 17 hours. The acid solution was filtered off and the graphite washed with 1 liter of dilute nitric acid and then 1 liter of twice distilled water. Drying was done under vacuum at 120°C for 10 hours. The resulting powder was submitted for spectrographic analysis to find out if purification was achieved. Electrodes will be made with the purified product, discharged, and analyzed.

2.2 Effect of Complexones on CuF_2 Cathode Performance

It was shown in an earlier investigation (1) that the use of certain complexing agents in $LiClO_4$/propylene carbonate solution improved the activated storage capability of the Li/CuF_2 cell, but at the expense of greatly reduced cell efficiency. These complexing agents, ethylene diamine and diethylene triamine, adversely affected cathode performance when used in sufficient concentration (approx 1%), to effect a prolonged activated storage. When it was found that the solubility of CuF_2 could be appreciably reduced in highly purified electrolyte (5) it was decided to re-evaluate complexones. It was thought that with the greatly suppressed solubility of CuF_2 in highly purified electrolyte, only a very small concentration of complexone would be needed to prevent copper migration. The adverse effect of complexone on cathode performance would then be appreciably reduced because of its low concentration.

2.2.1 Preparation and Testing of Electrolyte Containing Complexones

Solutions containing 0.05%, 0.10% and 0.15% of respectively ethylene diamine and diethylene triamine in 1 F $LiClO_4$/propylene carbonate were made. The $LiClO_4$ was a highly purified salt prepared as described in Section 1.5.2 of this report. The propylene carbonate was doubly distilled. These solutions

were evaluated in Li/CuF_2 cells of three plate construction using 30 mils of glass fiber filter paper insulation. Each electrolyte was tested, in replicates of two cells, which were discharged at a current density of 2 ma/cm^2. In addition, control cells (no complexone) were also tested. Cathode potentials were measured against a Ag/AgCl reference electrode and converted to measurements vs Li/Li^+electrode for purposes of reporting data in a manner consistent with previous studies.

The results of this experiment are shown in Figure 4 and 5. It can be seen that even with a very low concentration, 0.05% of complexone, the cathode efficiency is greatly decreased; approximately 30% with ethylene diamine and about 50% with diethylene triamine. An increase in complexone concentration generally resulted in a further decrease in cathode efficiency.

It would appear that the use of complexones, even at very low concentrations, would adversely affect cathode performance so as to make their use impractical. Therefore, the effect of complexones in cells on activated storage was not investigated. However, this study may be extended later in the contract to include even low (<0.05%) concentrations of complexone and will involve activated storage tests if the loss of cathode efficiency is found to be reasonably low.

2.3 Effect of Water in CuF_2 on Cathode Performance

This study was conducted to determine the effect, on cathode performance, of the addition to the CuF_2 of small amounts of water.

Anhydrous CuF_2 (-170 mesh) was placed in an evaporating dish over a steam bath 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 as described in Section 2.1 except that pressing was done at 500 $\#/cm^2$. As a control test, anhydrous CuF_2 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/cm^2, in 3 plate Li/CuF_2 cells, using 1 F $LiClO_4$/propylene carbonate (Purified) electrolyte.

The results of this experiment are shown in Table 3 and Figure 6. A comparison of the performance obtained with 2% water, with as received and dried CuF_2, appears to indicate there is no significant effect due to slight hydration of CuF_2. 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 differences observed are within experimental error, and that the effect of water, at least in the range tested, is insignificant.

2.4 Effect of Discharge Current Density and Electrolyte on AgO Cathode Performance

The effect of discharge current density on AgO cathode performance was evaluated in two electrolytes (i) 1.5F $LiClO_4$/dimethyl sulfite and (ii) 2.0 F $LiClO_4$/dimethyl carbonate. The performance of AgO cathodes in these electrolytes was previously shown (5) to be somewhat higher than in 1F $LiClO_4$/propylene carbonate when discharging at 2 ma/cm^2. Therefore, it was decided to extend the study to include the effect of current density on cathode performance.

2.4.1 Electrode Preparation and Testing

Silver II oxide cathodes were made using AgO powder prepared as previously described (5). The electrodes were made by die-pressing -325 mesh AgO powder at 350 #/cm^2. No binder or graphite was used since the conductivity of AgO is high, and it has been found that AgO prepared in this manner is capable of being easily compacted into a structurally strong electrode with no binder required.

The electrodes were assembled into three plate cells against pressed lithium ribbon anodes, and insulated with 30 mils of glass fiber filter paper. Replicates of two cells were used to test each current density and electrolyte variable. The cells were discharged at respectively 2, 4, 6 and 8 ma/cm^2. Cathode potentials were measured against a Ag/AgCl reference electrode, using a high impedance electrometer.

The results of this experiment are shown in Figures 7 and 8. In general, in both electrolytes, the effect of an increase in current density, from 2 to 8 ma/cm^2, was to decrease coulombic efficiency and operating potential and consequently cell energy density. A comparison of the performance in the two electrolytes is shown in Table 4. The energy density was calculated on the basis of the total weight of AgO in the electrode and the weight of lithium consumed in the discharge. The weight of all other components was not included. It can be seen that the performance of AgO cathodes, on an energy density basis, was consistently higher in 1.5F $LiClO_4$/dimethyl sulfite electrolyte over the current density range tested.

2.5 Particle Size Evaluation of CuF_2

Cupric fluoride (Ozark-Mahoning, Lot No. R5-131), which was very low in water content, was sieved to -170 mesh and tested in cells on discharge. However the performance was very low (35% utilization). It was thought that

this was a particle size problem, and therefore this was evaluated. The CuF_2 which had been sieved for 15 minutes on a mechanical shaker, was mixed with 10% graphite (SW 1651) and 5% polyethylene (-100 mesh) on a mechanical mixer for 1.5 hours, the electrodes with 5 Cu 14 2/0 copper grids were pressed at 90°C and 500 lbs per cm^2. Lithium anodes were used with a separator of 2 layers of 15 mil glass filter paper. The performance curves for the various fractions are in Figure 9. Duplicate tests were run with each particle size and an average performance curve is given.

From the results 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.

3. SEPARATOR STUDIES

Separator studies were continued in the second quarter in an attempt to obtain a material with a capability of eliminating or retarding considerably the migration of dissolved copper species from the cathode (CuF_2) to the anode (Li). Separators previously evaluated did not have this capability and consequently activated storage of the Li/CuF_2 system was very limited.

Investigations of microporous, ion exchange membrane, and polymer film separator materials were conducted in a search for materials with the desired selectivity toward the ionic species, and with a sufficiently high conductivity consistent with good cell efficiency.

3.1 Evaluation of Porothene Separators in Li/CuF_2 Cells

Most of the earlier investigations of electrode performance in three-plate cells involved the use of glass fiber filter paper as the separator. Although the resistivity of this material was very low, resulting in a minimum of IR losses and a high discharge efficiency, it was not satisfactory in activated storage applications of the Li/CuF_2 cell. Therefore, it was decided to evaluate other separator materials, of the conventional microporous variety, and of various thicknesses, to determine their effect on electrode and cell performance and on activated storage.

Porothene (Electric Storage Battery Company), a microporous Polyethylene separator, with a fine pore size and high porosity (approx. 70% porous), 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 material.

3.1.1 Effect of Separator Thickness on Performance of CuF_2 Cathodes

The Porothene material was dried at 40°C for 5 hours under vacuum. Cupric fluoride cathodes were prepared as described in Section 2.1, except that die-pressing was done at 500 #/cm². The cathodes were assembled against pressed lithium ribbon anodes in three plate cells, using various thicknesses of Porothene separator ranging from 2 to 30 mils. Replicates of two cells were made to test each thickness variable. The cells were discharged at 2 ma/cm², using 1 F $LiClO_4$/propylene carbonate (purified). Cathode potentials were measured against Ag/AgCl reference electrodes using a high input impedance electrometer. The percent utilization of CuF_2 was used as a criterion of performance.

The results of this experiment are shown in Figures 10 and 11.

An increase in separator thickness resulted in a decrease in performance; from 63% utilization with 2 mils of separation, to 11% with 30 mils. The high resistivity of the separator, especially at the higher thicknesses, appears to adversely affect performance, apparently by a combination of resistive and concentration polarization effects.

3.1.2 Effect of Porothene Separators on Activated Storage of Li/CuF_2 Cells

To determine the effect of porothene separator material on the activated storage characteristics of Li/CuF_2 cells, three plate cells were built incorporating 12 mils of porothene as insulation. The electrodes were insulated using a technique whereby an envelope of the separator material was formed to contain the anode, with an additional thickness of separator enclosing the cathode in a "U' type construction, with the edges of the electrode exposed.

Replicates of two cells were made for respectively one weeks activated storage and for immediate discharge. The cells were filled with 1 F $LiClO_4$/propylene carbonate (purified). All discharges were conducted at 2 ma/cm².

Results of this experiment revealed a 38% utilization of CuF_2 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 separators.

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

3.2 Evaluation of Ion Exchange Membranes

The activated storage capability of the Li/CuF_2 cell has been found to be very limited, and efforts have been made to discover the causes of and to find a solution for the problem. One of the major factors in this limitation appears to be the migration of dissolved copper species to the anode with consequent copper dendrite formation and eventual short-circuiting of the cell. All earlier studies have shown that conventional microporous separators are incapable of preventing migration of dissolved copper. It appears that a perm-selective type of membrane separator is required that will allow migration of the ionic electrolyte species required by the cell reaction, while preventing the transfer of the copper species. In aqueous systems this capability has already been demonstrated by the use of a perm-selective membrane in a type of Daniel Cell (6). In this case solutions of $CuSO_4$ and $ZnSO_4$ were separated by the membrane, and it was found that no copper was deposited on the zinc electrode in the $ZnSO_4$ compartment.

Therefore, it was decided to undertake a program of evaluation of various ion exchange membranes as one phase of a new separator study.

3.2.1 Preparation of Macroreticular Ion Exchange Membranes

One part of this study involved the preparation of membranes containing macroreticular ion exchange resins dispersed in a polyethylene binder. The macroreticular resins differ from conventional resins in that they have a truly macroporous structure with a high surface area, whereas the conventional exchangers do not have discrete pores but only an apparent porosity which is related to the intermolecular spacing between polymeric chains in the polyelectrolyte gel. Because of the greater porosity of the macroreticular resins they are capable of absorbing large amounts of organic materials. Therefore it was decided to evaluate the macroreticular resins in membranes, since it was thought that a capability of absorbing organic solvent molecules would cause the membrane to function similarly to conventional membranes in aqueous solutions, i.e., be able to swell, absorb electrolyte and become electrolytically conductive.

Macroreticular resins designated as IRA-904, a strong base anion exchanger, and Amberlite 200, a strong acid cation exchange resin, were obtained from the Rohm & Haas Co. These materials were dried at 140°F for 16 hours under vacuum. The resins 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 resin 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.

Samples of the membranes were equilibrated in 1 F $LiClO_4$/distilled propylene carbonate electrolyte for one day. The percent absorption and retention of electrolyte was determined. The resistivity was then measured using the technique previously described (7).

The results of this experiment are shown in Table 5. It can be seen that electrolyte absorption by these membranes was very low, and the resistivity extremely high. The use of such membranes, even at very low current densities, would result in extremely high IR losses and consequently loss of cell operating efficiency.

3.2.2 Evaluation of Various Ion Exchange Membranes

In addition to the preparation and testing of macroreticular ion exchange membranes various other ion exchange membranes were evaluated. These membranes are proprietary to the Electric Storage Battery Company so that only number designations for the materials are given in this report. These materials were the most readily available and were tested to obtain some background information on the performance of ion exchange membranes in organic electrolyte.

These membranes were equilibrated in purified 1 F $LiClO_4$/propylene carbonate for one day. The electrolyte absorption and electrolytic resistivity of the membranes was then determined. The results of this study are shown in Table 5. In general, the electrolyte absorption and retention characteristics were poor and resistivity extremely high for these membranes. Only membrane No. 1073 had a reasonably high absorption, and also the lowest resistivity of the membranes tested. Also noted throughout will be the absence of significant swelling of these membranes, which appears to be necessary for good conductivity. Future investigations with regard to activated storage of Li/CuF_2 cells may be conducted with membranes having the lowest resistivity.

3.3 Evaluation of Various Polymeric Material as Membranes in Organic Electrolyte

Another phase of the new separator study concerns the behavior of various polymeric materials in organic electrolyte. A screening test was initiated in an attempt to obtain materials with the following characteristics:

i) A capability of absorbing electrolyte without completely dissolving in the solution.

ii) Good electrolytic conductivity. This will be determined initially only for those materials available in film form.

iii) A capability of ionic selectivity, by allowing permeability of ionic species required by the electrode reactions, while preventing transfer of copper species.

Characteristics such as these are shown by cellophane in aqueous systems, in applications such as the Ag/Zn alkaline cell. The cellophane membrane, partially attacked but not completely dissolved by water, swells and absorbs electrolyte, becoming conductive. It is selective in that transfer of dissolved silver species from the cathode to the zinc anode apparently is prevented. If a material can be obtained capable of functioning similarly in organic electrolytes, except for the ability to be selective for copper species, it may be possible to prolong the activated storage life of the Li/CuF_2 cell.

Various polymeric materials, some in powdered or pelletized form, and others in film form, were equilibrated in 1 F $LiClO_4$/propylene carbonate (purified) electrolyte for one week. Visual observation of the behavior of these materials was made to determine if the materials were inert, partially attacked or completely dissolved. In the case of partial attack a cementing action on the powder particles, or gelling action were the characteristics observed. In the case of films, partial attack was measured by a swelling action. Also, for the film materials, electrolyte absorption and membrane resistivity were measured in 1 F $LiClO_4$/propylene carbonate. The results of these experiments are shown in Tables 6 and 7.

In Table 6 it can be seen that Methocel (4000 cps) gelled in the electrolyte, and the Saran F-120 was partially attacked, causing cementing of the particles of powder. The other materials were either essentially inert or completely soluble. Possibly Methocel and Saran in film form might have the desired membrane characteristics described above, and will be investigated as they become available in films.

In Table 7 the characteristics of various polymer films are shown. The resistivity of all of these materials was extremely high. Even for Orlex 310 film, which swelled considerably and absorbed an appreciable weight of electrolyte, the resistivity was very high. These results with polymer materials have not shown promise for application as perm-selective membranes, but further investigations of these and other polymers, for example Saran and Methocel as described above, will be conducted.

LIST OF MATERIALS AND SUPPLIERS

Methyl Nitrate,	K & K Laboratories
D-Xylitol,	" "
Succinonitrile,	" "
Dimethyl Carbonate, Highest Purity	Fisher Scientific Co.
Dimethyl Sulfite, " "	" " "
1,4-Dioxane, Fisher Certified	" " "
2,5-Dihydrofuran, Practical	" " "
1,3-Dioxolane, Highest Purity	" " "
Aluminum Trifluoride, anhyd., purified	Matheson, Coleman & Bell
Triethyl Phosphite, practical	" " "
Amberlite 200, Cation Exchange Resin	Rohm & Haas
IRA-904, Anion Exchange Resin	" "
Polyphenylene Oxide-531-801	General Electric
Surlyn A, Ionomer, ER 1552	DuPont
Zytel Nylon, code 101	"
Teslar (PVF) type 30	"
Methocel, 4000 cps	Dow Chemical Co.
Hostalit (PVC) C-260	Hoechst Chem. Co.
Cellulose Acetate E-398-3	Eastman Chem. Products
Cellulose Acetate E-398-10	" " "
Ethulose E-1200	Chemaster Corp.

LIST OF MATERIALS AND SUPPLIERS (cont'd)

Cellusize WP-09	Union Carbide
Phenoxy 8	" "
Saran F-120	Dow Chem. Co.
Nylon 6 (Capran)	Allied Chemical Corp.
Orlex 310 (PVC)	Nixon-Baldwin
Borden C-2 Film	Borden Chem. Co.
Borden C-3 Film	" " "

REFERENCES

(1) Boden, D. P., Buhner, H. R., Spera, V. J.
First Quarterly Report, Contract Nr. DA-28-043-AMC-01394(E)

(2) Boden, D. P., Buhner, H. R., Spera, V. J.
Final Report, Contract Nr. DA-28-043-AMC-01394(E)

(3) Berglund, U., and Sillen, L. G., Acta Chem. Scand. 2 (1948) 116-126

(4) Willard, H. W., and Smith, G. F., J. Am. Chem. Soc., 45 (1923) 286

(5) Boden, D. P., Buhner, H. R., Spera, V. J.
First Quarterly Report, Contract Nr. DA-28-043-AMC-02304(E)

(6) Ionics Incorporated (Juda, W., McRae, W. A.) Ger, 1,042,052 (1958)

(7) Boden, D. P., Buhner, H. R., Spera, V. J.
Third Quarterly Report, Contract Nr. DA-28-043-AMC-01394(E)

TABLE 1

Properties of Non-Aqueous Solvents

Solvent	Dielectric Constant	Viscosity (Centipoise)	Density (g/cc)	Melting Point (°C)	Boiling Point (°C)
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	--	156.5

TABLE 2

Solubility of CuF_2 in $LiClO_4$/Propylene Carbonate Solutions

Electrolyte	Concentration of Cu^{++} mg/ltr	g. ion/ltr
0.0025 F $LiClO_4$ in P.C.	6	9.4×10^{-5}
0.005 F $LiClO_4$ in P.C.	6	9.4×10^{-5}
0.010 F $LiClO_4$ in P.C.	6	9.4×10^{-5}
0.025 F $LiClO_4$ in P.C.	7	1.1×10^{-4}
0.05 F $LiClO_4$ in P.C.	7	1.1×10^{-4}
0.10 F $LiClO_4$ in P.C.	9	1.4×10^{-4}
0.25 F $LiClO_4$ in P.C.	9	1.4×10^{-4}
0.50 F $LiClO_4$ in P.C.	13	2.0×10^{-4}
1.0 F $LiClO_4$ in P.C.	25	3.9×10^{-4}

TABLE 3

EFFECT OF PARTIALLY HYDRATED CuF_2 ON CATHODE PERFORMANCE

Percent Water Added to CuF_2	Percent Utilization of CuF_2 (avg)
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	62
0.5	67.5
1.0	58
2.0	71

TABLE 4

EFFECT OF CURRENT DENSITY AND TYPE OF ELECTROLYTE ON AgO CATHODE PERFORMANCE

Current Density	1.5 F $LiClO_4$/Dimethyl Sulfite		2.0 F $LiClO_4$/Dimethyl Carbonate	
ma/cm^2	AgO Utilized (%)	Energy Density (Watt hrs/lb)	AgO Utilized (%)	Energy Density (Watt hrs/lb)
2	98	350	95	308
4	97	268	95	260
6	93	220	90	240
8	65	173	73	120

TABLE 5

ION EXCHANGE MEMBRANE CHARACTERISTICS IN ORGANIC ELECTROLYTE

Electrolyte: 1 F $LiClO_4$/Propylene Carbonate

Membrane Designation	Thickness (mils) Dry	Thickness (mils) Equilibrated	Electrolyte Absorption (%)	Electrolyte Retention (%)	Specific Resistance (ohm-cm)
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	$> 1.7 \times 10^4$
#1054-F	5	5	40	57	$> 5.5 \times 10^4$
#1072	7	7	72	90	7.3×10^3
#1073	8	8.5	88	68	1.8×10^3
#1074	6	7	40	57	$> 3.5 \times 10^4$

TABLE 6

CHARACTERISTICS OF POLYMERS IN 1F $LiClO_4$/PROPYLENE CARBONATE

Polymer	Effect of Immersion for One Week
Polyphenylene Oxide 531-801	Inert
Surlyn A-ER1552	Inert
Methocel, 4000 cps	Slight solubility - gelled
Hostalit C-260 (PVC)	Inert
Cellulose Acetate E-398-3	Completely dissolved
Cellosize WP09	Inert
Zytel, Code 101	Slight attack, electrolyte cloudy
Saran F-120	Slight attack, particles cemented
Cellulose Acetate E-398-10	Completely dissolved
Ethulose E1200	Inert

TABLE 7

CHARACTERISTICS OF POLYMER FILMS IN 1 F $LiClO_4$/PROPYLENE CARBONATE

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

Specific Conductance of $LiClO_4$ in Various Solvents

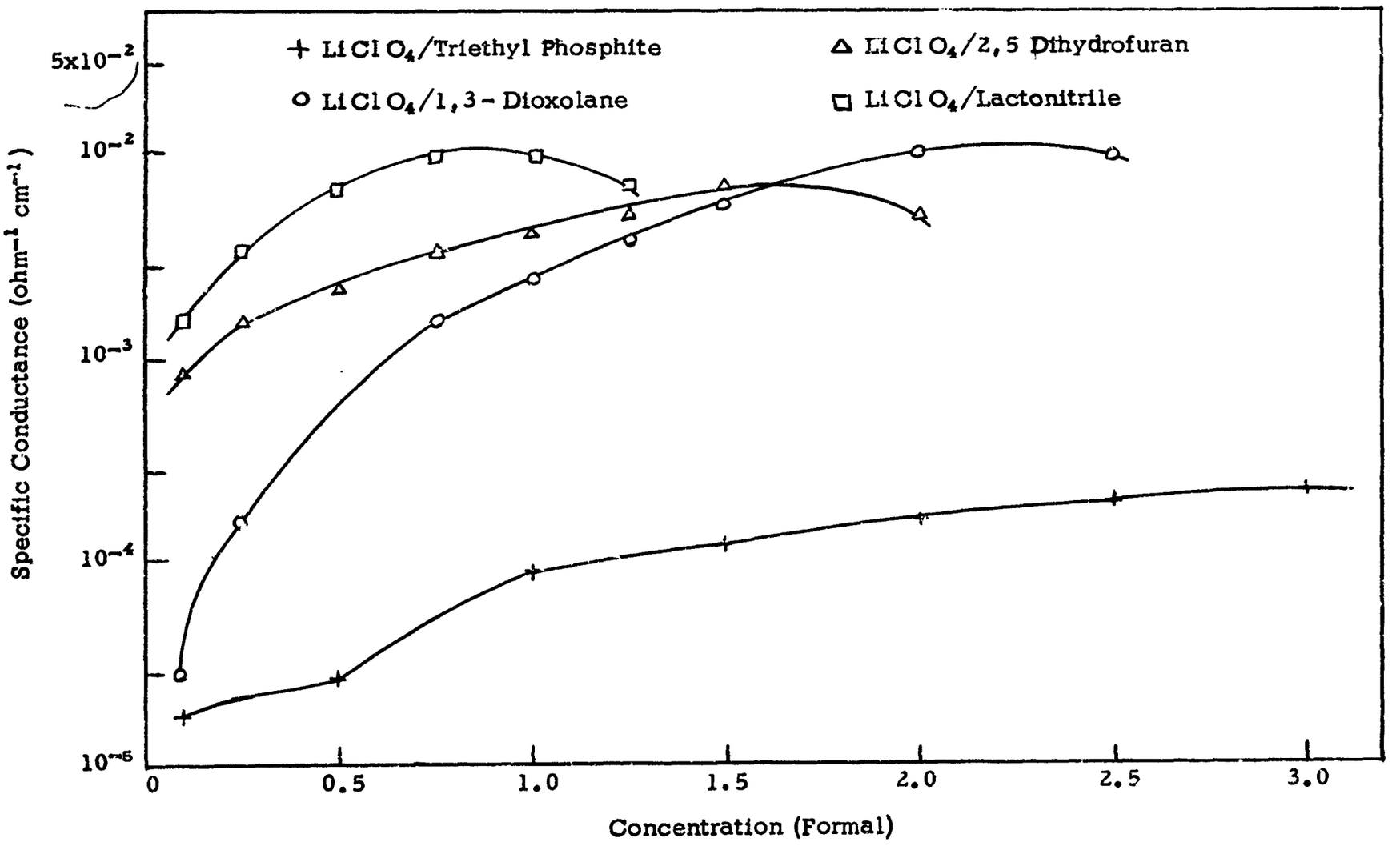

FIGURE 1

Corrosion of Lithium in Various Electrolytes
($LiClO_4$ as Electrolyte Solute)

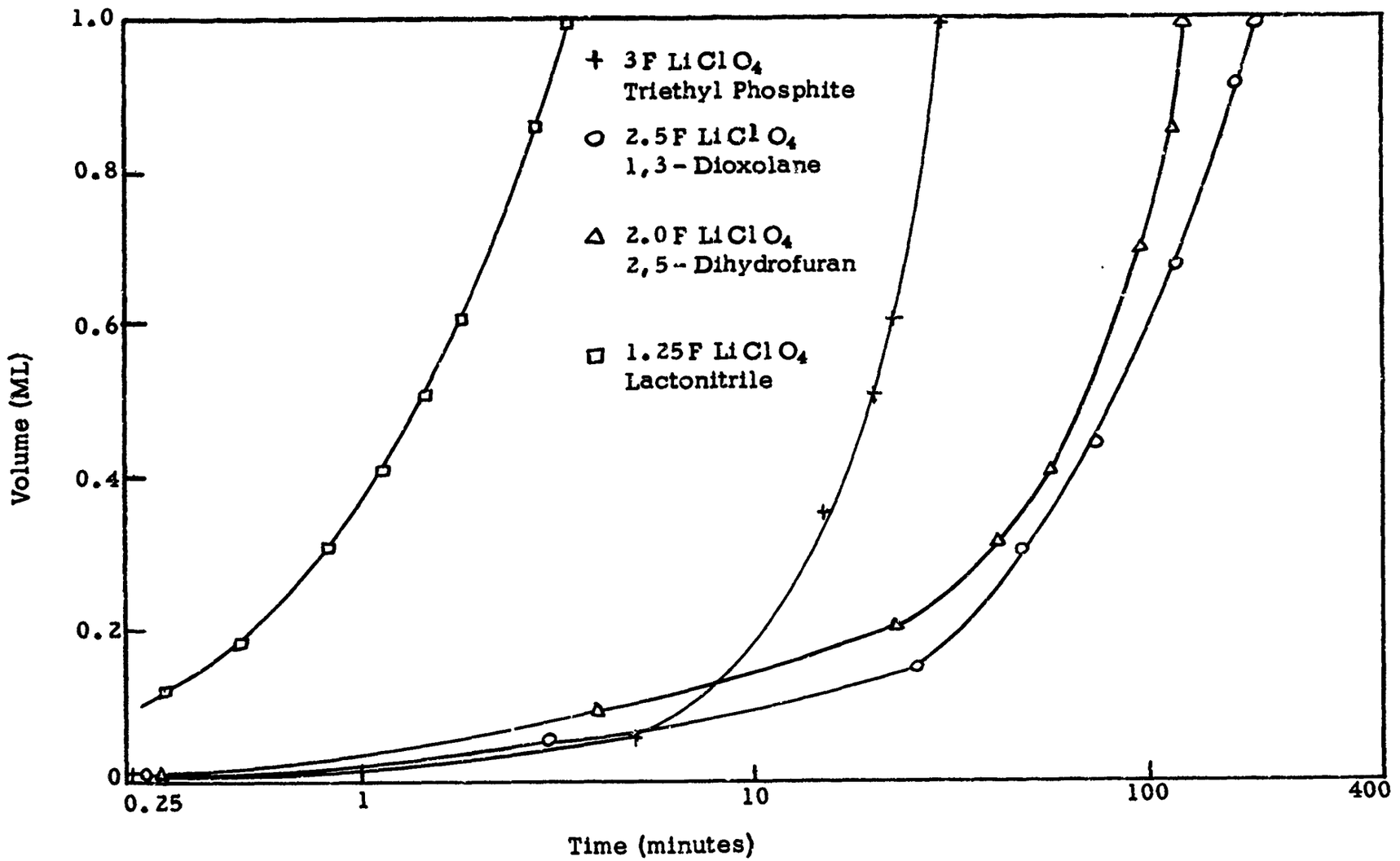

FIGURE 2

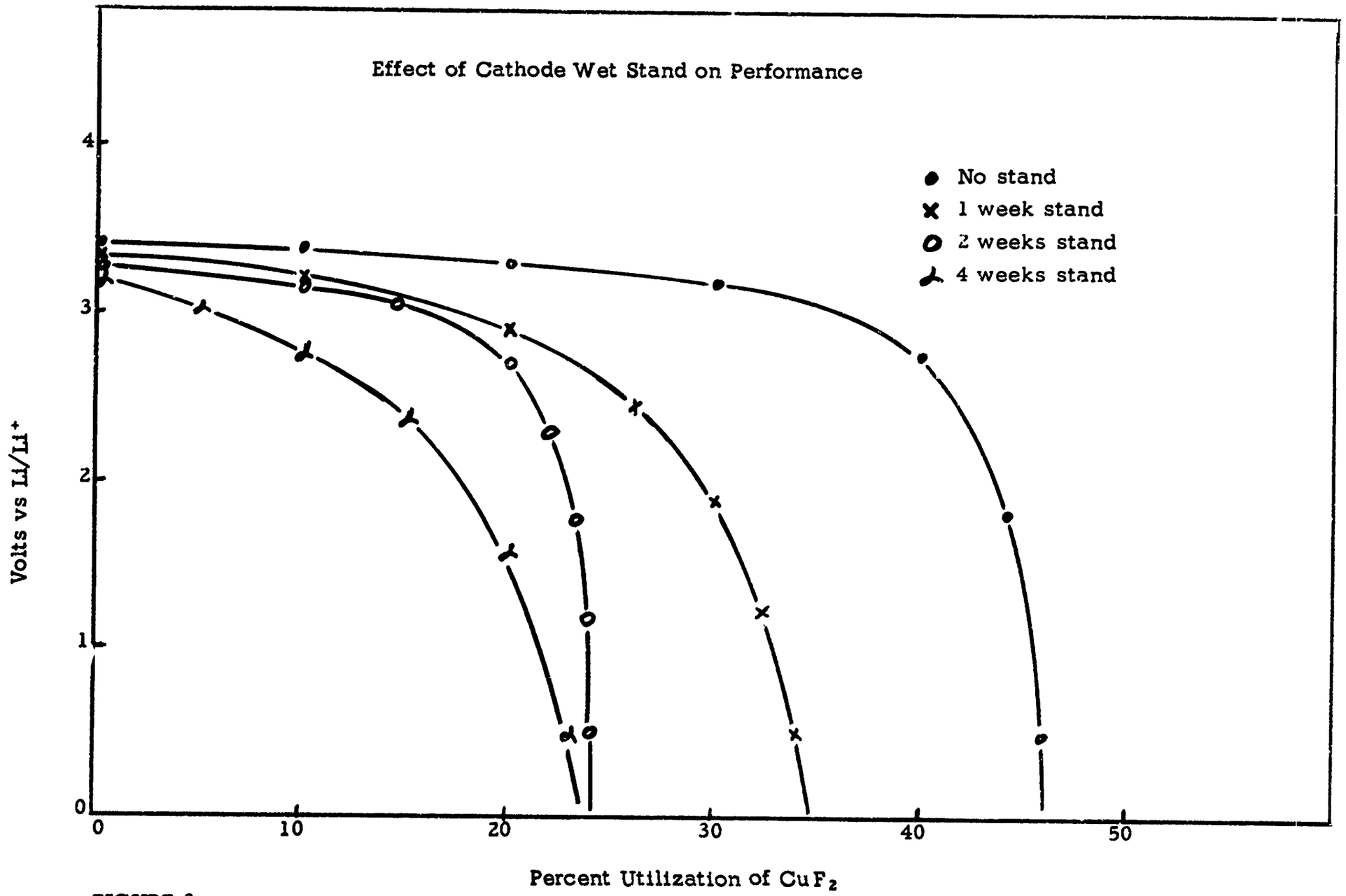
Effect of Cathode Wet Stand on Performance
No stand
1 week stand
2 weeks stand
4 weeks stand
Volts vs Li/Li+
Percent Utilization of CuF2
0
1
2
3
4
0
10
20
30
40
50

FIGURE 3

Effect of Ethylene Diamine Complexone on CuF_2 Cathode Performance
Electrolyte: 1 F $LiClO_4$ (Recryst)/Double Dist. P.C.

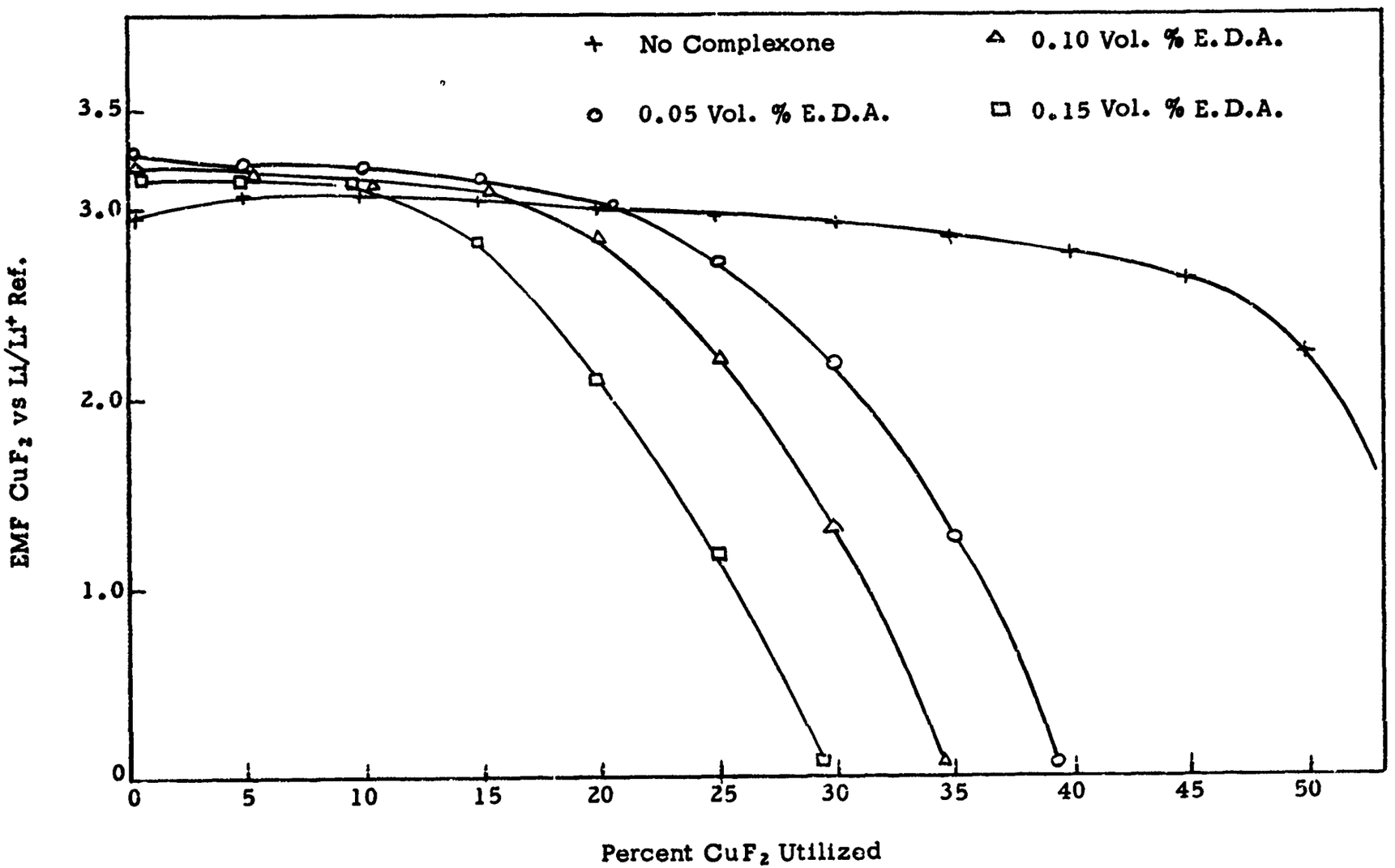

FIGURE 4

Effect of Diethylene Triamine Complexone on CuF_2 Cathode Performance
Electrolyte: 1 F $LiClO_4$ / Propylene Carbonate (Purified)

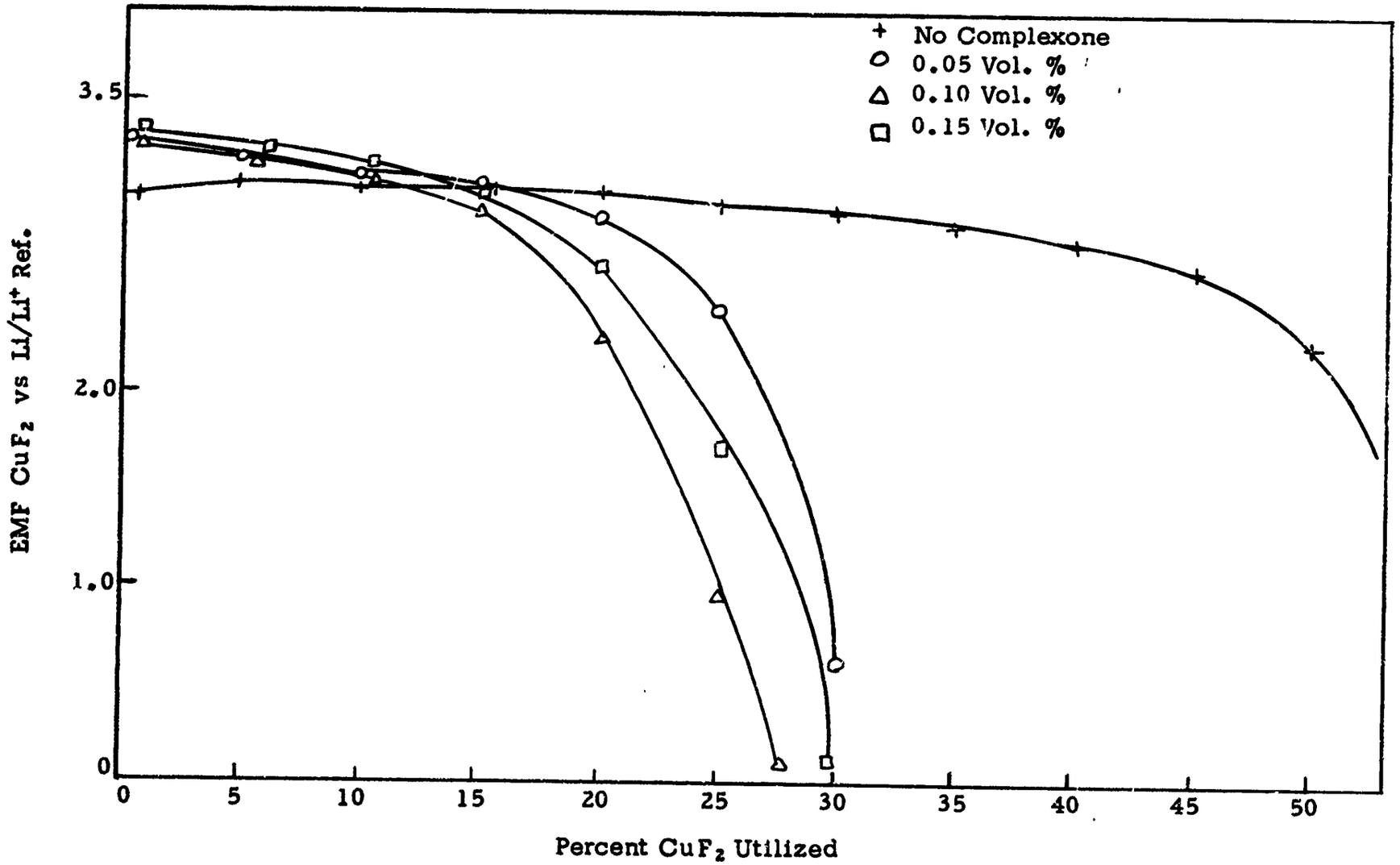

FIGURE 5

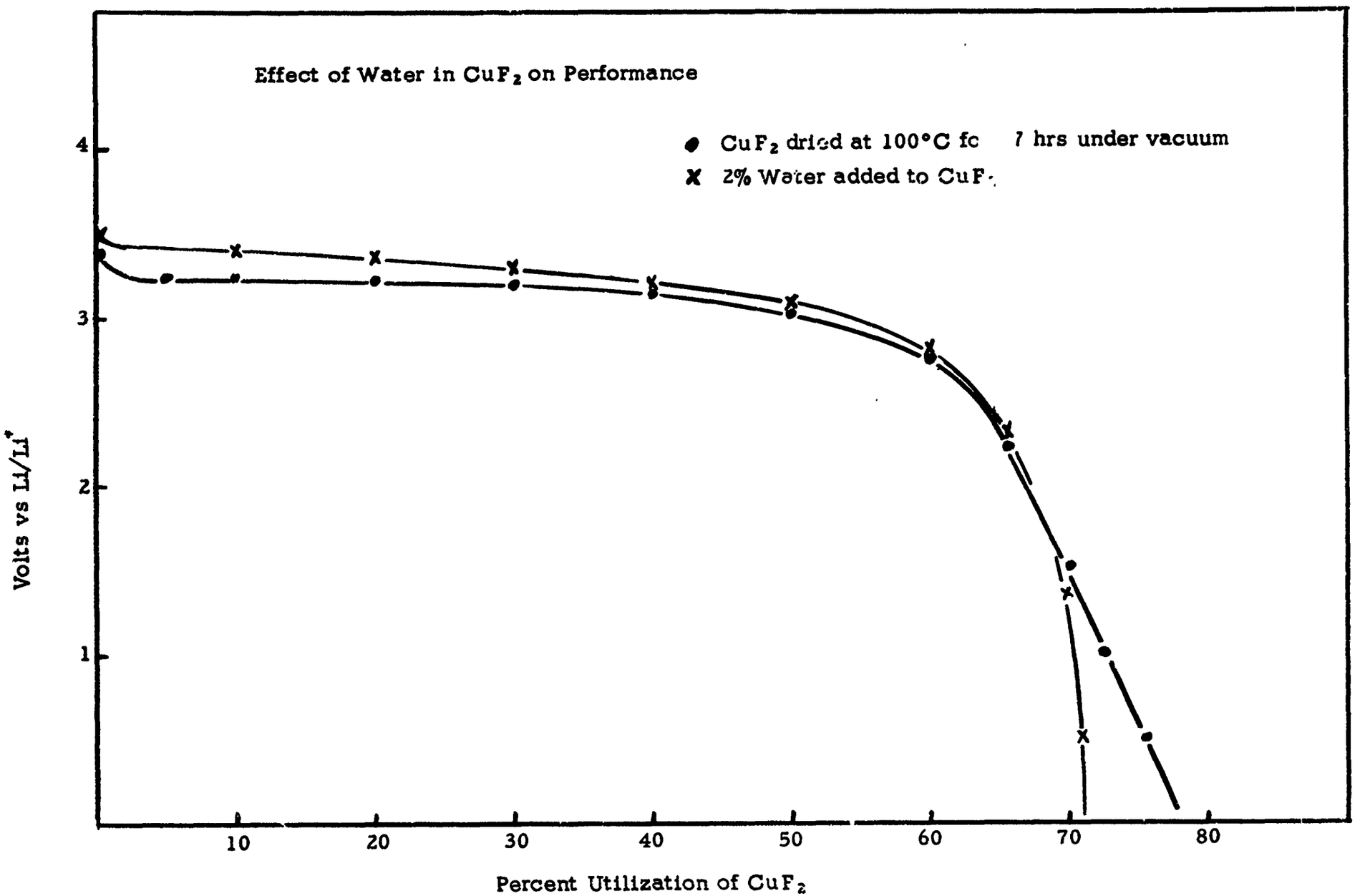
Effect of Water in CuF_2 on Performance
● CuF_2 dried at 100°C fc 7 hrs under vacuum
✕ 2% Water added to CuF_2
Volts vs Li/Li^+
4
3
2
1
10
20
30
40
50
60
70
80
Percent Utilization of CuF_2

FIGURE 6

Effect of Current Density on Ag O Cathode Performance
Electrolyte: 1.5F Li Cl O_4/Dimethyl Sulfite

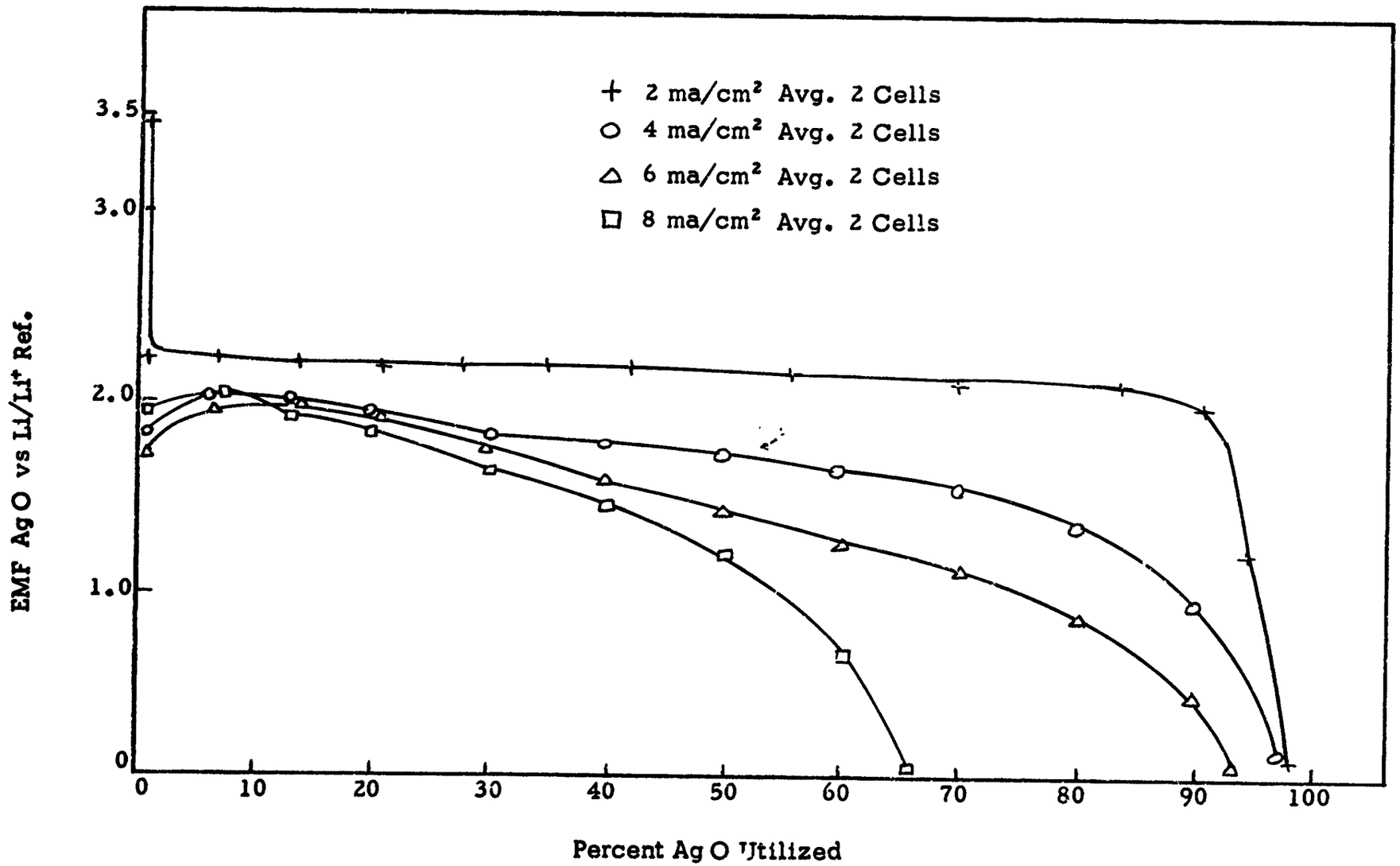

FIGURE 7

Effect of Current Density on Ag O Cathode Performance
2F Li Cl O_4/Dimethyl Carbonate Electrolyte

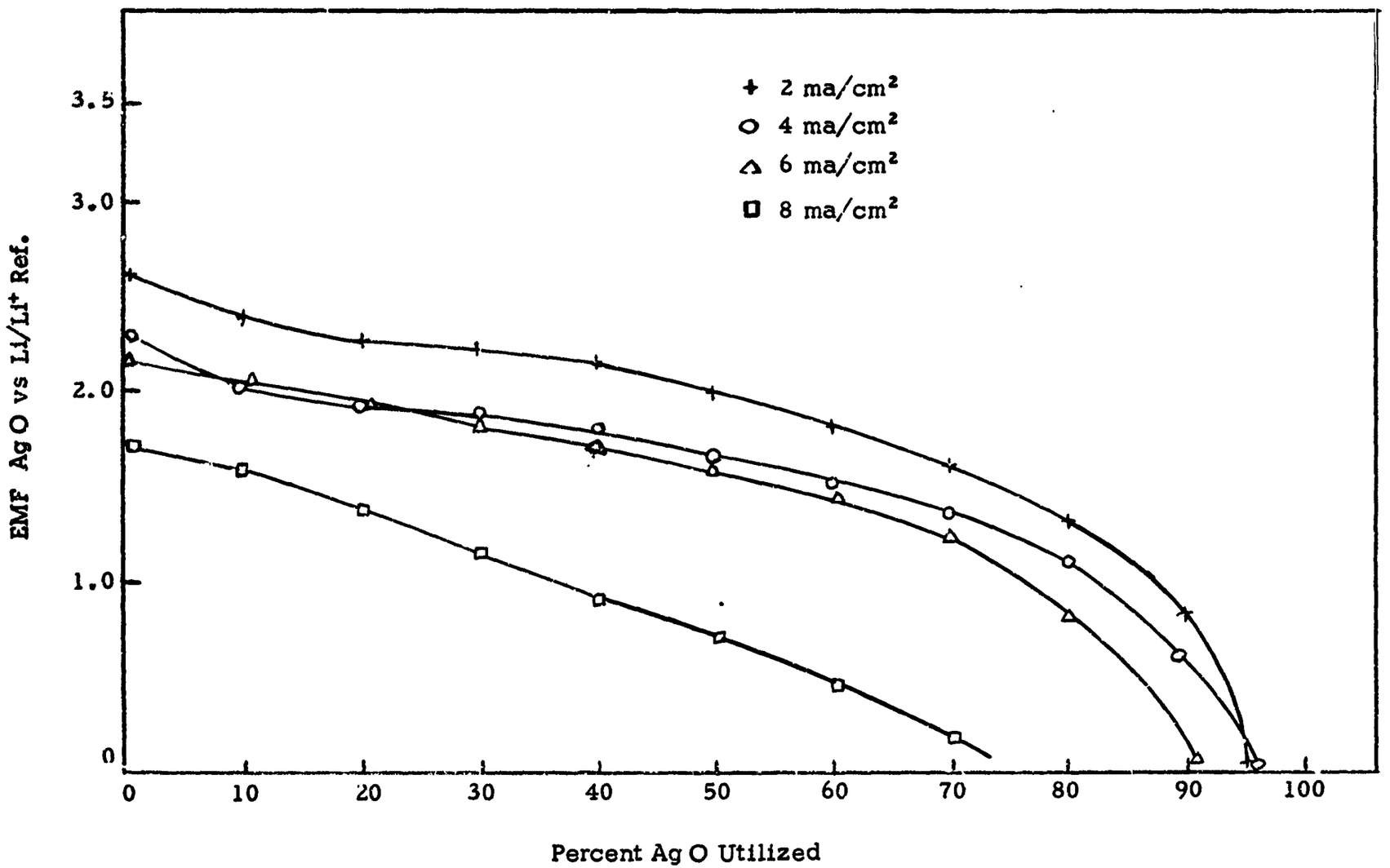

FIGURE 8

FIGURE 8

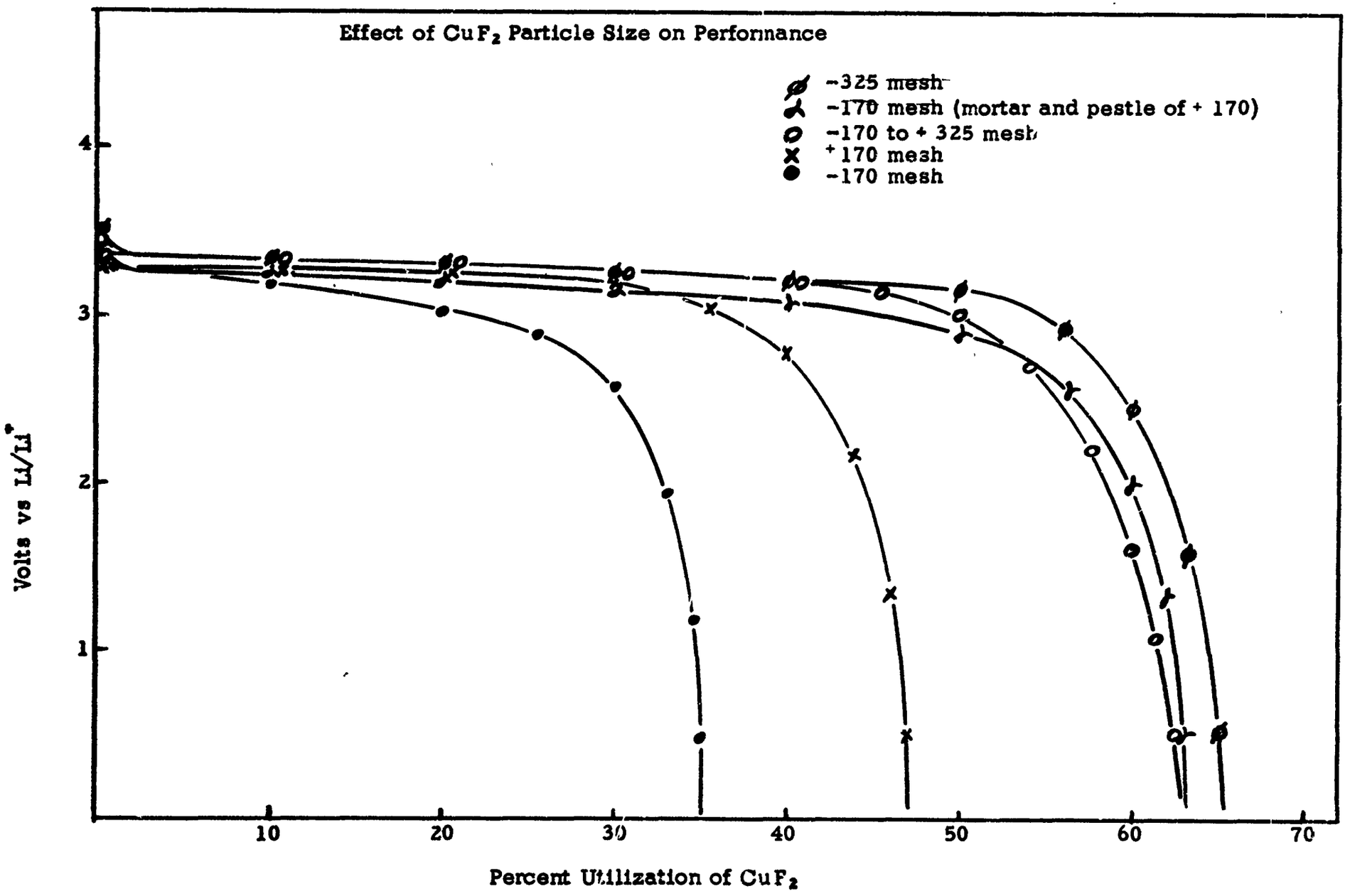

FIGURE 9

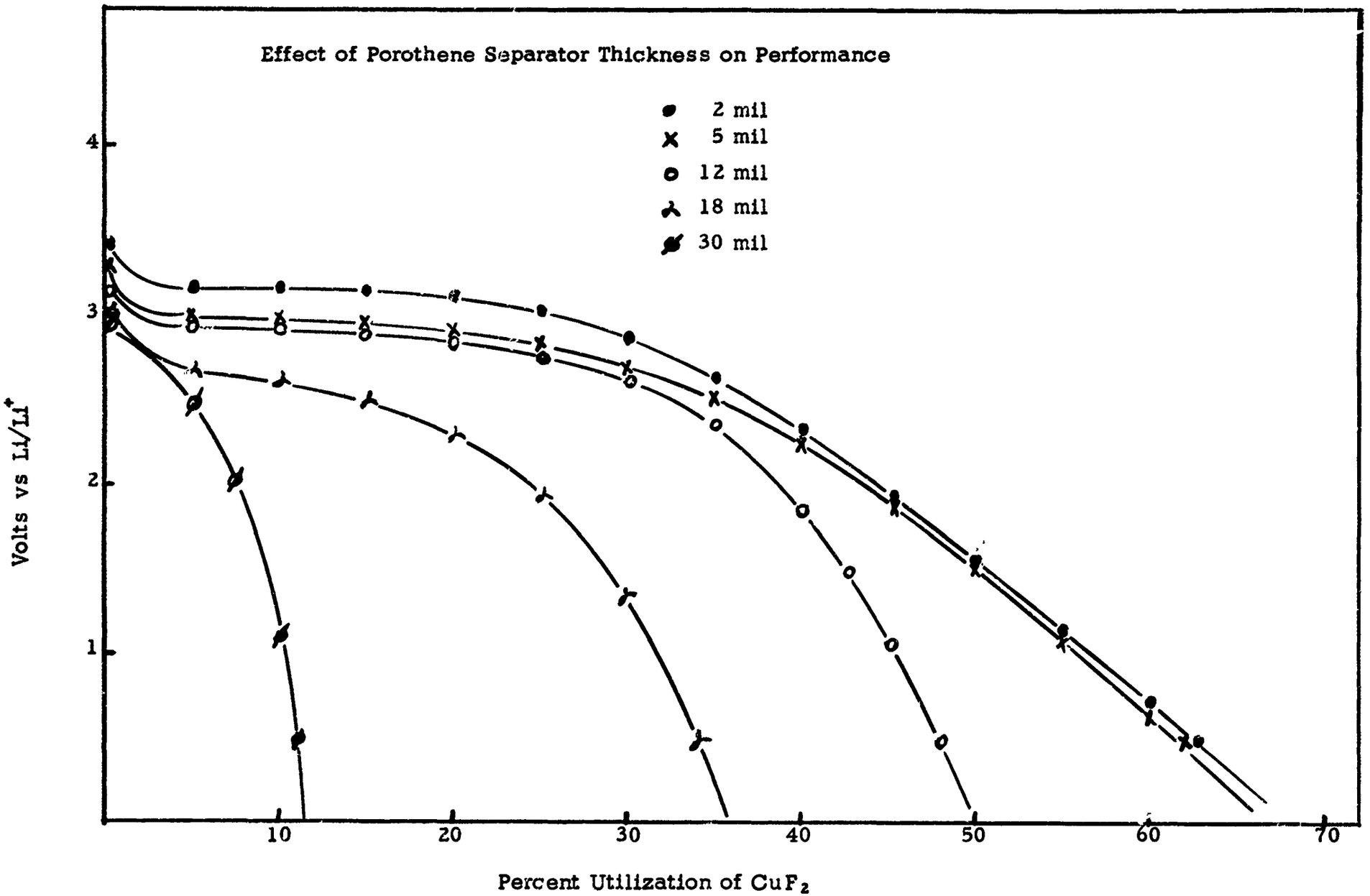
Effect of Porothene Separator Thickness on Performance
2 mil
5 mil
12 mil
18 mil
30 mil
Volts vs Li/Li+
4
3
2
1
10
20
30
40
50
60
70
Percent Utilization of CuF2

FIGURE 10

FIGURE 10

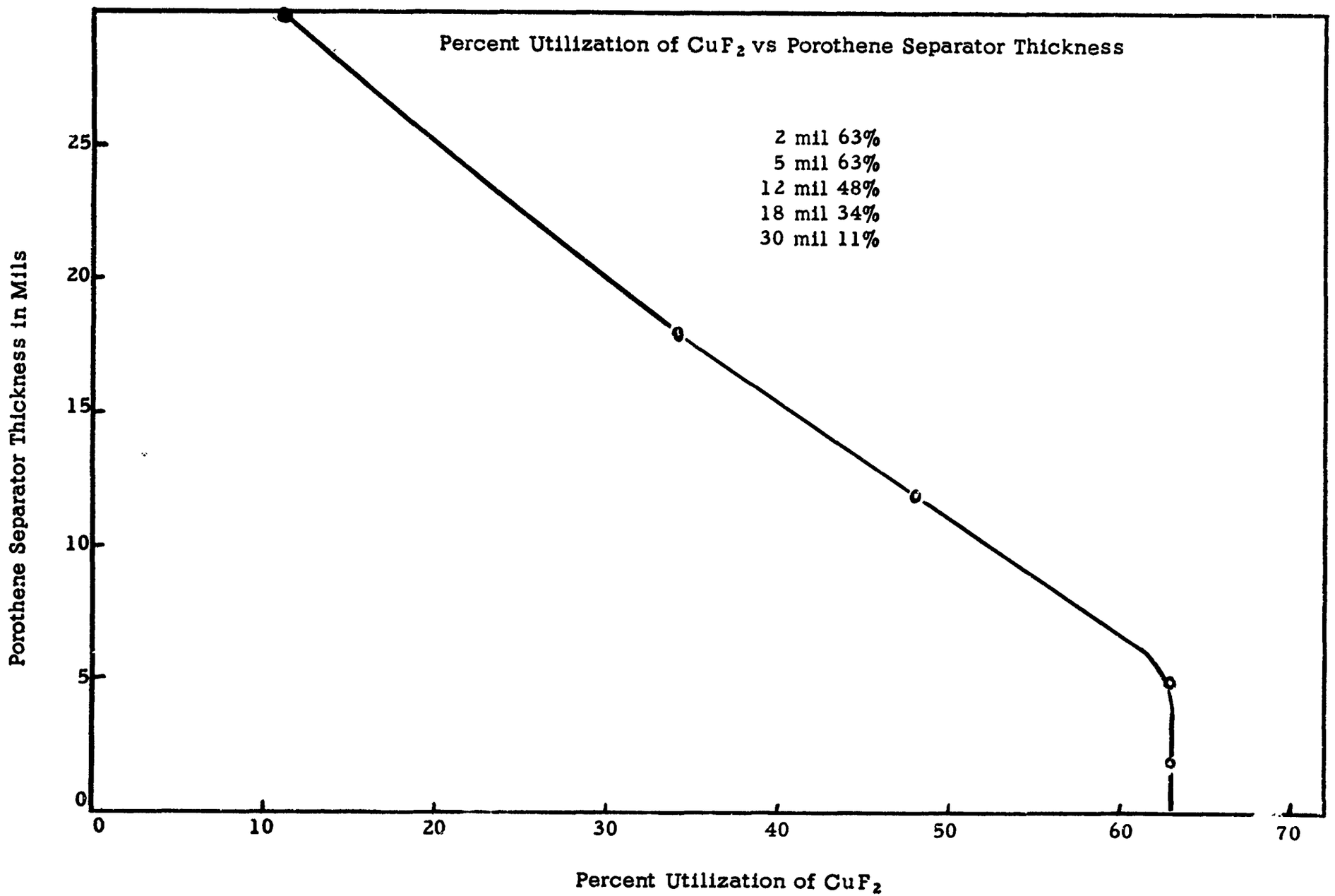

FIGURE 11

Security Classification

DOCUMENT CONTROL DATA - R&D

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

1. ORIGINATING ACTIVITY *(Corporate author)* The Electric Storage Battery Company The Carl F. Norberg Research Center Yardley, Pennsylvania	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Quarterly - 15 Sept 66 - 15 Dec 66

5. AUTHOR(S) *(Last name, first name, initial)*

Buhner, H. R.; Spera, V. J.

6. REPORT DATE February 1967	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
8a. CONTRACT OR GRANT NO. DA 28-043 AMC-02304(E) b. PROJECT NO. 1C0 14501 A 34A c. Task No. -00 d. Subtask No. -09	9a. ORIGINATOR'S REPORT NUMBER(S) 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* ECOM-02304-2	

10. AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Commanding General U.S. Army Electronics Command Fort Monmouth, N.J. ATTN: AMSEL-KL-PB

13. ABSTRACT

This report describes the work carried out during the second quarter of ~~contract No.~~ DA 28-043 AMC-02304(E), High Energy System (Organic Electrolyte). Several new electrolyte solvents were evaluated in an attempt to obtain a solution with properties superior to those of $LiClO_4$/propylene carbonate. Although high specific conductivities, greater than [illegible] $mho^{-1}cm^{-1}$, were obtained in a few instances, $LiClO_4$/lactonitrile and $LiClO_4$/1, 3, Dioxolane, these electrolytes were very corrosive toward lithium.

A new technique was used to prepare highly purified and anhydrous $LiClO_4$, by recrystallization from water and refluxing in ether. This process is based on the highly preferential solubility of anhydrous, as compared to hydrated, $LiClO_4$ in diethyl ether.

The effect of electrolyte ($LiClO_4$/propylene carbonate) concentration on CuF_2 solubility was re-evaluated, and contrary to previous findings, where solubility was found to be constant over the electrolyte concentration range studied, it was found to increase as concentration increased. This might have been caused by inadvertent use of electrolyte which was found to contain impurities.

Storage of CuF_2 cathodes in electrolyte was found to result in more than a 50% loss in discharge efficiency after only two weeks storage. There was an indication that certain impurities, especially iron, in the graphite, might have been responsible for this behavior, although reaction between electrode and electrolyte is also a possibility.

(Continued on Attached Sheet)

DD FORM 1 JAN 64 1473

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
High Energy Density Battery						
Organic Electrolyte						
Primary Battery						
Copper Flouride						

INSTRUCTIONS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

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

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

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

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

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

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

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

Security Classification

AD 473

13. ABSTRACT (CONTD)

Complexones were re-evaluated, at low concentrations, in highly purified electrolyte, to determine the effect on CuF_2 cathode performance. They were found to adversely affect the efficiency causing a 30-50% loss in performance with as little as 0.15% complexone.

Water was added, in amounts up to 2%, to anhydrous CuF_2 and found to have no appreciable effect on cathode performance.

Silver II oxide cathodes were discharged at current densities between 2 and 8 ma/cm^2 in $LiClO_4$/dimethyl sulfite and $LiClO_4$/dimethyl carbonate solutions. Energy density was found to decrease about 50% as current density increased over the range tested.

A study of the effect of CuF_2 particle size on cathode performance revealed generally increasing electrode efficiency with decrease in particle size.

Separator studies involving evaluations of microporous, ion exchange membrane, and polymer film materials revealed none that were satisfactory, with resistivities between 10^4 and 10^5 ohm-cm. Activated storage of Li/CuF_2 cells with microporous polyethylene (Porothene) separators was very poor, with short circuiting due to extensive copper dendrite penetration after only one week. (Author)