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HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

SECOND QUARTERLY REPORT

By

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

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CONTRACT DA-28-043-AMC-01394(E)

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

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SECOND QUARTERLY REPORT

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Report No. 2

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

The study of high energy density systems in the second quarter included: investigation of new electrolyte solvents; development of a technique for purifying propylene carbonate and other solvents; continued studies of corrosion and solubility of anode and cathode materials in various electrolytes; investigation of the effect of various fabrication and operating parameters on cathode performance; development of Li anode fabrication methods; and construction and testing of compact Li/CuF_2 cells.

Propylene carbonate of high purity was obtained by vacuum distillation from a basic oxide (Ca O) or an alkali metal (Li).

Various new electrolyte solvents were screened to determine their compatibility with the Li CuF_2 couple, but none were found to be comparable to propylene carbonate.

A re-evaluation of solubility of CuF_2 in various electrolytes, using purified solvents, revealed generally low solubility, except in $LiClO_4$/acetonitrile, $LiClO_4$/nitromethane, and $AlCl_3$/propylene carbonate. Corrosion rates of Li in these electrolytes were high except for $LiClO_4$/propylene carbonate and $LiClO_4$/nitromethane.

Investigation of new CuF_2 cathode binders revealed that none of those tested was superior to polyethylene.

A re-evaluation of CuF_2 particle size, with regard to its effect on cathode performance, revealed that material of -170 mesh was the best of all fractions tested.

Cupric fluoride cathode performance was found to increase with an increase in operating temperature between 0°C and 30°C and decreased with further increase in temperature to 60°C.

Attempts to develop new CuF_2 cathode fabrication techniques, by electroforming copper fluoride in a fluoride containing electrolyte, and by chemical treatment of sintered Cu O with BrF_3 were unsuccessful.

A study of various anode fabrication methods, including pressed Li ribbon and powder, and electroformed Li, revealed that the pressed ribbon method was by far the best, with regard to both performance and simplicity of fabrication.

A separator study was initiated to develop a material suitable for use in the Li/CuF_2 system, and having the characteristic of low electrical resistance, resistance to chemical attack, and the capability of acting

as a barrier to migration of copper ions to the anode. Thus far, only asbestos filter paper has been used as a separator in cell construction but it is not completely satisfactory.

Li/CuF$_2$ cells of compact construction, containing two Li anodes and one CuF$_2$ cathode, and with asbestos filter paper insulation, have been tested. An energy density of 525 watt hours per lb (based on active materials consumed only) has been obtained with a current density of 1.7 ma/cm^2. Charged stand capability is limited to about 16 hours because of migration of copper ions to the anode, with consequent short circuiting of the cells.

LIST OF TABLES

LIST OF FIGURES

Figure

LIST OF FIGURES (cont'd)

Figure

TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd)

INTRODUCTION

This report describes the work carried out in the second quarter of Contract No. DA-28-043-AMC-01394(E), the aim of which is to conduct investigations leading to the development of an organic electrolyte battery with an energy density greater than 200 watt hours/lb.

The work carried out in the first quarter indicated that good CuF_2 electrodes could be made by the hot pressing technique and that lithium electrodes could be made by pressing lithium ribbon into a conducting grid. Considerable effort was devoted to the development of a suitable electrolyte which led to the adoption of 1F $LiClO_4$ in propylene carbonate because of its inertness and fairly good conductivity.

It was decided in this quarter that we should further investigate the preparation and optimization of the CuF_2 and Li electrodes and begin the assembly of small prototype cells. Since the conductance of the $LiClO_4$/propylene carbonate electrolyte leaves something to be desired, a continuing search was made for other promising solvents. Work was also started on the investigation and characterization of various separator materials to determine their suitability for cell construction.

EXPERIMENTAL

1) ELECTROLYTE STUDIES

The work conducted in the last quarter consisted of screening a number of solvent and solute systems which led to the selection of 1F $LiClO_4$ in propylene carbonate as a promising electrolyte. A detailed investigation of the conductance function indicated that the solute was essentially completely dissociated and that the ions were unsolvated by the propylene carbonate.

Corrosion studies indicated that both CuF_2 and Li were attacked to some extent by propylene carbonate. The solvent used in these experiments was as received material from Eastman Organic Chemicals and it was thought that the observed corrosion may be a function of the impurities present in it. Since the electrolyte must be inert towards the electrode materials to give a reasonable chance of a long activated stand life, it was decided to investigate methods of obtaining very pure propylene carbonate from the as received stock.

1.1 Purification of Propylene Carbonate

The propylene carbonate used in these experiments was Eastman Organic Chemical Company practical grade. The solvent was investigated by vapour phase chromatography and by voltammetry at controlled potential. Purification was carried out by the following procedures.

1.1.1 Drying with a Desiccant

Linde Co. No. 5A molecular sieve was activated by drying at 120°C in a vacuum oven for 16 hours. About 50 g of the activated sieve was added to a 3 kg bottle of propylene carbonate which was then tightly stoppered and shaken periodically for one week.

1.1.2 Vacuum Distillation

Propylene carbonate was distilled at one millimeter pressure through a modified Vigreux column 12 in. long. The first fraction started to come over at 60°C after which the temperature rapidly increased to 70-72°C at which the main fraction was distilled off. The distillation was terminated when the temperature exceeded 72°C. The middle fraction was collected while the others were discarded.

1.1.3 Vacuum Distillation from Drying Agents

The method was essentially identical to the above except that the propylene carbonate was refluxed over a drying agent for one hour before any solvent was collected. The drying agents examined were:

i) Calcium oxide
ii) Silica
iii) Lithium ribbon

It was observed that the temperature increased from 60°C to 66°C during refluxing indicating that some impurity was reacting with the drying agent. The temperature at which fractions were collected were approximately the same as when drying agents were absent.

Volumetric flasks, filled to the brim to exclude air, were used to store the samples.

1.2 Determination of Impurities by Vapour Phase Chromatography

The samples were analyzed by means of an F and M Model 700 gas chromatograph equipped with a Model 240 temperature programmer. The concentration of vapour was determined by a thermal conductivity detector whose response was recorded on a Honeywell 1 mv recorder. The columns were stainless steel tubes 6 ft long packed with Chromosorb W (an acid washed diatomaceous earth) coated with 10% Carbowax 20 M.

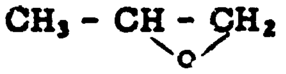
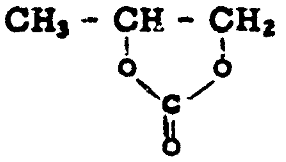
Initially it was thought advisable to inject the propylene carbonate at a temperature above its boiling point to insure complete vapourization. With the column at 50°C a 2μ ltr sample was injected at 280°C. The temperature programmer was set to raise the column temperature at 15°/minute. When the column was at 210°C the temperature was held constant for 20 minutes to ensure complete elution of the sample. The carrier gas was helium flowing at 60 ml/min at an inlet pressure of 30 psig.

Chromatograms were obtained from the following samples using sensitivities that gave a meaningful peak height.

i) Eastman propylene carbonate as received
ii) Propylene carbonate dried over Linde No. 5A molecular sieve
iii) Propylene carbonate distilled at 1 mm Hg
iv) Propylene carbonate distilled at 1 mm Hg from Ca O
v) Propylene carbonate distilled at 1 mm Hg from SiO_2
vi) Propylene carbonate distilled at 1 mm Hg from Li wire

The chromatograms are shown in Figures 1 to 6.

It can be seen that all the curves show a variety of peaks indicating the presence of several impurities. A qualitative analysis of the peaks was carried out by running blanks of compounds which might reasonably be expected to be present as impurities in propylene carbonate. Where the peak due to the known test material coincided with a peak from the propylene carbonate, it was deduced that the compounds were identical. In this way the principal peaks were identified as follows.

Peak No.	Temperature	Time	Tentative Identification	Formula
1	65-68°C		Carbon dioxide	CO_2
2	89°C		Propylene oxide	
3	103°C		Not identified	
4	139°C		Not identified	
5	159°C		Water	H_2O
6	170°C		Allyl alcohol	$CH_2{=}CH - CH_2OH$
7	210°C	3 min	Propylene glycol	$CH_3 - CHOH - CH_2OH$
8	210°C	8-10 min	Propylene carbonate	

The as received propylene carbonate is seen to contain CO_2, propylene oxide, allyl alcohol and propylene glycol as major impurities together with a small amount of water. On drying over Linde No. 5A molecular sieve, it appears that no significant improvement in the purity of the propylene carbonate is obtained. The small peak due to the presence of a trace of water is still present and the amount of propylene glycol has actually increased.

After distilling at 1 mm Hg a trace very similar to the undistilled samples was obtained although there was a slight reduction in the peak height. The samples which were distilled under vacuum from Ca O and Si O_2 show a new peak at 103°C which has not yet been identified although it may be acetone. This peak is very small in the sample distilled from lithium ribbon. The amount of propylene glycol has been considerably reduced in the propylene carbonate distilled from Ca O, Si O_2 and Li.

In general the traces are remarkably similar, no significant difference was observed with any of the purification techniques. This common property of the chromatograms led us to suspect that the source of the impurities was not in the original material but in our analytical technique. It is known that propylene carbonate when heated decomposes to give propylene oxide, propionaldehyde, allyl alcohol and carbon dioxide (1). Since all of these compounds except propionaldehyde were found it was suspected that at some stage the propylene carbonate was being decomposed. The most likely point is when the sample is introduced into the chromatograph at 280°C. If decomposition occurred here the analyses would all be expected to be similar. It was decided to test this hypothesis by repeating the experiment using an injection temperature of 110°C at which propylene carbonate should be stable. The chromatograms are shown in Figures 7 to 12.

It can be seen that in general there are fewer peaks than when the sample is injected at 280°C. The as received propylene carbonate shows peaks characteristic of carbon dioxide, propylene oxide and propylene glycol. The carbon dioxide peak is extremely small and the sensitivity had to be increased to 4x to record a meaningful wave. Standing the propylene carbonate over molecular sieve increased both the number and concentration of the impurities. A fairly large unidentified wave was found at 103°C and the amount of propylene glycol was increased. This may be due to decomposition of the propylene carbonate by the basic complex alumino silicate since this is known to occur at elevated temperatures (1). When the propylene carbonate was distilled under vacuum, only a trace of carbon dioxide and propylene oxide remained in the distillate. The amount of propylene glycol was not affected and it thus appears that this cannot be removed by distillation alone.

The samples of solvent distilled from Ca O, Si O_2 and lithium ribbon were all found to be extremely pure, only a trace of CO_2 was evident. This may have come from inclusion of a trace of air in the sampling syringe. The increase in base line current around 200°C is attributed to "bleeding" of the Carbowax 20 M which is slightly volatile at these temperatures.

It thus appears that distillation from a basic oxide or alkali metal is necessary to remove the propylene glycol by reaction to form the alcoholate of the metal. By this method extremely pure propylene carbonate can be obtained. The numerous peaks observed when a high injection temperature is used are attributed to decomposition of the propylene carbonate in the chromatograph.

1.3 Decomposition Potential Studies

Although the decomposition potential of an electrolyte has no exact theoretical significance, it can provide a useful tool for the detection of electroactive species in the solution. The method used was that of voltammetry at controlled potential. A Pyrex glass cell of conventional design was used for the measurements. This is shown in Figure 13. The cell was filled with propylene carbonate in an argon filled dry box and continuously flushed with dry argon during the measurements. A Wenking potenticstat was used to control the potential, between the reference electrode and the cathode, in conjunction with a bias box where potentials greater than 3 volts were desired. The potential was controlled manually in steps of 0.1 volts and five minutes was usually allowed for the current to become steady before the next increment was made. Voltammograms were recorded on identical samples to those subjected to vapour phase chromatography. The results are shown in Figure 14.

The untreated Eastman propylene carbonate is seen to have a large reduction wave at -2.00 volts with respect to a silver/silver chloride electrode. Vacuum distilled material does not show this wave although a reduction current starts to be observed at -3.00 volts. Referring to the chromatographic experiments the main difference between as received and distilled propylene carbonate is the elimination of propylene oxide. It thus seems probable that this is the cause of the wave at -2.00 volts. To investigate this possibility a voltammogram was obtained from vacuum distilled propylene carbonate which had been doped with 0.05% propylene oxide. A wave was observed at approximately -2.00 volts which coincides with the waves observed in the as received and molecular sieve treated material. We may thus tentatively conclude that reduction of propylene oxide is the cause of the large cathodic current. The propylene carbonate distilled from CaO shows an extremely small current up to -5.5 volts, which is considered to be its decomposition potential, and thus appears to be extremely pure.

Summarizing the investigation of purification techniques it has been found that several impurities exist in practical grade propylene carbonate which can be removed by vacuum distillation from CaO, SiO_2 or Li. The source of the large reduction wave at -2.00 volts has been traced to propylene oxide present as an impurity in the solvent.

1.4 Investigation of Other Solvents

Studies carried out in the last quarter on a variety of solvent/solute systems indicated that 1F $LiClO_4$ in propylene carbonate was a promising electrolyte from the point of view of conductance and compatibility with the electrode materials. Although the dielectric constant of propylene carbonate is high, its high viscosity limits the conductance of its solutions to moderate values. In addition there does not seem to be any solubility of lithium fluoride in its solutions, thus, when a CuF_2 electrode is discharged in $LiClO_4$ solution, LiF builds up in the cathode which probably blocks up the pores and reduces transport of the Li^+ to the reaction site. It is thought that significant improvements in the behaviour of the electrodes would result if a more suitable electrolyte were available which was inert towards the electrode materials, had high conductivity and was capable of dissolving LiF. For these reasons a further search was made for solvents which might be expected to form highly conducting solutions with inorganic salts. Solvents were chosen on the bases of their dielectric constants and viscosity which are the most influential parameters on the conductance of a solution. The solvents chosen together with some of their physicochemical properties are shown in Table 1. (2)(3)

As an initial screening test the solvents were added to a piece of freshly oleaned lithium ribbon. If the reaction was extremely fast the solvent was rejected for further consideration. Those solvents which showed only slight or no reaction towards lithium were further examined conductometrically. This rapid screening test eliminated formamide, ethanolamine and N-methyl formamide from further consideration.

1.4.1 Determination of Conductance

The solvents used were the purest commercially available and were not purified before use. It was decided to initially examine $LiClO_4$ as a solute to obtain a direct comparison with previous results (4). The $LiClO_4$ was obtained from G. Frederick Smith and Co., Columbus, Ohio and was dried at 120°C under reduced pressure for 16 hours. All solutions were prepared in a glove box filled with dry nitrogen or argon with the exception of methyl thiocyanate which had to be used in a fume hood because of its nauseating odor. It was found that ethylene dichloride was a very poor solvent and its use was discontinued. The conductance of the solutions was determined at 25°C at a frequency of 1000 cps in a cell of constant 0.926. The bridge used was an E.S.I Universal Impedance Bridge, Model 291.

Curves of the specific conductance are shown in Figure 15, and the equivalent conductances are shown in Figure 16.

The curves are quite conventional in that the specific conductance tends to pass through a maximum around 1 Formal. An interesting feature of the curve of ethylene dipropionate is that the equivalent conductance increases with concentration rather than decreases as is usually observed.

If we assume that the electrolyte is associated into triple ion according to:

$$\text{i)}\quad LiClO_4 \rightleftharpoons Li^+ + ClO_4^-$$
$$\text{ii)}\quad Li^+ + ClO_4^- \rightleftharpoons [Li^+ClO_4^-]$$

iii) $[Li^+ClO_4^-] + Li^+ \rightleftharpoons [LiClO_4Li]^+$

iv) $[Li^+ClO_4^-] + ClO_4^- \rightleftharpoons [LiClO_4ClO_4]^-$

Fuoss and Kraus (5) postulated that these triple ion should be stable since the potential energy due to the third ion is greater than the mean thermal energy of the ions in a solvent of low dielectric constant.

From the equilibrium

$$[Li^+ClO_4^-] \rightleftharpoons Li^+ + ClO_4^-$$

$$K = \frac{[Li^+][ClO_4^-]}{[LiClO_4]}\gamma_\pm^2 \qquad \gamma_\pm = \text{mean ionic activity coefficient}$$

If $\alpha = [Li^+]/C$

$\alpha_1 = [LiClO_4Li]^+/C$, then the concentration of the single, double and triple ions is given by $C\alpha$, $C(1-\alpha-3\alpha_1)$ and $C\alpha_1$ respectively.

If it is assumed that the two types triple ion are formed to the same extent

$$\frac{[LiClO_4][ClO_4^-]}{[LiClO_4ClO_4]^-} = \frac{[LiClO_4][Li^+]}{[LiClO_4Li]^+} = K_1$$

It is easy to obtain

$$\alpha = \sqrt{K/C}\,(1-\alpha-3\alpha_1)^{1/2}\,\gamma_\pm^{-1}$$

It can be seen that as the concentration increases the fraction of triple ions increases and thus the conductivity must increase.

If Λ_0 is the contribution of the simple ions to the conductance and λ_0 that due to the triple ion

$$\Lambda = \alpha\Lambda_0 + \alpha_1\lambda_0$$

and

$$\Lambda = (\sqrt{K/C}\,(1-\alpha-3\alpha_1)^{1/2}\,\gamma_\pm^{-1})\Lambda_0 + (\frac{\sqrt{KC}}{K_1}(1-\alpha-3\alpha_1)^{3/2}\,\gamma_\pm^{-1})\lambda_0$$

This is of the form

$$\Lambda = Ac^{-1/2} + Bc^{1/2}$$

The formation of a triple ion shifts the ion-ion pair equilibrium in the direction of a higher free ion concentration. The net result is an increase in conductance with concentration. When the conductance of the free ions becomes small $(Ac^{-1/2})$

the increasing term $(Bc^{1/2})$ takes over and the total concentration of ions increases. To explain the shape of the conductance curve of $LiClO_4$ in ethylene dipropionate considerable ion association must be postulated even at very low concentrations.

The conductance of acrylonitrile and propionitrile solutions was quite high and so it was decided to examine their effect on the performance of the CuF_2 electrode.

1.4.2 Effect of Acrylonitrile and Propionitrile on the Discharge of CuF_2

Cupric fluoride electrodes were prepared from a mix of 85% CuF_2 (-170 to + 325 mesh), 10% Southwestern 1651 micronized graphite and 5% polyethylene powder (-100 mesh). The dry mix was tumbled for 16 hours before the electrodes were fabricated. Approximately two grams of dry mix were hot pressed at 4000 lbs per cm^2 into a 5 Cu 14 2/0 expanded grid. Two electrodes were discharged at 1.7 ma per cm^2 in

i) 1F $LiClO_4$ in propylene carbonate
ii) 1F $LiClO_4$ in propionitrile
iii) 1F $LiClO_4$ in acrylonitrile

The results are shown in Figure 17. In order to compensate for the slightly different electrode weights, the potential has been plotted against percent CuF_2 discharged based on the reaction being $CuF_2 + 2Li^+ + 2e = Cu + 2LiF$. The capacity of the electrodes can be seen to be reduced by the acrylonitrile and propionitrile, in addition the polarization is much more severe. An interesting feature of the discharge in acrylonitrile was that as the reaction proceeded the electrolyte began to polymerize and after two hours was completely solid. In spite of this, the electrode still continued behaving normally, indicating that the polymerized $LiClO_4$/acrylonitrile had appreciable electrolytic conductance. This observation may be of significance since it may be a possible way of producing solid electrolytes for cells.

Because the performance of the CuF_2 electrode was adversely affected by discharging in acrylonitrile or propionitrile, these solvents were deleted from further consideration.

2. Corrosion and Compatibility Studies - Cathode and Anode Materials

The corrosion and solubility experiments carried out in the first quarter had simply been a rapid visual screening of the solubility of cupric fluoride in conjunction with gassing tests on lithium ribbon. In these experiments, no particular care was taken in purifying the electrolytes and thus the observations could have been markedly influenced by the impurities present in the solvents. Since the vapour phase chromatographic experiments carried out with propylene carbonate had shown a fairly high level of impurities, it was decided to repeat the corrosion-tests using purified materials.

2.1 Solubility of CuF_2 in Organic Electrolytes

The following solvents were chosen for the investigation:

i) Propylene carbonate
ii) Acetonitrile
iii) Nitromethane
iv) Dimethyl sulfoxide
v) Epichlorohydrin
vi) Furfural
vii) Acrylonitrile
viii) Propionitrile

The solvents were all distilled before use, a middle cut being taken. Those solvents with high boiling points were distilled under reduced pressure whereas the low boiling solvents were distilled at one atmosphere. The solute chosen was in all cases lithium perchlorate which had been vacuum dried for 16 hours at 120°C before use. In some cases other solutes were investigated where it seemed appropriate. The solutions were all prepared and the CuF_2 was added in a glove box filled with dry argon. The flasks were then shaken periodically for one month and then submitted to complexometric analysis for total copper. The results together with some visual observations are shown in Table 2.

The solubility of CuF_2 in the various electrolytes can all be seen to be quite low with the exception of $LiClO_4$ in acetonitrile and nitromethane and $AlCl_3$ in propylene carbonate. On the basis of these results one would expect 1M $LiClO_4$ in propylene carbonate or acetonitrile to be a suitable electrolyte.

2.2 Corrosion of Lithium in Organic Electrolytes

The rate of corrosion was determined as described previously (4) by use of the special micro gassing pipettes. The solvents were distilled to remove impurities and the solute was dried for 16 hours at 120°C under vacuum. A piece of lithium ribbon 1 in. by 1/4 in. by 1/16 in. was cut from a sheet and kept clean by immersion in heavy white oil. Immediately before use, the foil was degreased in distilled hexane and dried with facial tissue. The gassing pipettes were filled with the electrolyte, the lithium was added and the top replaced to exclude all the argon. The rate of attack on the lithium by the electrolytes was determined by measuring the amount of gas evolved and by visual inspection. The results are shown in Figure 18.

It can be seen that in general the rate of gas evolution is quite high. With acetonitrile, acrylonitrile, propionitrile and epichlorohydrin the rate can be considered too high to permit their use in practical cells. Dimethyl sulfoxide and furfural gave rates which were intermediate while nitromethane and propylene carbonate gave extremely low gassing rates with the lithium remaining bright for upwards of 10^4 minutes. It is probable that only propylene carbonate and nitromethane are sufficiently inert to be useable in practical cells.

All the curves show the presence of an induction period during which the lithium appears quite stable. If the evolved gas is hydrogen this might simply be the length of time it takes for the lithium surface to become saturated with hydrogen or to form LiH. On the other hand incubation periods are often associated with autocatalytic processes in which the products catalyze the reaction (6), thus giving rise to a steadily increasing rate of reaction.

3. Cathode Studies

3.1 Cupric Fluoride Cathodes

This quarters work was continued to improve the electrochemical and structural properties of the hot pressed cathodes.

3.1.1 Effect of Various Binders on the Performance

It had been thought that the type of binder employed in the fabrication of the electrodes exerted an important effect on their performance. The binder can be expected to influence the degree of wetting of the electrode, the mechanical strength, the pressure required to produce a strong compact and consequently the electrochemical properties. We thus decided to investigate several binders in the hot pressed electrode formulation to determine their effect on the strength and discharge characteristics of the electrodes. The binders investigated were

i) Polyvinylchloride
ii) Klucell G
iii) Polyethylene oxide
iv) Vinylidine fluoride
v) Polystyrene
vi) Polyvinylchloride - polyvinyl acetate copolymer
vii) Polyvinylchloride - polyvinyl acetate (28%), diatomaceous earth (72%) (Blend 119)
viii) Teflon
ix) Polyethylene

The binders were all obtained as powders and sieved past a 100 mesh standard sieve. Electrodes were prepared from a mix containing

i) 85% CuF_2 (-170 to + 325 mesh)
ii) 10% Southwestern 1651 graphite (dried at 120°C)
iii) 5% binder (-100 mesh)

To insure complete dispersion, the powders were tumbled in a Fisher-Kendall mixer for 16 hours. All sieving, electrode preparation, weighing and discharging was carried out in an argon filled dry box. The powders were pressed into electrodes on 5 Cu 14 2/0 Exmet copper screen at a pressure of 4,000 lbs per cm^2 for 3 minutes at 90°C. They were then given an overnight soak in 1F $LiClO_4$ in propylene carbonate and discharged against pressed Lithium counter electrodes in fresh electrolyte at a current of 50 ma (1.7 ma per cm^2). The electrode potentials were measured against a silver/silver chloride reference electrode having a potential of + 3.48 volts with respect to lithium. The results are shown in Figure 19, where the potentials have been converted to the lithium scale for easy reference. The performance in some cases simply reflects the degree of shedding of the electrodes. For example, in the case of Klucell 6, the active material fell off the grid within one hour of open circuit stand. With the other binders shedding occurred during discharge which is the usual state of affairs. An estimate was made of the amount of shedding during the stand and discharge. This is shown below.

Binder	Amount of shedding on O.C. stand	Amount of shedding on discharge
Polyvinylchloride	0	8%
Klucell 6	95%	not discharged
Polyethylene oxide	0	63%
Vinylidine fluoride	0	88%
Polystryrene	0	90%
PVC - PVAC	0	80%
Blend	0	75%
Teflon	0	0
Polyethylene	0	5%

In several instances the utilization of CuF_2 exceeds the amount of material left on the grid, which is surprising, until one considers that the material does not fall off until it is discharged. In fact, dimensional changes during discharge appear to be the principal cause of shedding. In general the performance was either equal to or worse than usually obtained with the standard polyethylene mix. The result obtained with Teflon was quite encouraging since very little shedding was observed. Because of the good performance obtained with the PVC - PVAC copolymer binder, it was decided to investigate this further.

3.1.2 Effect of Compacting Pressure on Electrodes Containing PVC - PVAC

It had been observed that the performance of hot pressed electrodes containing polyethylene was markedly affected by the compacting pressure. It was decided, therefore, to investigate whether this was also the case with electrodes containing PVC - PVAC as a binder.

A number of electrodes were prepared as above using three different compacting pressures. The electrodes were soaked overnight in 1F $LiClO_4$ in propylene carbonate and then discharged at 1.7 ma per cm^2. The results are shown in Figure 20. The electrodes pressed at 4,000 lbs per cm^2 gave the best performance as was the case with polyethylene binder. It was then decided to investigate the effect of current density on the electrode performance.

3.1.3 Effect of Current Density on Performance

Hot pressed CuF_2 electrodes were prepared from a mix containing 85% CuF_2 (-170 to +325 mesh), 10% graphite (SW 1651) and 5% PVC-PVAC copolymer. The electrodes were pressed at 4,000 lbs per cm^2 for 3 minutes at 90°C. Replicates of three were discharged at different current densities. The results are shown in Figure 21. The results are quite conventional in that a decrease in utilization and an increase in polarization accompanies an increase in current density.

3.1.4 Effect of Pore Formers on Performance

It had been thought for some time that the performance of the electrodes was controlled by the progressive accumulation of lithium fluoride in the pores. It was concluded that if the porosity of the electrodes could be increased, better performance should be obtained due to prevention of pore blocking.

Two pore formers were investigated: i) $LiClO_4$
ii) $AlCl_3$

3.1.4.1 Lithium Perchlorate as a Pore Former

Hot pressed electrodes were prepared from a mix containing 82.7% CuF_2, 8.2% graphite, 4.1% polyethylene and 5% lithium perchlorate (-200 mesh powder). The electrodes were placed in distilled propylene carbonate to leach out the $LiClO_4$ and form pores. Electrodes were soaked for periods varying from 16 hours to 168 hours and then discharged at 1.7 ma per cm^2 in 1F $LiClO_4$ in propylene carbonate. The results are shown in Figure 22. It can be seen that the performance was considerably reduced by this technique.

3.1.4.2 Aluminum Trichloride as a Pore Former

Electrodes were prepared as above but with 10% $AlCl_3$ as a pore former. The aluminum trichloride was removed by placing the electrodes in a vacuum oven at 170°C for 2 hours at 20 mm of mercury pressure which caused the $AlCl_3$ to be sublimed. The electrodes were then discharged as before. The results are shown in Figure 22. Again the performance was adversely affected by the process.

3.1.5 Effect of Water on Electrode Performance

The steps which have to be taken to ensure that the electrodes are completely anhydrous are very tedious and it would considerably simplify electrode manufacture if a little water could be tolerated. X-ray diffraction studies had indicated a rapid pick up of water from the atmosphere by cupric fluoride, and it was decided to investigate whether electrodes allowed to stand in air or discharged in electrolyte contaminated with water were able to function efficiently.

A number of cupric fluoride electrodes were prepared from a formulation containing 85% CuF_2, 10% graphite and 5% PVC - PVAC. The electrodes were all prepared in a dry argon atmosphere to exclude water and then discharged under different conditions. Two electrodes were discharged in the usual way, two in electrolyte to which 2% water had been added, two were allowed to stand in the atmosphere for 5 hours (R.H 25%) and the final two were stood in air of 100% humidity for 5 hours. They were then discharged at 1.7 ma per cm^2. The results are shown in Figure 23. In all cases the presence of water caused the capacity to fall off. This experiment stresses the need to eliminate water from the electrodes. Although the conditions of this experiment were more severe than would normally be encountered in practice, it is thought that the effect is sufficiently marked to be manifest even at low degrees of water contamination. When cupric fluoride electrodes are stood in moist air, $CuF_2 \cdot 2H_2O$ is formed which has a larger molar volume than CuF_2. This causes the active material to swell and close the pores thus reducing the diffusion of Li^+ to the reaction sites and increasing the polarization.

3.1.6 Effect of Particle Size

The cupric fluoride powder as supplied by Ozark-Mahonning Inc. consists of a small amount of fine particles together with a large amount of agglomerated "pebbles". In the past, only the fine powder had been used to make electrodes and this resulted in the accumulation of a large quantity of coarse lumpy material. It was decided to grind this in a ball mill to reduce it to a fine powder that could then be used for electrode preparation. The coarse cupric fluoride was loaded into a ceramic mill with pebbles under a dry argon atmosphere and tightly sealed with tape to prevent exposure to water vapour. The cupric fluoride was then ground for 16 hours. This was carried out in air because the size of the machinery involved precluded its use in a dry box. A fine powder was obtained which was sieved and subsequently used to make electrodes. When these electrodes were discharged, it was found that the polarization was excessively high and that the utilization was only about one third of that of an electrode made from unground powder. A typical result is shown in Figure 24 where an electrode prepared from ground CuF_2 is compared with one prepared from (powder) as received.

In another experiment cupric fluoride electrodes prepared from powder which had been mechanically sieved for one hour were compared to electrodes prepared from hand sieved cupric fluoride nominally of the same size. It was found that the electrodes fabricated from hand sieved cupric fluoride gave a typical result (72% utilization at 1.7 ma per cm^2) whereas those prepared from mechanically sieved powder gave only 37% utilization.

It thus appears as if the method of treating the cupric fluoride is very critical. Photomicrographs showed that the cupric fluoride was composed of flat semi-transparent crystals together with a large number of very small fractured bits. When the material was ground, the flat crystals were broken down into very small pieces which then agglomerated to form clusters of various sizes. On sieving this material, the various size fractions represented, not discrete particles, but agglomerates and it is conceivable that when this powder was used to make electrodes the agglomerates were broken down in the mixing operation into very small particles. Thus, the electrode performance would be independent of the apparent particle size produced by sieving. The difference in performance between hand sieved and machine sieved material probably is due to a similar effect. The violent agitation of a sieving machine is probably sufficient to fracture the particles, whereas a gentle hand sieving may not.

It was thus decided to investigate more closely the effect of the cupric fluoride pre-treatment. We thought it necessary (if only for economy) to devise methods of using the coarse pebbled CuF_2 and so this was used in the experiment. We also concluded that since hand sieving is inefficient, better reproducibility would be obtained by machine sieving and this procedure was adopted also.

Coarse, pebbled cupric fluoride was gently broken down by grinding in a morter and pestle for five minutes and then sieved on a mechanical shaker for 15 minutes to isolate the desired fraction. The following fractions were obtained

i) -325 mesh
ii) -170 mesh
iii) - 80 mesh
iv) -170 to + 325 mesh
v) - 80 to + 325 mesh

Samples of the powders were submitted to microscopic examination and photographed at a magnification of 300. The photomicrographs are shown in Figure 25. The results can be summarized as follows.

Particle Size (mesh)	Total Particle Size Range (micron)	Range of > 50% of sample (micron)	Size of Smallest Particles (micron)
-325	1 - 45	8 - 30	1 - 5
-170	1 - 100	10 - 70	1 - 5
- 80	1 - 200	20 - 120	1 - 5
-170, +325	1 - 100	30 - 80	1 - 5
- 80, +325	1 - 200	60 - 120	1 - 5

The samples consisted of polycrystalline aggregates composed of very small particles.

Electrodes were prepared by the standard hot pressing method and discharged at 1.7 ma per cm^2 in 1F $LiClO_4$ in propylene carbonate. The results are shown in Figure 26. All the results are quite good and in general the best utilization is obtained from those size fractions containing a mixture of coarse and fine particles. Extremely high utilization was obtained from the electrodes prepared from -80 mesh CuF_2 but the polarization was also quite high. Taking into account both utilization and polarization the -170 mesh CuF_2 gave the best result. These results indicate that it is possible to use the coarse lumpy CuF_2 if care is taken not to grind it too severely.

3.1.7 Effect of Temperature on Performance of CuF_2 Cathodes

Cupric fluoride cathodes were discharged at various temperatures over the range 0°C to 60°C to determine the effect of operating temperature on performance.

3.1.7.1 Experimental

Cathodes were made from a blend of 85% CuF_2 (-170 + 325 mesh), 10% graphite, and 5% Polyethylene (-100 mesh). Approximately 0.5 grams of this blend was pressed into one inch square grids of 5Cu 14 2/0 expanded copper, at 4,000 lbs per cm^2 for 3 minutes at 90°C.

The cathodes were tested in a glass cell, the construction and use of which were described in the first quarterly report. The cell was partially immersed in a thermostatically controlled water bath, in which temperature was maintained within ± 1°C of a preset temperature in the range 0°C to 60°C. The electrolyte used in cell testing was 1F $LiClO_4$ in propylene carbonate. The propylene carbonate was dried over molecular sieve but was not further purified. Cathodes were discharged at 1.7 ma per cm^2 using a constant current d.c. power supply.

The cathode potentials were measured against an Ag/AgCl reference electrode in the same electrolyte, using a high impedance electrometer. Discharge was terminated when the potential of the cathode was -3.5 volts vs the Ag/AgCl reference. The percentage of the theoretical CuF_2 capacity utilized on discharge was taken as a criterion of performance.

The results of this experiment are shown in Figure 27. On first analysis the utilization of CuF_2 appears to increase from about 30% at 0°C to 60% at 30°C, then decreases to about 55% at 40°C and finally increases again to about 70% at 60°C. However, results of recent investigations of decomposition potentials of solvents and electrolytes suggest that the capacity usually ascribed to discharge of CuF_2, as represented by the second plateau in the discharge curve, is in reality due to reduction of an impurity in the solvent. Since the electrolyte used was not purified, this impurity was present in this study. Therefore the discharge of CuF_2 is essentially complete after the first break in the voltage-time (capacity) curve.

A re-analysis of the above results, based on a correction for the capacity due to solvent impurity, would be as follows: Utilization of CuF_2 increases from about 30% at 0°C to about 60% at 30°C, and then decreases, with further increase in temperature to about 50% at 60°C. The reason for this kind of behavior is not immediately evident. However, it may be that the propylene carbonate, or the electrolyte becomes reactive with the CuF_2 at elevated temperatures and results in a loss of CuF_2 coulombic efficiency.

3.2 Electroformed CuF_2 Cathodes

As already stated in the first quarterly report, it would be desirable to produce a CuF_2 electrode with a minimum of electrochemically inactive components, in order to increase the energy density of the cathode. It was suggested that this might be accomplished by investigations of methods for electroforming CuF_2 on porous, sintered copper structures. The results of initial experiments, reported in the first quarterly report, were unsatisfactory, and further efforts were made during the second quarter. A search of the literature failed to reveal any previous investigation of methods of electroforming fluorides. An electrolyte containing arsenic trifluoride was investigated in an attempt to anodically form CuF_2 on copper.

3.2.1 Experimental

Experiments were conducted using arsenic trifluoride, alone and as an electrolyte in propylene carbonate and anhydrous ether. When used in solution, one ml of arsenic trifluoride was added to 5 ml of each of the solvents indicated.

Two half inch square sheet copper electrodes were immersed in each of the electrolytes tested, and a current of 2.5 ma (1.5 ma per cm^2) was passed through the cell. The current was interrupted after 20 minutes, and the electrodes were analyzed by x-ray diffraction to determine the products formed.

3.2.2 Results and Conclusions

The results of this test revealed that CuF_2 could not be anodically formed on copper in any of the electrolyte containing arsenic trifluoride. Arsenic was cathodically formed in all electrolytes as a black deposit. It appears that arsenic trifluoride does not ionize to produce the simple fluoride ions which are probably required in order to anodically form CuF_2 on metallic copper.

3.3 Bromine Trifluoride (BrF_3) Treatment of Sintered CuO

In another attempt to produce a CuF_2 cathode by other than the pressed powder technique, conversion of a porous, sintered CuO matrix to CuF_2 was investigated. Emeleus and Woolf (6) described a method of converting various oxides to fluorides by reaction of the oxides with BrF_3. The process was reported as being quantitative for several of the oxides investigated, and the reaction products, other than the fluorides formed, were volatile and easily separated from the desired product. A method was proposed, whereby a porous, sintered CuO electrode would be converted to CuF_2 simply by reaction with BrF_3 and with a minimum of subsequent processing.

3.3.1 Experimental

Porous, sintered CuO compacts were made, 1½ in. square by the following method: a) -325 mesh copper powder was placed in a die, pressed at 5,000 lbs and the resulting compact sintered at 600°C in hydrogen. This produced a structurally sound, porous copper plate. b) The sintered copper was oxidized at 670°C and was found to be nearly 100% converted to CuO. c) The CuO plate was treated with BrF_3 by thoroughly wetting the porous matrix with the reagent, and after 10 minutes evaporating the excess BrF_3 on a hot plate at 250°C. This procedure was repeated twice. The specimens were then submitted for x-ray analysis.

3.3.2 Results and Conclusions

Results of this experiment revealed that CuF_2 was not produced by treatment of CuO with BrF_3, even after repeated treatment of the oxide with reagent.

Because of the hazards involved in handling BrF_3, it was decided to discontinue investigations with this material.

4 Anode Studies

This study was conducted to develop a method of fabricating lithium anodes capable of 1) high coulombic efficiency with minimum polarization, 2) ease of fabrication and 3) storage after fabrication with a minimum loss of efficiency.

Three fabrication techniques were investigated, including pressed lithium ribbon, pressed lithium powder, and electroformed lithium.

4.1 Pressed Lithium Ribbon Anodes

The material used in this phase of the anode study was lithium ribbon, 0.015 in. thick by 2 in. wide. The conducting and supporting grid was expanded copper designated as 3 Cu 7 3/0. The grid size was 1½ in. by 1⅝ in., with a copper contact wire spot-welded along one edge. The lithium was cut to the approximate size of the grid which was pressed into the lithium at 1,000 lbs per cm^2 between steel plates coated with petrolatum. The excess lithium was trimmed from the grid and the electrodes were then stored in paraffin oil in a tightly sealed preserving jar. It should be noted that nearly all of the work with lithium was done in a dry-box under an argon atmosphere. Because of practical limitations the pressing operation was performed outside the dry-box, but the operation was very rapid and resulted in no detectable oxidation of lithium.

Anodes were made by the pressed ribbon technique for immediate testing and for storage for various intervals in paraffin oil.

4.1.1 Effect of Current Density on Performance

In one series of tests the anodes were prepared for discharge using the cleaning operation described in the first quarterly report. This involved degreasing in hexane, etching in absolute methanol and rinsing in distilled propylene carbonate.

In another experiment the paraffin oil was simply wiped from the electrode surfaces using absorbent tissues and the electrode placed immediately in electrolyte.

All half-cell testing was done in polypropylene jars of the type described in the first quarterly report. The anode was positioned between two sheet copper cathodes, allowing a ¼ in. spacing between the electrodes. Potentials were measured against Ag/Ag Cl reference electrodes, using a high impedance electrometer. A constant current d.c. power supply was used in all cell testing. The anodes were discharged in 1F $LiClO_4$ in distilled propylene carbonate, at current densities ranging from 1.5 to 10 ma per cm^2.

4.1.2 Results

The results of testing pressed lithium ribbon anodes etched with methanol are shown in Figure 28. Anode polarization is extremely high initially, but decreases as discharge proceeds, reaching a somewhat stable level for a considerable portion of the total discharge, and finally increasing rapidly again at termination of discharge. It appears that increasing current density from about 3 to 10 ma per cm^2 does not appreciably affect the percent utilization of lithium which ranged between 55 and 60%.

The results of testing pressed ribbon anodes from which the paraffin oil was removed, but with no additional cleaning or etching, are shown in Figure 29. In this series of curves there is no initial high polarization as obtained with methanol etched anodes. The initial, relatively small polarization remained practically constant throughout discharge and increased sharply at the end of discharge. The utilization of lithium ranged from about 75% to 85% of the theoretical capacity over the range of current densities used, with some evidence of better utilization at the higher current densities. Polarization does not appear to increase appreciably with increase in current density, at least over the current density range tested, suggesting that this type of anode may be capable of sustaining far greater current densities with high efficiency.

4.1.3 Conclusions

A highly efficient lithium anode can be fabricated by pressing lithium ribbon into a supporting and conducting grid. No special cleaning or etching operation is required before the electrodes can be discharged, and in fact, etching in methanol appears to adversely affect the performance. It appears that a passive film is formed during the etching operation, possibly a lithium methoxide film. Anodes stored in paraffin oil have remained bright and clean, even after weeks of storage, when proper care is taken to exclude air and moisture from the container.

4.1.4 Effect of Storage on Lithium Electrode

It is considered to be of prime importance that the electrodes are capable of prolonged active stand. If this can be achieved the battery should be able to be stored in the activated condition for a considerable time without much loss in capacity. This is of obvious benefit to the user in that the battery is ready for service the instant it is wanted.

Three types of storage test were constructed as follows:

i) Storage of electrodes in heavy white oil
ii) Storage of electrodes in 1F $LiClO_4$ in propylene carbonate
iii) Storage of electrodes in cells with CuF_2 counter electrodes

4.1.4.1 Storage of Electrodes in Heavy White Oil

A number of pressed foil electrodes prepared as previously described were immersed in heavy white oil contained in screw top jars. The lids were tightly sealed and taped to exclude air and moisture and then the electrodes were allowed to stand for the specified time periods. Periodically the jar was opened under dry argon and an electrode was removed for test. Excess oil was removed from the surface by wiping with a facial tissue and the electrode was then weighed to determine its active material weight. A thin film of oil was still present on the electrode at this stage but since this did not appear to affect the performance no more refined cleaning methods were examined. The electrode was then discharged at 2 ma per cm^2 (60 ma) in 1F $LiClO_4$ in propylene carbonate. So far electrodes have been subjected to two months storage. The results are shown in Figure 30.

The performance of the electrodes has held up well for up to two months storage. The variation in the results is not considered significant enough to be attributed to the effect of storage since a 5% variation in capacity of identical electrodes is not unusual.

4.1.4.2 Storage of Electrodes in 1F $LiClO_4$/Propylene Carbonate

Since it was felt likely that the main cause of self discharge of lithium electrodes in a cell would be the transfer of copper from the cathode to the anode, it was thought advisable to determine the effect of the electrolyte alone on the capacity so that in cell work this could be separated from the effect due to copper transfer.

The experiment was carried out as described previously except the electrodes were stored in 1F $LiClO_4$/Propylene carbonate which had been prepared from distilled solvent and vacuum dried salt. This experiment has only been underway for one month and thus not many results have been acquired. The results taken to date are shown in Figure 31.

It is obvious that so far the electrodes remain unaffected by storage. The difference between the curves is within experimental error.

4.1.4.3 Storage of Electrodes in Cells with 1F $LiClO_4$/Propylene Carbonate

This phase of the work has only just begun and will be fully reported in the next quarter.

4.2 Pressed Lithium Powder Anodes

4.2.1 Fabrication

Lithium powder obtained as a dispersion in hexane (100 microns by down), was used as the anode material in this study. Again, as stated in section 4.1, all work, except electrode pressing, was done in a dry argon atmosphere.

A portion of the dispersion was removed from the container, the hexane allowed to evaporato and the dry powder mixed with twice distilled propylene carbonate to form a paste. The paste was applied to a grid of 3 Cu 7 3/0 expanded copper with dimensions $1\frac{1}{2}$ in. by $1\frac{6}{8}$ in. The grid was supported on filter paper during the application of the paste. The pasted electrode was then covered with another sheet of filter paper and pressed between steel plates at 70 lbs/cm^2. The pressed electrode was then rinsed twice in hexane and stored in lithium treated hexane in a tightly sealed jar.

4.2.2 Discharge of Pressed Lithium Powder Anodes

The electrodes were discharged using the technique already described for pressed ribbon anodes. Before testing, the anodes, wet with hexane, were allowed to dry in a dry argon atmosphere before immersion in electrolyte. The electrolyte used was 1F $LiClO_4$ in distilled propylene carbonate.

Discharge characteristics of pressed lithium powder anodes are shown in Figure 32. Curve #1 shows the performance of an anode which was prepared for discharge as described in 4.2.2. There is an initial extremely high polarization of about 3.0 volts, and then a rapid decrease to about 1.5 volts after only a small interval of discharge. As discharge proceeds, polarization again increases steadily to terminal voltage after only about 30% of the lithium has been utilized.

This was considered to be very unsatisfactory performance, especially when compared with that obtained from pressed ribbon anodes. It was thought that a passive oxidation product prevented more efficient performance, and on this basis it was decided to attempt to remove this film by chemical etching in methanol. A pressed lithium powder electrode was etched in 30% (by volume) absolute methanol in distilled propylene carbonate, rinsed twice in distilled propylene carbonate and immersed immediately in electrolyte. The electrode was etched for only ten seconds to avoid excessive loss of lithium. The performance of an anode cleaned in this manner is shown in curve # 2 of Figure 32. Only a slight improvement in performance was obtained, with about 39% utilization of lithium.

4.2.3 Conclusions

It appears that the very fine lithium powder used in these experiments oxidizes very easily, even with the extreme care taken to avoid contact with air and moisture. A passive film is formed on the lithium which adversely affects the electrochemical utilization at any practical current density. Removal of a part of the passive film by chemical etching results in only small improvement in performance, and in any case appears to be an impractical technique.

4.3 Electrodeposited Lithium Electrodes

Electrodes prepared by electrodeposition of the electroactive material would be expected to have the properties usually considered most desirable for efficient operation. They will be porous, have a high surface area and would be reasonably assumed to be electroactive. It would thus be expected that higher current densities could be withdrawn than from a corresponding pressed foil electrode. We decided, therefore, to carry out a series of experiments to determine the conditions under which lithium could be deposited from non-aqueous solutions and to determine its electrochemical properties on subsequent anodic discharge.

4.3.1 Electrodeposition of Lithium

Lithium has been deposited from a variety of organic solutions of lithium salts and few problems exist providing the decomposition potential of the solvent is greater than the potential at which lithium is deposited. In spite of the ease of deposition of lithium metal, a wide variation in the type and quality of the deposits has been observed. At different times workers have reported spongy, dendritic, grainy and powdery deposits. It was thought worth-while, therefore, to investigate the types of deposits produced when lithium is deposited from various electrolytes over a wide range of current densities. The usual apparatus used in plating range tests is an electrochemical cell of special design so that the cathode is subjected to a variable current density along its length. Two common types of such cell are the Hull (7) and Gilmont (8) cells. In the Hull cell the current density varies in a non-linear manner along the cathode, whereas the Gilmont cell is so designed as to provide a linear variation of current density. In our experiments the Hull cell was used primarily because it is far easier to make than the Gilmont cell and commercial cells were not available in polypropylene. The cell used is shown in Figure 33. The volume of the cell was 267 mls which gave the relationship between current, current density and cathode length shown in Table 3.

The test consisted of placing 267 ml of the electrolyte into the cell together with a lithium foil anode and copper cathode. A fixed current was passed for a prescribed length of time and then the cathode was withdrawn and photographed. Initial screening tests indicated that a current of 0.5A flowing for about an hour gave a deposit suitable for examination. This was equivalent to a variation in current density of 0.25 to 20 ma/cm^2 along the cathode length. Some typical results are shown in Figures 34 and 35.

The panel obtained in 1F LiClO$_4$ in propylene carbonate shows an extremely uniform deposit over a wide range of current densities. A slightly more dull deposit is formed at the lower current densities while a deposit of higher reflectivity is formed as the current density is increased. When 1F LiClO$_4$ in acetonitrile was used as the electrolyte a wide variation in the quality of deposit was obtained. At the low current density end little or no lithium was deposited, a flaky plate being produced at about 2 ma/cm^2. Above 4 ma/cm^2 a fairly good, very spongy, deposit is produced. The panel obtained from dimethyl formamide electrolyte shows a poor deposit which was yellowed due to solvent decomposition. A more dilute solution of LiClO$_4$ in propylene carbonate produced a spotty deposit at low current densities finally yielding a smooth powdery deposit at around 2 ma/cm^2. The deposit obtained in LiCl in propylene carbonate was fairly smooth and dark showing striations due to convective effects.

Since the best looking deposits were obtained from 1F LiClO$_4$ in propylene carbonate, it was decided to carry out some experiments to determine the current efficiency and reproducibility of the deposits. A number of copper electrodes were plated at 5 ma/cm^2 for 5 hours. The amount of lithium was determined by dissolving the deposit in water and titrating with dilute sulphuric acid. It was found that the current efficiency varied from 93 - 98%. It is thought that the true current efficiency is actually 100% and that the difference between this and the experimental value reflects the small fragments which become detached when the electrode is transferred from the cell to the water. These results seemed encouraging so it was decided to investigate the anodic behaviour of the electrodeposited lithium.

4.3.2 Discharge of Electrodeposited Lithium Anodes

Lithium was deposited on copper cathodes in two series connected cells. One of the electrodeposited plates was discharged immediately in the same electrolyte, the other was withdrawn from the cell, the deposit dissolved in water and titrated with 0.8698 N H_2SO_4 to determine the weight of lithium. Initially the electrodes were deposited at 5 ma/cm^2 and discharged at 2 ma/cm^2. It was found that the efficiency of the electrodeposition approached 100%, whereas when the electrodes were discharged only from 46 - 53% of the theoretical capacity was obtained. A typical result is shown in Figure 36.

Why the utilization of the lithium was not greater is not understood. When the electrodes were examined at the end of discharge it was seen that a considerable amount of lithium was still left on the electrode.

The deposit obtained at 5 ma/cm^2 was fairly spongy and so it was decided to repeat the experiment with electrodes deposited at 2 ma/cm^2 at which a more dense deposit is obtained. Again the efficiency of the deposition was between 95 and 98%. When the electrodes were discharged capacities ranging from 51.5% to 67.5% of the calculated values were obtained. A typical result is shown in Figure 37. Although the utilization was slightly better than that obtained from electrodes plated at 5 ma/cm^2 the improvement was only marginal and was not thought significant enough to warrent further examination of the effect of current density. It was observed that the lithium still present on the electrode at the end of discharge was extremely loosely adherent which perhaps indicates that the deposit is becoming detached from the copper sheet as it is discharged.

Some discharges were performed on electrodes where the lithium had been deposited from a saturated solution of lithium chloride in propylene carbonate. The efficiency of the deposition was quite high ranging from 90 to 94% of the expected weight of lithium. However, when the electrodes were discharged the polarization increased very rapidly and the electrodes failed within a few minutes.

In view of the poor performance obtained with the pressed lithium powder and electrodeposited lithium electrodes, it was decided to concentrate future work on the pressed foil type which have shown very encouraging performance.

5. Separator Studies

It is thought that the separator will play an important part in the development of the Li/CuF$_2$ system for practical use. In order to achieve the highest energy density an excess of electrolyte cannot be tolerated but the separator will have to absorb sufficient electrolyte to allow efficient working of the electrodes. The wetted separator must have a low resistance to avoid excessive IR losses in the cell and lastly, should not be subject to attack by the electrolyte. It may also be necessary that the separator act as a barrier to the migration of copper ions to the lithium electrode where they will be discharged to form dendrites with subsequent short circuiting.

We decided to use four standard screening tests for the suitability of a material as a separator. These were:

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

5.1 Electrolyte Absorption and Retention Studies

Compatibility studies carried out in the last quarter had indicated that very few plastic materials were corrosion resistant towards propylene carbonate. Among those found to be inert were, polyethylene, polypropylene, glass fibre, Teflon and asbestos. It was decided to choose separators first from this class of materials and investigate their electrolyte absorption and retention.

The following materials were examined:

i) Webril EM 476
ii) Webril SM 91
iii) Cellophane PUDO 193
iv) Asbestos filter paper

The absorption was determined by immersing a weighed sample of the material in propylene carbonate for 70 hours, holding vertically for 30 seconds to drain off excess propylene carbonate, and finally reweighing. The absorption was defined as:

$$A = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100\%$$

The retention was determined by placing the soaked separator on a glass plate inclined at 45° and allowing it to drain for 30 minutes. The separator was then weighed. The retention was defined as:

$$R = \frac{\text{Drained wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100\%$$

The results are shown in Table 4 and are averages of three replicates.

The greatest degree of electrolyte absorption and retention was achieved with the asbestos filter paper. This has subsequently been investigated in cells. This work is continuing and will be reported further in the next report.

5.2 Determination of Separator Resistance

A cell is presently being constructed to evaluate the electrical resistance and capacitance of separators. This is a cylindrical plastic vessel of polypropylene and is shown in Figure 38. The separator is clamped between the two halves exposing a separator area of 1 cm^2 to the electrolyte. The cell has two pairs of electrodes. The two working electrodes are discs of platinized platinum mesh which are welded to platinum wire leads. Two platinized platinum wires, one in each cell section serve as voltage electrodes. They are located so that the center of the wire is 0.050 in. from the separator.

A Wayne-Kerr No. B-222 A.C impedance bridge with low impedance adaptor is used to measure the real and reactive components of the separator resistance by the use of a four terminal method. The adaptor is required to extend the range of the bridge to the very low values of electrical resistance which are a necessary characteristic of a useful separator.

The resistance of the separator is found by the formula

$$R_s = R_t - R_o$$

Where

R_s = separator resistance
R_t = total resistance
R_o = cell resistance

The capacitance is calculated from

$$\frac{1}{C_s} = \frac{1}{C_t} - \frac{1}{C_o}$$

Where the subscripts have the meaning given above, the specific resistivity of the separator is obtained from

$$\rho = \frac{R_s \times a}{b} \quad \text{ohm-cm}$$

Where

a = exposed area cm^2
b = thickness cm

At the present time the cell is still under construction and will be tested and used in the next quarter.

6. Lithium - Cupric Fluoride Cells

After a satisfactory level of performance was obtained with lithium and cupric fluoride electrodes, as determined from half cell studies, it wa decided to build and test small Li - CuF_2 cells of compact design. This was done to study the compatibility of the cell components, and to determine if individual electrodes perform as well as they do in half cells, in a configuration requiring closely spaced elements and a minimum electrolyte volume.

6.1 Cell Fabrication - General

The electrode size remained as already described, $1\frac{1}{2}$ in. by $1\frac{5}{8}$ in., for anodes and cathodes. The cells were made with two anodes and one cathode, with the total theoretical capacity of the anodes more than twice that of the cathodes. This construction causes the cell performance to be limited by the cathodes, and was intended as a method of evaluating the performance of the CuF_2 cathode, the less efficient of the two electrodes. By design then, the compact cell was used to further evaluate cathodes, as well as to determine the compatibility of the various cell components.

The separator material used in the original work was 15 mil asbestos filter paper. At first, only one thickness of separator was used, but was increased to two thicknesses when test results indicated the need for thicker insulation. A rectangular piece of asbestos paper, $1\frac{3}{4}$ in. by $4\frac{1}{2}$ in., was folded in half along its length, and a cathode was positioned in the fold. This assembly was then sandwiched between the anodes, and the element was inserted into a polypropylene jar with inside dimensions $1\frac{3}{4}$ in. by $2\frac{1}{2}$ in. by 0.40 in. Polypropylene and polyethylene spacers were used to produce a compact cell, with a minimum of spacing between adjacent elements.

A small hole, drilled in the jar wall, connected the cell and reference electrode compartments, and functioned as a Luggin capillary. The capillary opening in the cell compartment was within $\frac{1}{16}$ in. of the electrode edges. A Ag/Ag Cl reference electrode was used to measure anode and cathode potentials.

All of the anodes used in cell testing were of the pressed ribbon type described in section 4.1 of this report. The anode grid weight was about 0.54 grams and the lithium metal weight averaged 0.27 grams/electrode, with a theoretical capacity of 1.0 A.H.

6.1.1 Fabrication and Testing of Cells No. 1 and 2

The cathodes used in cells No. 1 and 2 were of the hot-pressed type, made by the technique described in the first quarterly report and were pressed at 4,000 lbs per cm^2. A cathode blend of 85% CuF_2 (-170 + 325 mesh), 10% graphite and 5% PVC - PVAC copolymer was used. A grid of 5 Cu 14 2/0 expanded copper, weighing about 0.92 grams was used in cathode fabrication. The total weight of blend per electrode averaged 1.80 grams, containing 1.53 grams of CuF_2 with a theoretical capacity of 0.80 A.H.

The cells were assembled as described in section 6.1, using one thickness of separator, and filled with about 10 ml of 1F $LiClO_4$ in distilled propylene carbonate. They were then discharged at 50 ma (1.7 ma/cm^2) using a constant current d.c. power supply.

6.1.1.2 Results

The test results for cells No. 1 and 2 are shown in Figure 39. Only about 14 to 16% of the CuF_2 was utilized in this test, the performance being limited by the cathodes. The anode potential remained nearly constant at about 0.5 volts vs Li/Li$^+$ throughout the discharge.

It was found that the CuF_2 blend used at this time was performing at far below the expected level, in half cell testing. After a thorough investigation, it was found that the average particle size of the CuF_2 powder was a critical factor. This was brought under control and a new cupric fluoride blend was used to fabricate cathodes for additional cell testing.

6.1.2 Fabrication and Testing of Cells No. 3 and 4

A cupric fluoride blend was used containing CuF_2 powder with an average particle size smaller than that used in the first cells. The new blend was made with 85% CuF_2 (−170 + 325 mesh), 10% graphite, and 5% Polyethylene (−100 mesh). The use of polyethylene as a binder was a variation in composition but this had been found to produce very little difference in cathode performance as compared to the use of PVC - PVAC binder. The cathodes were pressed at 4,000 lbs per cm^2 for 3 minutes at 90°C. The cells were assembled with one thickness of separator as described for cells No. 1 and 2. Approximately 10 mls of 1F $LiClO_4$ in distilled propylene carbonate were used in each cell. The cells were discharged at 50 ma (1.5/cm^2).

6.1.2.1 Results

The performance characteristics of cells No. 3 and 4 are shown in Figure 40. The utilization of CuF_2 ranged from about 34 to 63%. Again the cathodes were the performance limiting electrode with considerable variation in efficiency. Anode performance was excellent with only about 50 mv polarization throughout the discharge.

Although cells No. 3 and 4 performed with 2 to 4 times the efficiency of cells No. 1 and 2, there was too great a variation in cathode efficiency, and further efforts were required to determine the cause of this behaviour. It should be mentioned that cathodes with identical construction revealed the same variability when tested in half cells, and with performance almost identical to that obtained from cathodes in cells No. 3 and 4.

It was decided to re-evaluate the effect of compacting pressure on performance of CuF_2 cathodes.

6.1.3 Evaluation of the Effect of Cathode Compacting Pressure on Performance

All of the electrode testing, until the last half of the second quarter on this contract, was done in half cells. This technique required that the electrodes be structurally sound, with a minimum of shedding of active material during discharge, in order to properly evaluate performance. Therefore, it was necessary to compact cathodes at pressures of about 4,000 lbs per cm^2 before active material erosion was controlled. However, the real effect of compacting pressures could not be determined over a wide range of pressures, and especially at very low pressures, where erosion was extreme. It was decided to re-evaluate the effect of compacting pressures on cathode performance by testing the electrodes in a cell designed to reduce active material erosion to a minimum. The cell construction described in section 6.1 was considered satisfactory for the work.

6.1.3.1 Cell Construction and Testing

Cathodes were made with CuF_2 powder of -170 mesh, in a blend containing 85% CuF_2, 10% graphite and 5% Polyethylene powder (-100 mesh). All cathodes were pressed at 90°C for 3 minutes with compacting pressures as follows:

Cells 11 and 12 - 4,000 lbs per cm^2
Cells 19 and 20 - 2,000 lbs per cm^2
Cells 17 and 18 - 500 lbs per cm^2

A variation in cell construction as compared to cells No. 1-4 was that two thicknesses of 15 mil asbestos filter paper were used as insulation.

The cells were filled with about 10 ml of 1F $LiClO_4$ in distilled propylene carbonate and discharged at 50 ma (1.7 ma/cm^2)

6.1.3.2 Results

The effect of compacting pressure on cathode performance is shown in Figure 41. Percent utilization of CuF_2 increased from about 40% (average) at 4,000 lbs per cm^2 to about 80% at 500 lbs per cm^2, an increase in performance of 100%.

In addition, a reduction in cathode compacting pressure appeared to effect an improvement in reproducibility of cathode performance.

In Figure 42, cell voltage vs percent CuF_2 utilized is shown. From this set of curves the energy density (watt hours/lb) was calculated. In these calculations the energy density was based 1) on the weight of active materials consumed in the reaction only, and 2) on the total material on the three electrodes, except grid weights. The weight of separation, electrolyte and jar are also excluded. The results were as follows and are averages of performance of paired cells:

	Energy Density (watt hours/lb)	
	Active Mat'ls Consumed	Total Electrode Mat'l
Cells No. 11 and 12	526	157
Cells No. 17 and 18	605	370

From a practical viewpoint the results shown in the last column are of most interest, and show that an increase of more than 100% in energy density was obtained by reduction in cathode compacting pressure from 4,000 to 500 lbs per cm^2.

This study has revealed that, contrary to earlier findings, low compacting pressures yield cathodes with far better performance than those formed at high pressures. The important factor in this investigation was the method of cathode testing, in which a compact cell design was used to avoid the erosion of cathode material, which precluded proper evaluation in half cell testing.

The fact that performance improves as the compacting pressure is reduced, suggests that electrolyte diffusion, and consequently concentration polarization, are important factors in cathode performance. In tightly compacted structures the pore size is probably much smaller than that obtained in a loosely compacted electrode. Therefore, better electrolyte diffusion and thereby less concentration polarization is to be expected in a loosely as compared to a tightly compacted cathode.

6.1.4 Evaluation of Sulfur Additive in CuF_2 Cathodes

An investigation by Amlie and Ruetschi (9) revealed that both the operating potential and coulombic efficiency of cuprous chloride cathodes were appreciably improved by the addition of small amounts of sulfur to the cuprous chloride. In an attempt to further improve the operating characteristic of the CuF_2 cathode, it was decided to investigate the effect of the addition of sulfur.

6.1.4.1 Experimental

A blend containing 87% CuF_2 (-170 +325 mesh), 8.7% graphite, and 4.3% Polyethylene (-100 mesh), was used as a basic cathode material in this study. Precipitated sulfur powder was added to this blend to yield a mixture containing 85.3% CuF_2, 8.5% graphite, 4.2% Polyethylene and 2% sulfur. Electrodes were pressed at 4,000 lbs per cm^2 at 90°C for 3 minutes. Control electrodes were made with the first mentioned blend (no sulfur) and were fabricated in the same manner as the sulfur bearing cathodes.

Cells were built using the construction technique described in section 6.1 with one thickness of 15 mil asbestos as insulation. The cells were filled with 10 ml of 1F $LiClO_4$ in distilled propylene carbonate and discharged at 1.7 ma/cm^2.

6.1.4.2 Results

The characteristics of sulfur bearing and sulfur-free CuF_2 cathodes are compared in Figure 43. There appears to be better reproducibility of performance with cathodes containing sulfur than with sulfur-free cathodes. However, if the best sulfur-free cathode is compared with both sulfur bearing cathodes, there does not appear to be a sufficient difference in either operating potential or CuF_2 efficiency to justify a conclusion as to the overall effect of sulfur.

Another characteristic immediately seen is the step-wise increase in polarization with sulfur bearing cathodes, as compared to the steadily increasing polarization obtained with sulfur-free cathodes. It appears that the sulfur, and its decomposition products in this system, are being reduced at different potentials depending on their respective decomposition potentials. There is evidence of reactivity of the sulfur in this system, as revealed by the strong odor, somewhat like that of mercaptans, given off by the electrolyte after test.

6.1.5 Effect of Sulfur Addition to Lightly Compacted Electrodes

An experiment was conducted to further evaluate the effect of sulfur additive on the performance of CuF_2 cathodes. In this test the cathode was pressed at 500 lbs per cm^2 rather than at 4,000 lbs per cm^2 as in the previous test. In cathodes with no sulfur addition, the best performance thus far has been obtained by compacting at 500 lbs per cm^2. Also, reproducibility of performance appeared to be better at low pressures. Therefore, a more reliable evaluation of the effect of sulfur was expected in a cathode pressed at 500 lbs per cm^2 rather than 4,000 lbs per cm^2.

6.1.5.1 Experimental

The cathode blend, containing 2% sulfur was the same as that described in section 6.1.4.1. The cathode was fabricated by pressing at 500 lbs per cm^2 for 3 minutes at 90°C.

Cell fabrication was as described in 6.1.4.1 except that two thicknesses of 15 mil asbestos separator were used.

The cell was filled with 10 ml of 1F $LiClO_4$ in distilled propylene carbonate and discharged at 1.5 ma per cm^2.

6.1.5.2 Results

The results of this test are shown in Figure 44 wherein the performance of a CuF_2-S cathode is compared with that obtained from control cathodes.

The percent utilization of CuF_2 appears to be about the same for both types of cathode. The open circuit potential was about 0.2 volts higher with CuF_2 sulfur cathodes. The discharge potential, for about 10% of the discharge, was also higher with CuF_2-S cathodes. As already shown in the previous experiment with sulfur in CuF_2, the potential of the CuF_2-S cathodes decreased in a step-wise manner near the end of discharge, as compared with a steadily decreasing potential of control cathodes.

6.1.5.3 Conclusions

The addition of a small amount of sulfur to the CuF_2 cathode appears to increase open circuit potential by about 0.2 volts as compared to CuF_2 alone. This improvement in cathode potential persists, but for only a small interval, on discharge. There appears to be no significant effect on percent utilization of CuF_2 due to the addition of sulfur.

6.1.6 Evaluation of CoF_3 as a Cathode Material

Cobalt trifluoride (CoF_3) was investigated as a cathode material in the first quarter, but as indicated in the first quarterly report, the performance was unsatisfactory. Only about 20% utilization of the CoF_3 in an electrode was obtained and operating voltages were much lower than those obtained with CuF_2. However, it was thought that cathode fabrication technique or electrolyte solvent impurity may have influenced these results. It was indicated therefore, that further work would be done with CoF_3.

6.1.6.1 Experimental

A CoF_3 cathode was made using a blend composed of 86.9% CoF_3 (−170 +325 mesh), 8.7% graphite, and 4.4% Teflon powder (7x). In this fabrication the cathode was pressed at 500 lbs per cm^2 and at room temperature, rather than 90°C as with CuF_2 cathodes. Heat was avoided when it was found, in previous tests, that at elevated temperature the CoF_3 reacted with the release paper used in the pressing operation. Teflon was used in the cathode blend since it has the characteristic of functioning as a binder simply by application of pressure, and does not require heat as do the thermoplastic material used in the CuF_2 cathodes.

A cell was built using the construction described in section 6.1 and with two thicknesses of 15 mil asbestos separator. The cell was filled with 10 ml of 1F $LiClO_4$ in distilled propylene carbonate and discharged at 50 ma (1.7 ma per cm^2).

6.1.6.2 Results

The performance of a cell with a CoF_3 cathode is shown in Figure 45. Cell performance was limited by the cathode which yielded only about 35% of its theoretical capacity. The voltage characteristics of the cathode also were very unsatisfactory with a high polarization from open circuit potential almost immediately after the start of discharge.

6.1.6.3 Conclusions

Cobalt trifluoride has not been found to be a satisfactory cathode material in the investigations thus far conducted, showing a low coulombic efficiency and high polarization under load.

6.2 Effect of Activated Storage on Cell Performance

A number of cells comprising two lithium electrodes and one cupric fluoride electrode were assembled using asbestos filter paper separator. The cells were primed with 1F $LiClO_4$ in propylene carbonate, entrapped argon removed by suction and stored in argon filled desiccators for various periods of time. The lithium electrodes were prepared by the pressed foil technique and the cupric fluoride electrode was prepared by hot pressing at 4,000 lbs per cm^2 for 3 minutes at 90°C, a mixture of 85% CuF_2, 10% graphite and 5% polyethylene.

The first test involved standing two cells overnight (16 hrs) that contained one thickness of asbestos paper as the separator. They were then inspected and discharged at 50 ma (1.7 ma/cm^2). During the night the average cell E.M.F. had dropped from 3.50 volts to 2.90 volts. On inspection, it was seen that the surface of the CuF_2 electrodes had been reduced to copper and that numerous dendrites of copper had penetrated the separator. The lithium electrode had a slight coppery sheen indicating that dissolved CuF_2 from the positive electrode had been galvanically reduced by the lithium. The performance of the cells on discharge was poor, the cupric fluoride electrode failing after only 31.6% of its nominal capacity. It was decided to increase the amount of separator from one to two thicknesses in the hope of delaying the dendrite formation. A group of cells was assembled as before and stood for various periods of time. They were then discharged at 50 ma, the individual electrode potentials being measured with respect to a Ag/Ag Cl reference electrode. The results are shown in Table 5.

Both electrodes appear to have suffered from the activated stand. The lithium electrodes show an initial increase in polarization and after a time start to recover. This is presumably due to removal of a thin film of copper which has formed on the electrode during stand. The cupric fluoride electrodes show a progressive decline in performance until complete failure has occurred after seven days activated stand.

The cells were opened for inspection before and after discharge. After one day of storage the CuF$_2$ electrodes had small spots of copper present on the surface and there were a few copper dendrites growing through the separator. The appearance of cells after two days storage was very similar to the above. A considerable amount of self discharge had taken place in the cells which had been stored for one week. The CuF$_2$ electrodes were completely covered with copper on the surface and numerous dendrites could be seen penetrating the separator. The lithium electrodes were covered with black patchy deposits which may have been finely divided copper. From evidence of these results it thus seems that a simple porous barrier will not suffice to allow an activated stand of any appreciable time. Cellulosic separators, such as cellophane or Viscon, which react with copper may be required. It may be possible to add a complexing agent or precipitating agent to the separator to prevent copper being transferred to the lithium electrode.

LIST OF MATERIALS AND SUPPLIERS

CuF_2, anhydrous		Ozark-Mahoning Co.
CoF_3, anhydrous		" " "
$LiClO_4$, anhydrous		G. Frederick Smith Co.
Propylene Carbonate		Eastman Organic Chemicals Jefferson Chemical Co.
Formamide, 99%		Matheson, Coleman & Bell
$AlCl_3$, anhydrous	Fisher certified -	Fisher Scientific Co.
LiCl	" "	" " "
Ethanolamine	" "	" " "
N-Methyl Formamide	Highest Purity	" " "
Methyl Thiocyanate	" "	" " "
Ethylene Dichloride	Fisher certified	" " "
Ethylene Dipropionate	" "	" " "
Acrylonitrile	" "	" " "
Propionitrile	Highest Purity	" " "
Acetonitrile	Fisher certified	" " "
Nitromethane	" "	" " "
Dimethyl Sulfoxide	" "	" " "
Epichlorohydrin	" "	" " "
Furfural	" "	" " "
Molecular Sieve, Linde #5A		" " "
Calcium Oxide	Fisher certified	" " "
Silica, Floated Powder		" " "
Ether, anhydrous	Fisher certified	" " "
N-Hexane	" "	" " "
Methanol	" "	" " "

LIST OF MATERIALS AND SUPPLIERS (cont'd)

Paraffin Oil	Fisher Scientific Co.
Petrolatum	" " "
Sulfur, Precipitated, U.S.P.	J. T. Baker Chemical Co.
Lithium Ribbon	Foote Mineral Co.
Lithium Dispersion	" " "
Graphite, Micronized	Southwestern #1651
Teflon Powder #7x	Du Pont Co.
Arsenic Trifluoride	K & K Laboratories
Bromine Trifluoride	Matheson Co.
Webril EM476	Kendall Mills Co.
Webril SM91	" " "
Cellophane PUDO 193	Du Pont Co.
Asbestos Filter Paper	Raybestos - Manhattan
Polyethylene Powder	U.S.I. Chemicals
Polyvinyl Chloride Powder	Naugatuck
Klucel 6 Powder	Hercules Powder Co.
Polyethylene Oxide Powder	Union Carbide Chemical Co.
Vinylidene Fluoride Powder	Pennsalt Co.
Polystyrene Powder	Koppers Co.
PVC - PVAC Copolymer Powder Type VYHH	Union Carbide Chemical Co.

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TABLE I

Non Aqueous Solvents

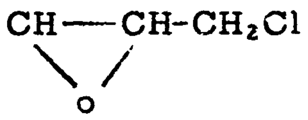
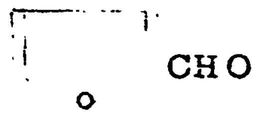
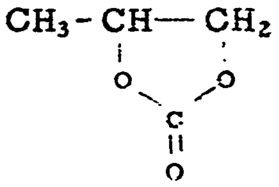
Solvent	Formula	Dielectric Constant	Viscosity (centipoise)	Density (g/cc)
Formamide	$H-CO-NH_2$	111.5	3.76	1.1334
Ethylene dichloride	$ClCH_2 \cdot CH_2Cl$	10.23	0.78	1.28034
Ethanolamine	$H_2N \cdot CH_2 \cdot CH_2OH$	37.72	19.346	1.022
N-methyl formamide	$H \cdot CO \cdot NH \cdot CH_3$	182.4	1.65	1.011
Epichlorohydrin	 $\underbrace{CH - CH}_{O}-CH_2Cl$	22.9	1.031	1.1801
Propionitrile	CH_3-CH_2-CN	27.7	0.413	0.7770
Furfural		41.9	1.49	1.1594
Glycolic Nitrile	$HO-CH_2-CN$	69	--	--
Methyl thiocyanate	$CH_3\,CNS$	35.9	--	1.0765
Acrylonitrile	$CH_2 = CHCN$	38	--	0.8060
Propylene carbonate	 $CH_3-CH-CH_2$	64.4	2.20	1.0610

TABLE 2

Solubility of Cupric Fluoride in Organic Electrolytes

Solution	Total Cu^{++} (gm/l)	Equivalent CuF_2 (gm/l)	Visual Observations
Propylene carbonate	0.00012	0.000192	Solution colorless
Prop. carbonate/$LiClO_4$	0.003	0.0048	Very pale green
Prop. carbonate/1F $AlCl_3$	0.005	0.0080	Dark brown
Nitromethane	0.00046	0.000735	Pale green
Nitromethane 1F $LiClO_4$	0.0096	0.01535	Emerald green
Acetonitrile	0.00017	0.000272	Colorless
Acetonitrile/1F $LiClO_4$	0.0021	0.00336	Very pale green
Acetonitrile/1F KCNS	0.0102	0.0163	Red solution
Acetonitrile/1F $AlCl_3$	0.0100	0.0160	Pale green
Dimethyl sulfoxide	none found	--	Colorless
DMSO/1F $LiClO_4$	0.0062	0.00991	Very pale green
Furfural	0.0006	0.00096	Pale brown
Furfural/1F $LiClO_4$	--	--	Solution polymerized
Epichlorohydrin	0.00014	0.000224	Very pale green
Epichlorohydrin/2F $LiClO_4$	0.0092	0.0147	Dark brown
Epichlorohydrin/1F $Mg(ClO_4)_2$	--	--	Solution exploded
Acrylonitrile/1M $LiClO_4$	--	--	Solution polymerized
Propionitrile/1F $LiClO_4$	0.135	0.216	Solution deep blue

TABLE 3

Hull Cell Current Density Scale

Panel Length (inches)	Current Density at Specified Total Current						
	0.25A	0.50A	1.00A	2.00A	3.00A	4.00A	5.00A
0.18	0.125	0.25	0.5	1.0	1.5	2.0	2.5
0.42	0.250	0.50	1.00	2.00	3.00	4.00	5.00
0.60	0.50	1.00	2.00	4.00	6.00	8.00	10.00
0.78	0.75	1.5	3.00	6.00	9.00	12.00	15.00
0.90	1.00	2.00	4.00	8.00	12.00	16.00	20.00
1.20	1.50	3.00	6.00	12.00	18.00	24.00	30.00
1.38	2.00	4.00	8.00	16.00	24.00	32.00	40.00
1.60	2.50	5.00	10.00	20.00	30.00	40.00	50.00
1.85	3.00	6.00	12.00	24.00	36.00	48.00	60.00
2.15	3.75	7.50	15.00	30.00	45.00	60.00	75.00
2.50	5.00	10.00	20.00	40.00	60.00	80.00	100.00
2.80	6.25	12.50	25.00	50.00	75.00	100.00	125.00
3.1	7.50	15.00	30.00	60.00	90.00	120.00	150.00
3.5	10.00	20.00	40.00	80.00	120.00	160.00	200.00

TABLE 4

Absorption and Retention of Propylene Carbonate by Separators

Separator	Absorption %	Retention %	R/A %
Webril EM 476	205	133.7	65.2
Webril SM 91	150	116	77.6
Asbestos filter paper	988	908	91.9
Cellophane PUDO 193	131	29	22.0

TABLE 5

Effect of Storage on Performance of Lithium/Cupric Fluoride Cells

Time	Results after Specified Storage Period (Days)								
	1 day			2 days			7 days		
	Cell Volts	Li elec.	CuF_2 elec.	Cell Volts	Li elec.	CuF_2 elec.	Cell Volts	Li elec.	CuF_2 elec.
O.C.V									
Initial	3.50			3.50			3.50		
Final	3.375	-3.45	+0.03	3.40	-3.50	-0.04	2.87	-3.50	-0.63
5 min	3.120	-3.25	-0.14	2.53	-2.96	-0.44	1.32	-3.15	-1.90
30 min	3.00	-3.16	-0.14	2.02	-2.78	-0.77	--	-3.10	-3.25
1 hour	2.97	-3.12	-0.13	1.85	-2.625	-0.815			
1 ½ hrs	2.90	-3.00	-0.10	1.70	-2.52	-0.800			
2 hrs	2.86	-2.98	-0.105	1.70	-2.55	-0.825			
2 ½ hrs	2.82	-2.92	-0.130	1.62	-2.47	-0.870			
3 ½ hrs				1.78	-2.80	-1.01			
4	2.78	-3.00	-0.215	1.70	-2.67	-0.98			
4 ½ hrs	2.675	-2.95	-0.260	1.85	-2.90	-1.05			
5 hrs	2.66	-2.96	-0.290	1.80	-2.90	-1.10			
6 hrs	2.525	-2.81	-0.250	1.71	-2.90	-1.18			
6 ½ hrs	2.430	-2.72	-0.305						
7 hrs	2.275	-2.70	-0.430	1.65	-2.90	-1.25			
7 ½ hrs	2.02	-2.73	-0.690						
8 hrs	0.95	-2.80	-1.800	1.50	-2.90	-1.40			
8 ¼ hrs	0.00	-2.80	-2.80						
9 hrs				1.11	-2.95	-1.84			
9 ½ hrs				0.0	-2.93	-2.95			
Utilization of CuF_2			54%			55.3%			1.5%

Vapor Phase Chromatogram of
~~As Received Propylene Carbonate~~

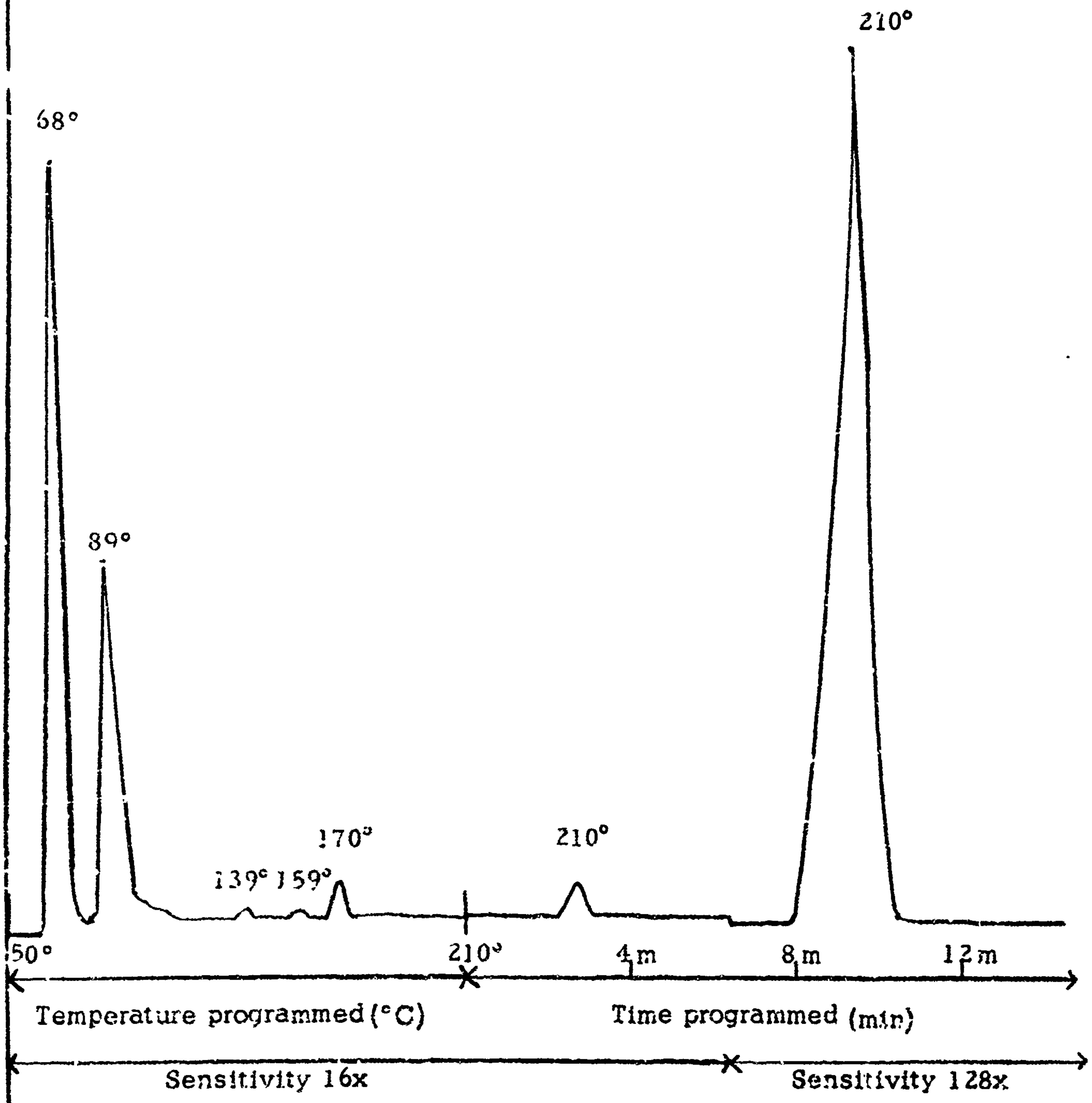


FIGURE 1

Vapor Phase Chromatogram of
Propylene Carbonate Dried with Molecular Sieve

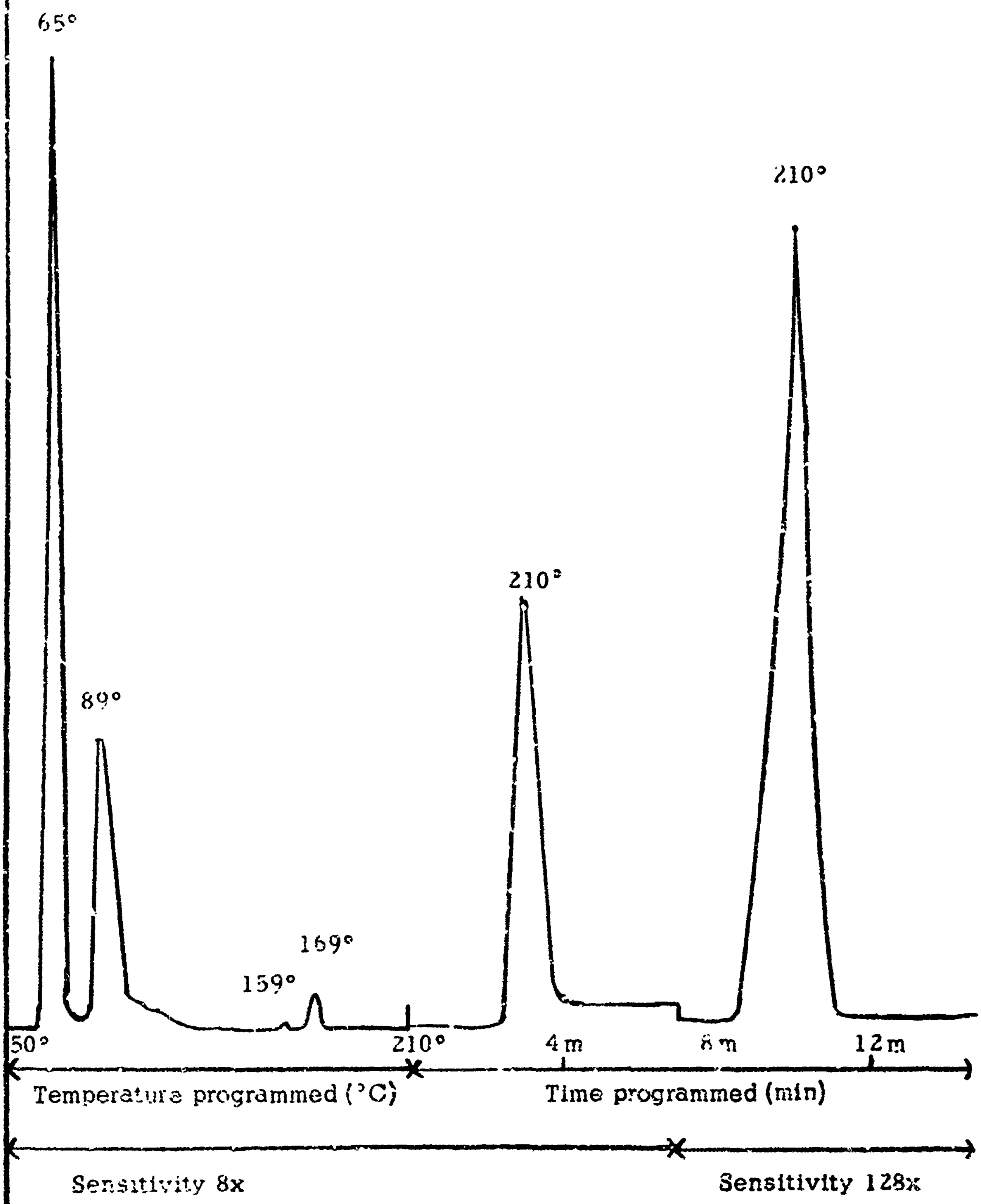
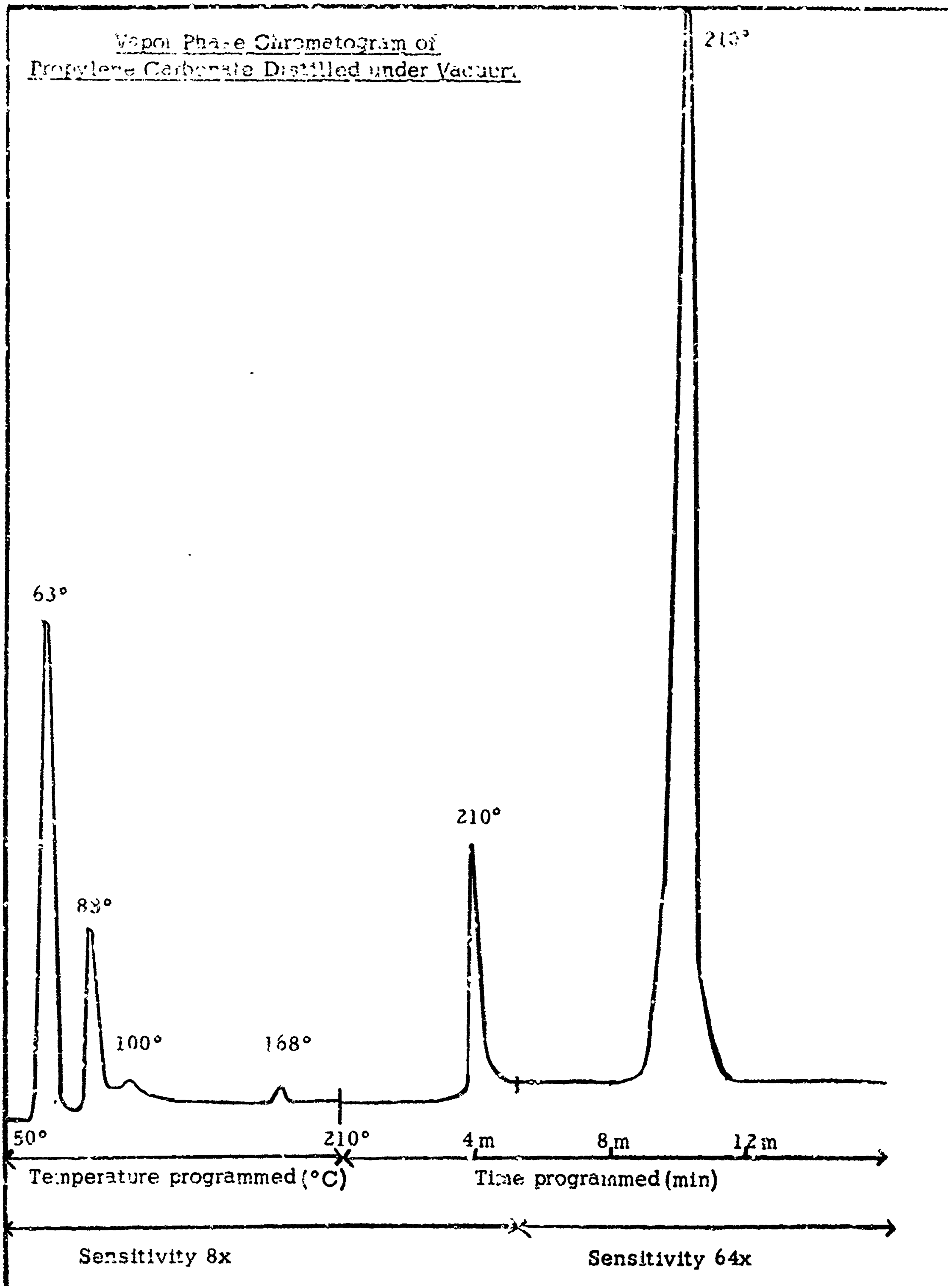
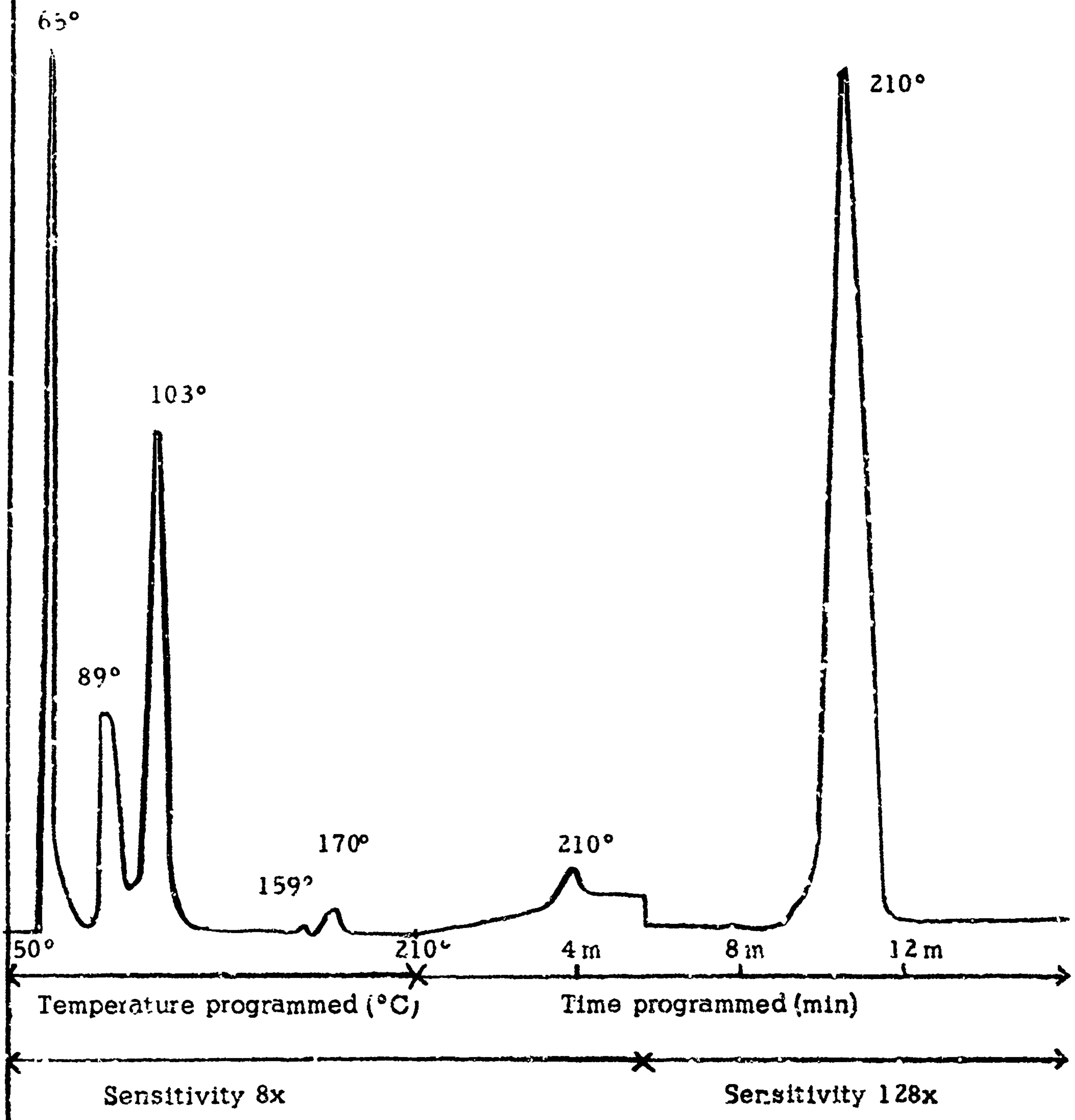


FIGURE 2



Vapor Phase Chromatogram of Propylene Carbonate Distilled under Vacuum

FIGURE 3



Vapor Phase Chromatogram of Propylene Carbonate Distilled From CaO

FIGURE 4

Vapor Phase Chromatogram of Propylene Carbonate Distilled From SiO_2

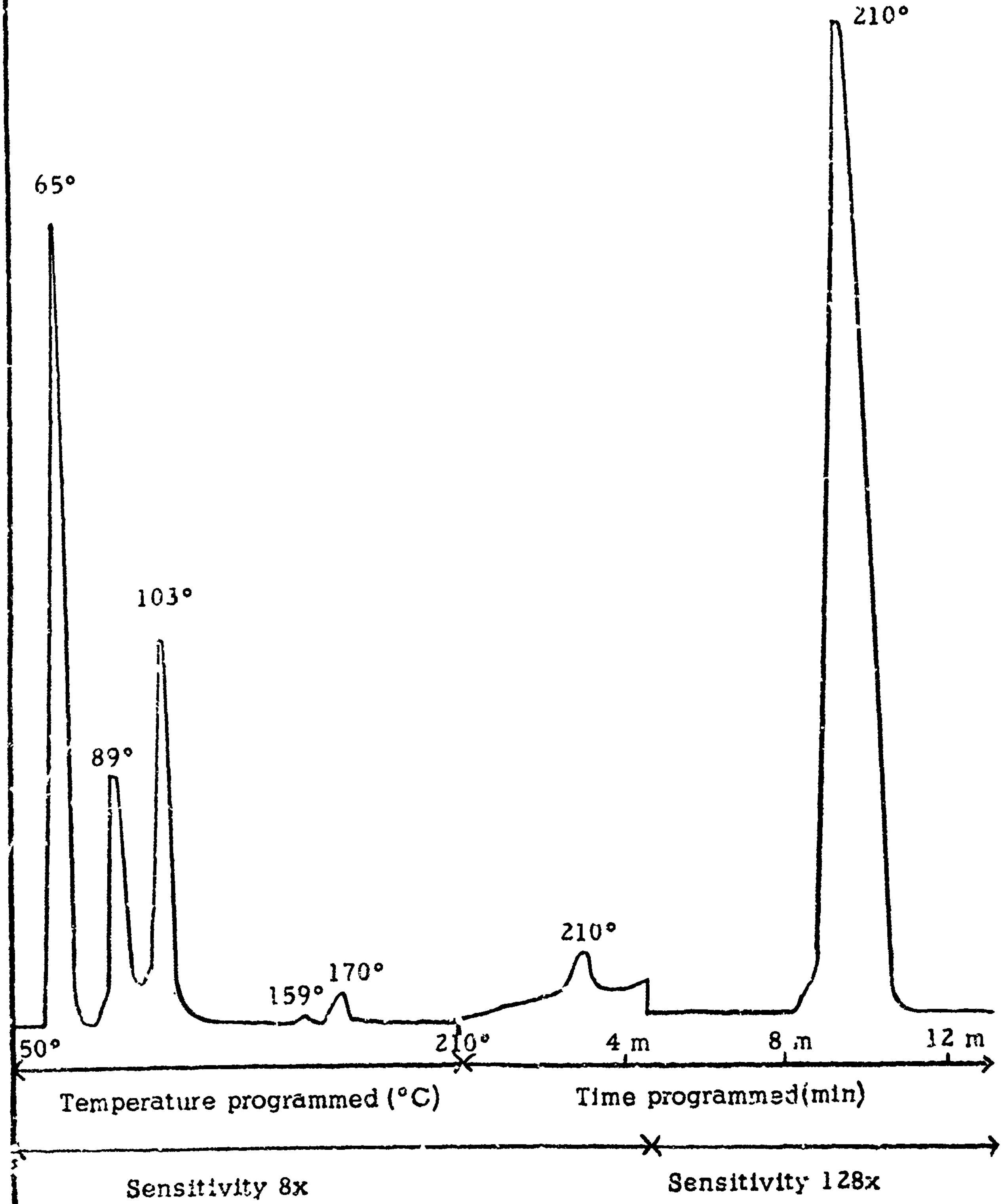


FIGURE 5

Vapor Phase Chromatogram of Propylene Carbonate
Distilled From Lithium

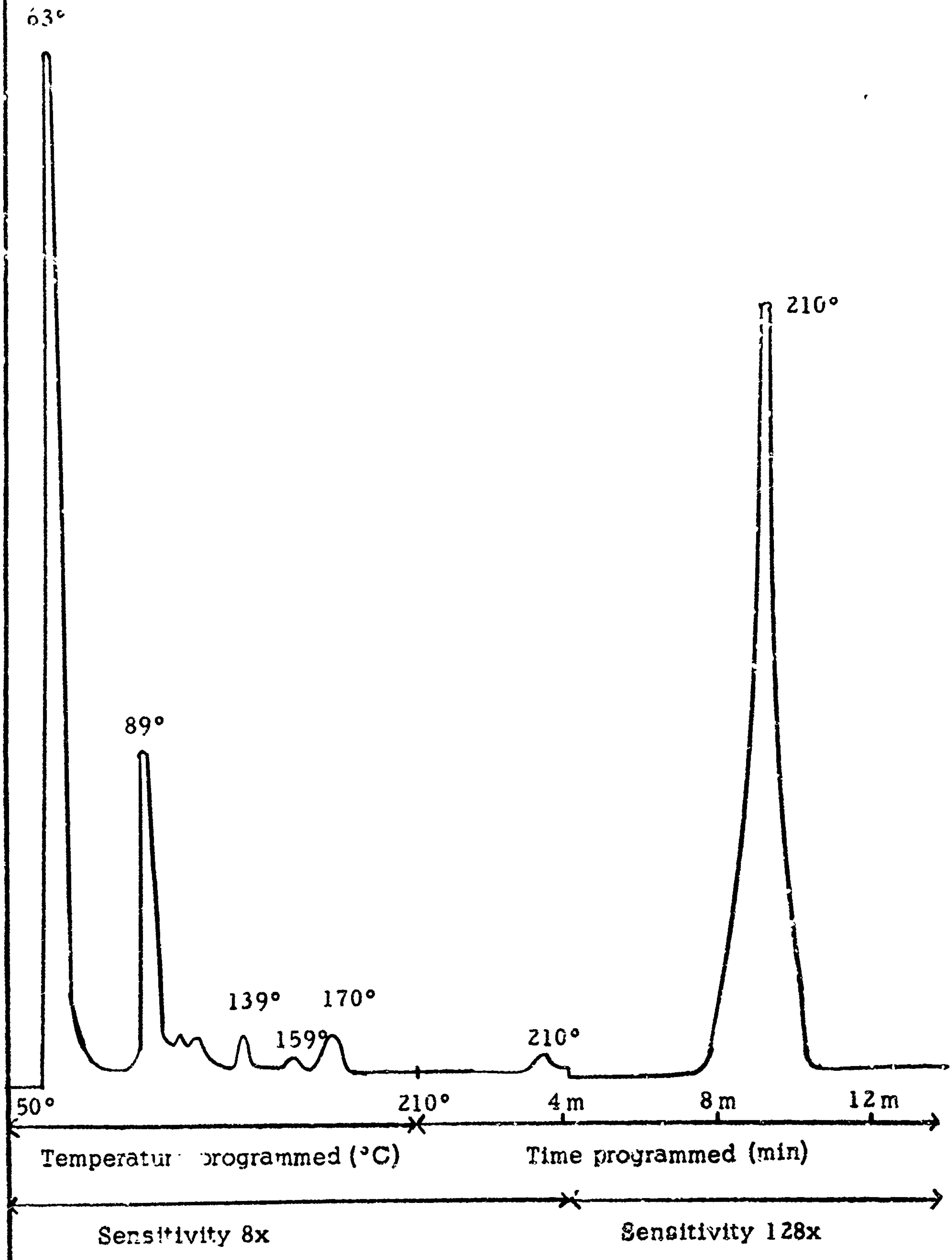


FIGURE 6

Vapor Phase Chromatogram of As Received Propylene Carbonate

Injection Temperature 110°C

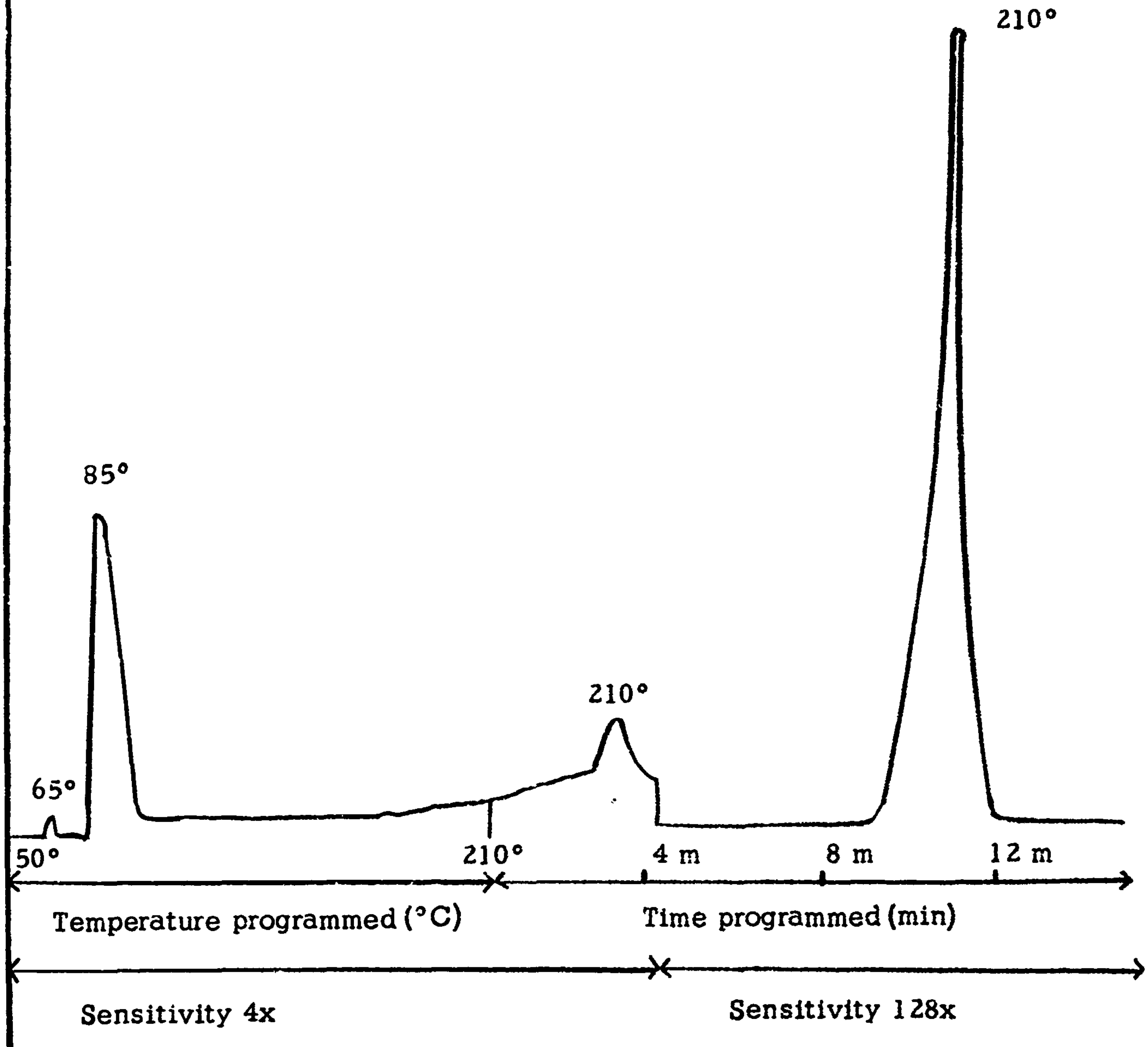


FIGURE 7

Vapor Phase Chromatogram of
Propylene Carbonate Dried with Molecular Sieve

Injection Temperature 110°C

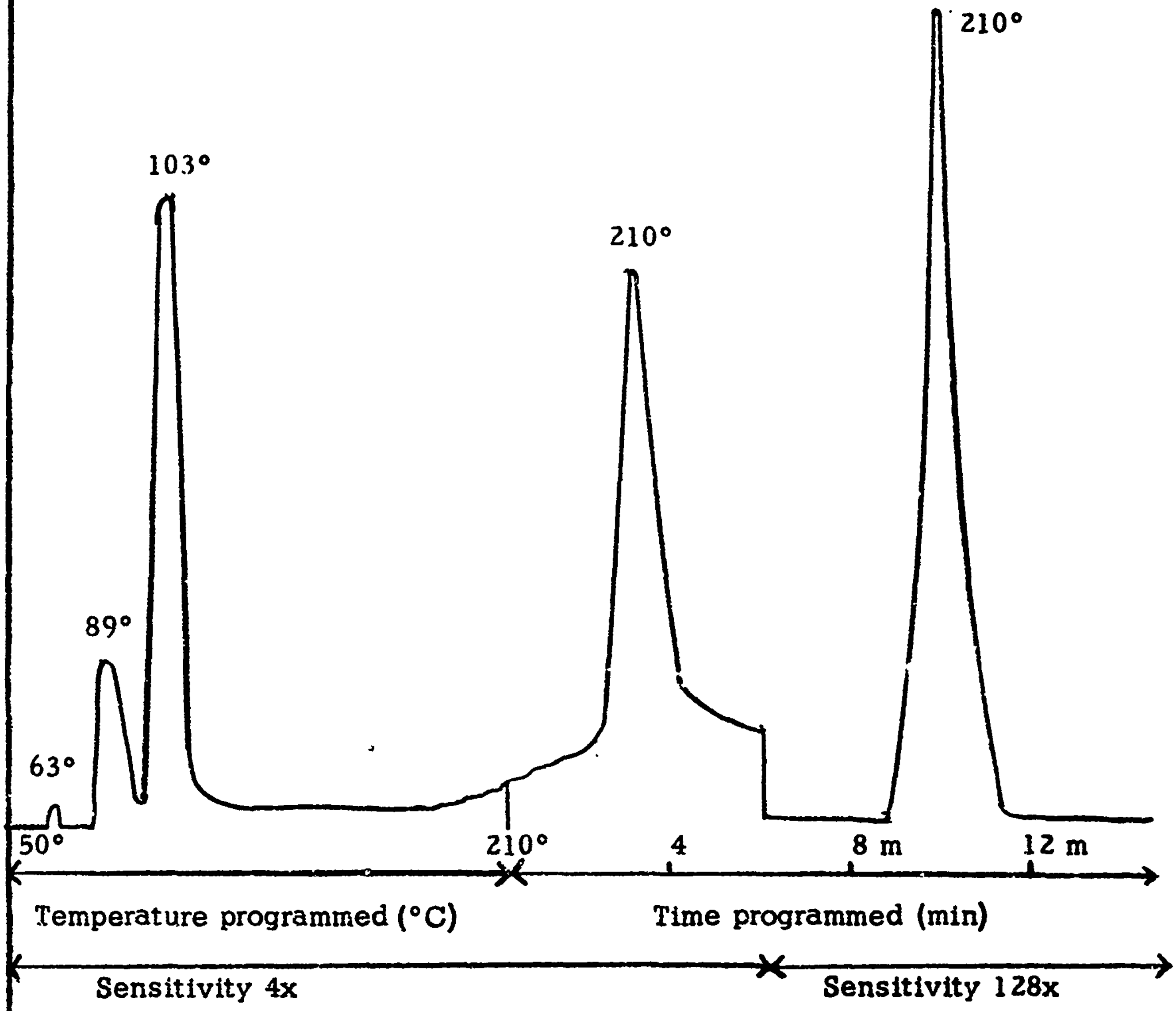


FIGURE 8

Vapor Phase Chromatogram of Propylene Carbonate
Distilled under Vacuum
Injection Temperature 110°C

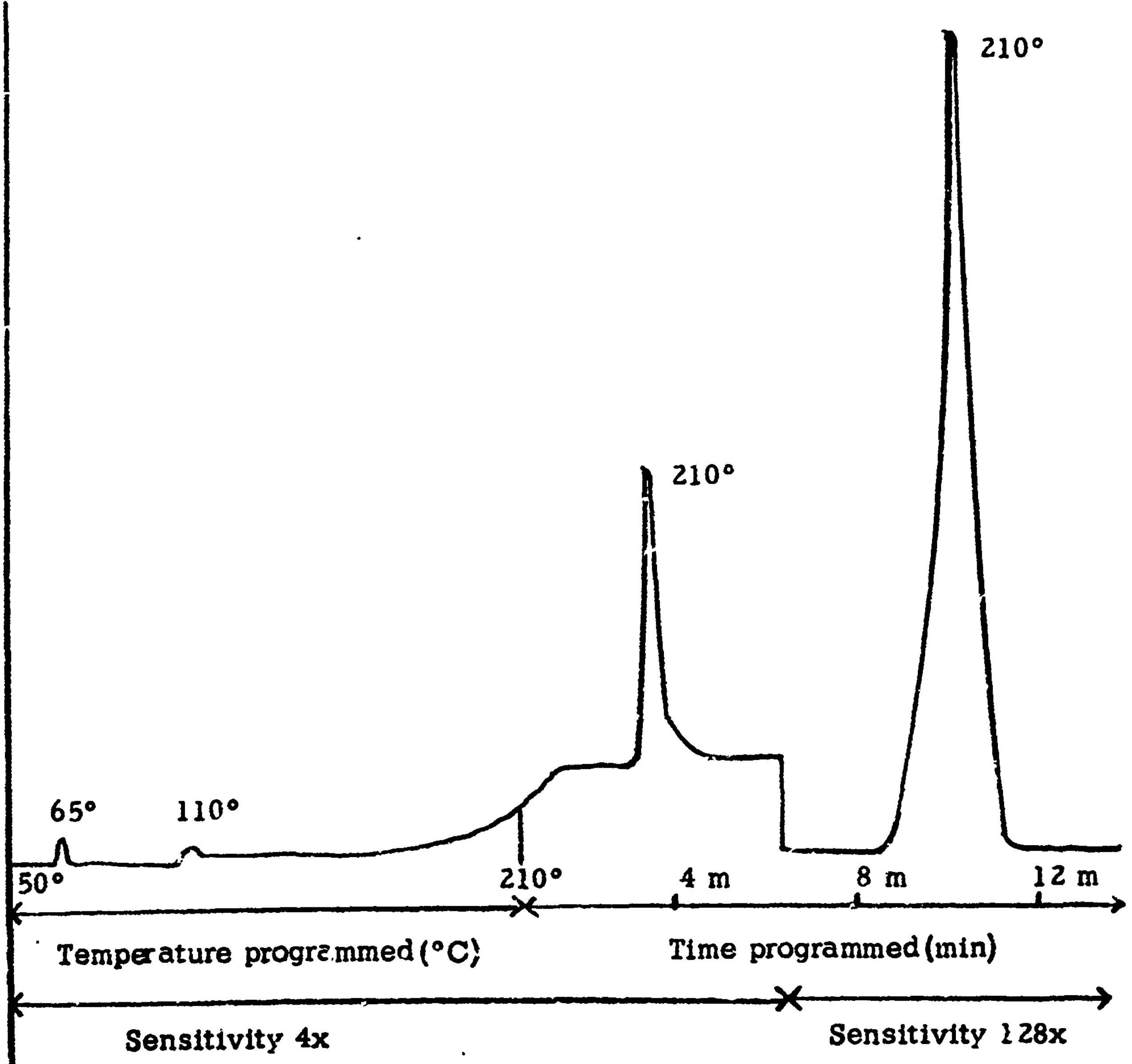


FIGURE 9

Vapor Phase Chromatogram of Propylene Carbonate
Distilled from Ca O
Injection Temperature 110°C

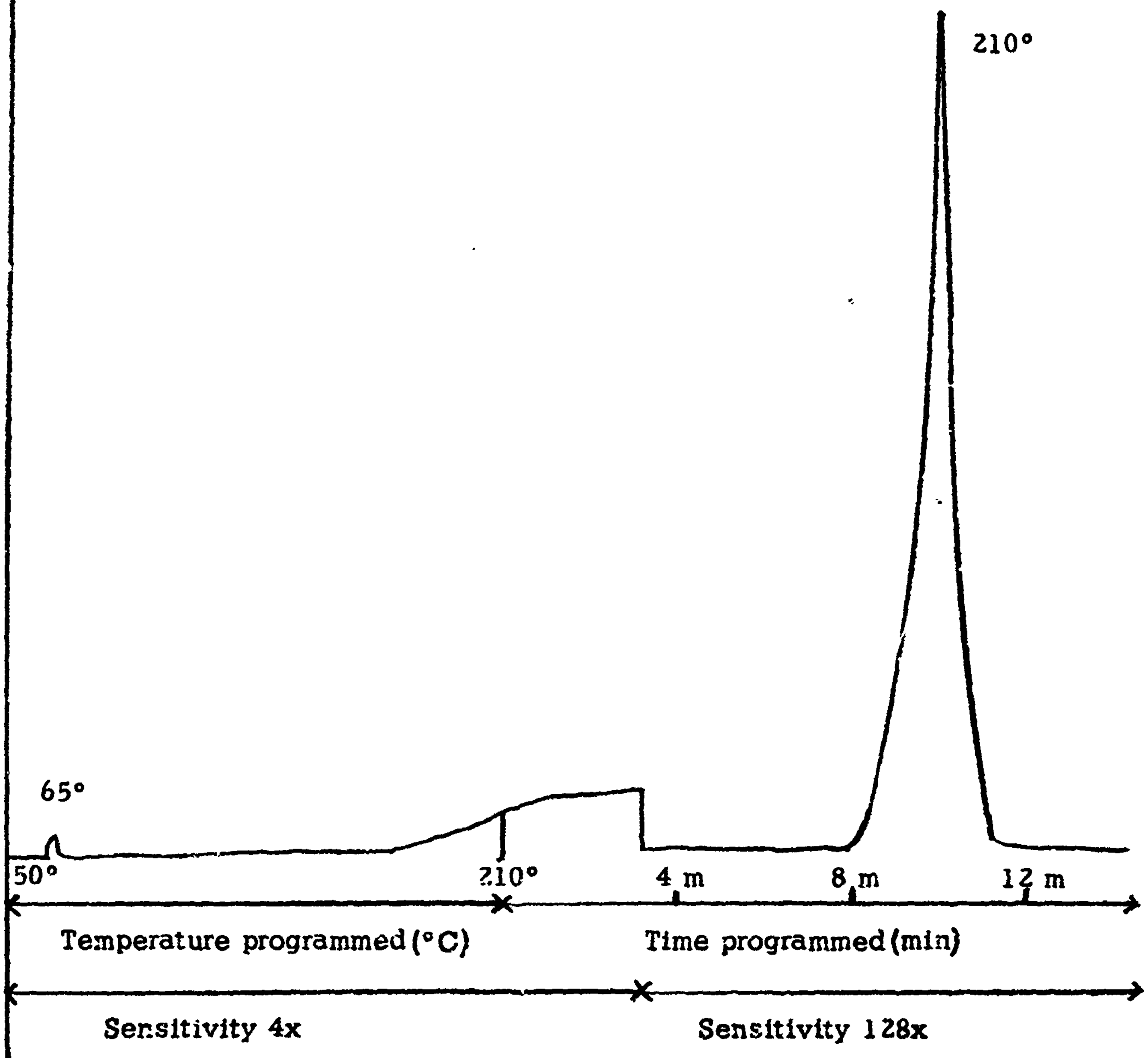


FIGURE 10

Vapor Phase Chromatogram of Propylene Carbonate
Distilled from SiO_2
Injection Temperature 110°C

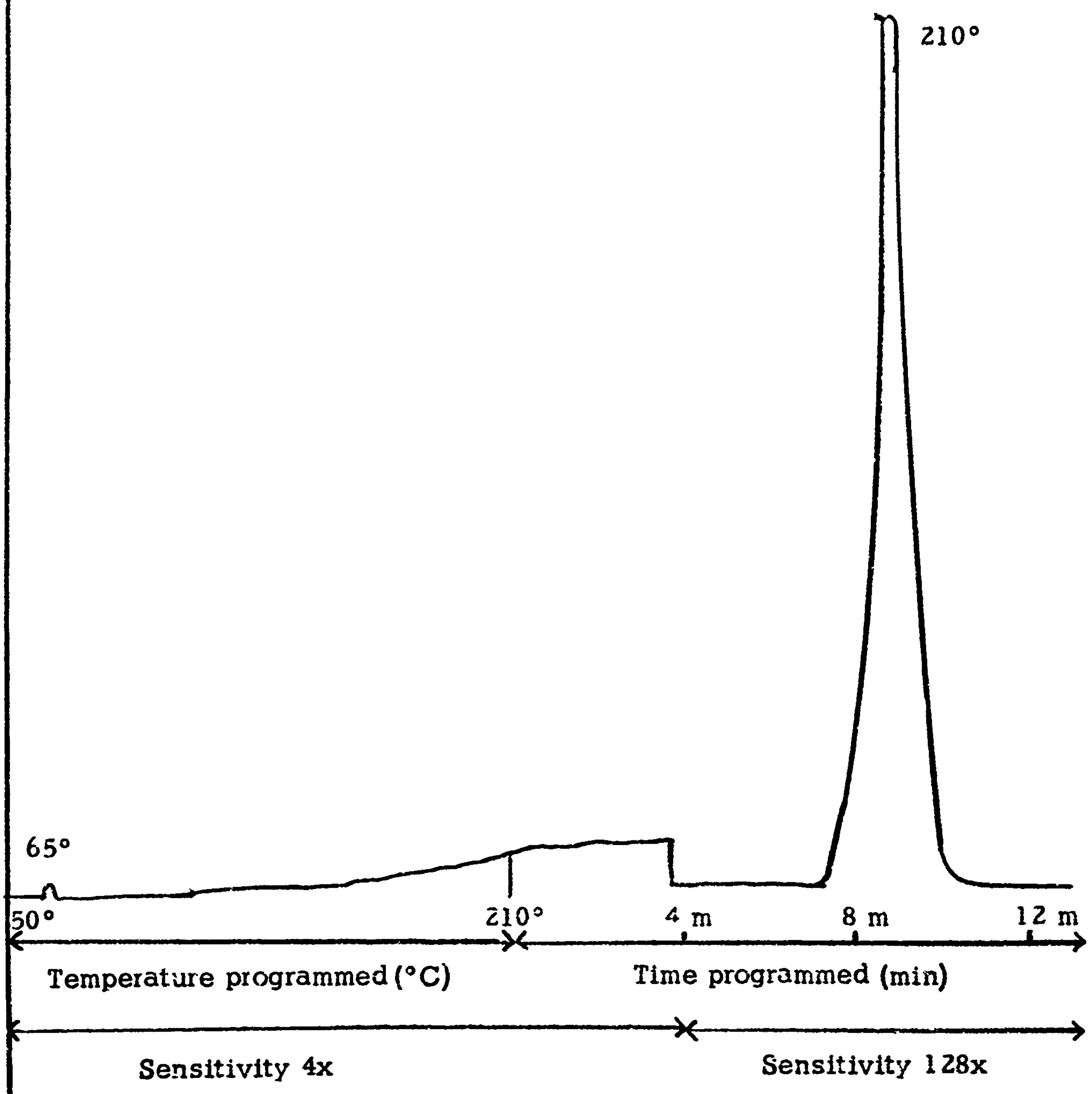


FIGURE 11

Vapor Phase Chromatogram of Propylene Carbonate
Distilled from Lithium
Injection Temperature 110°C

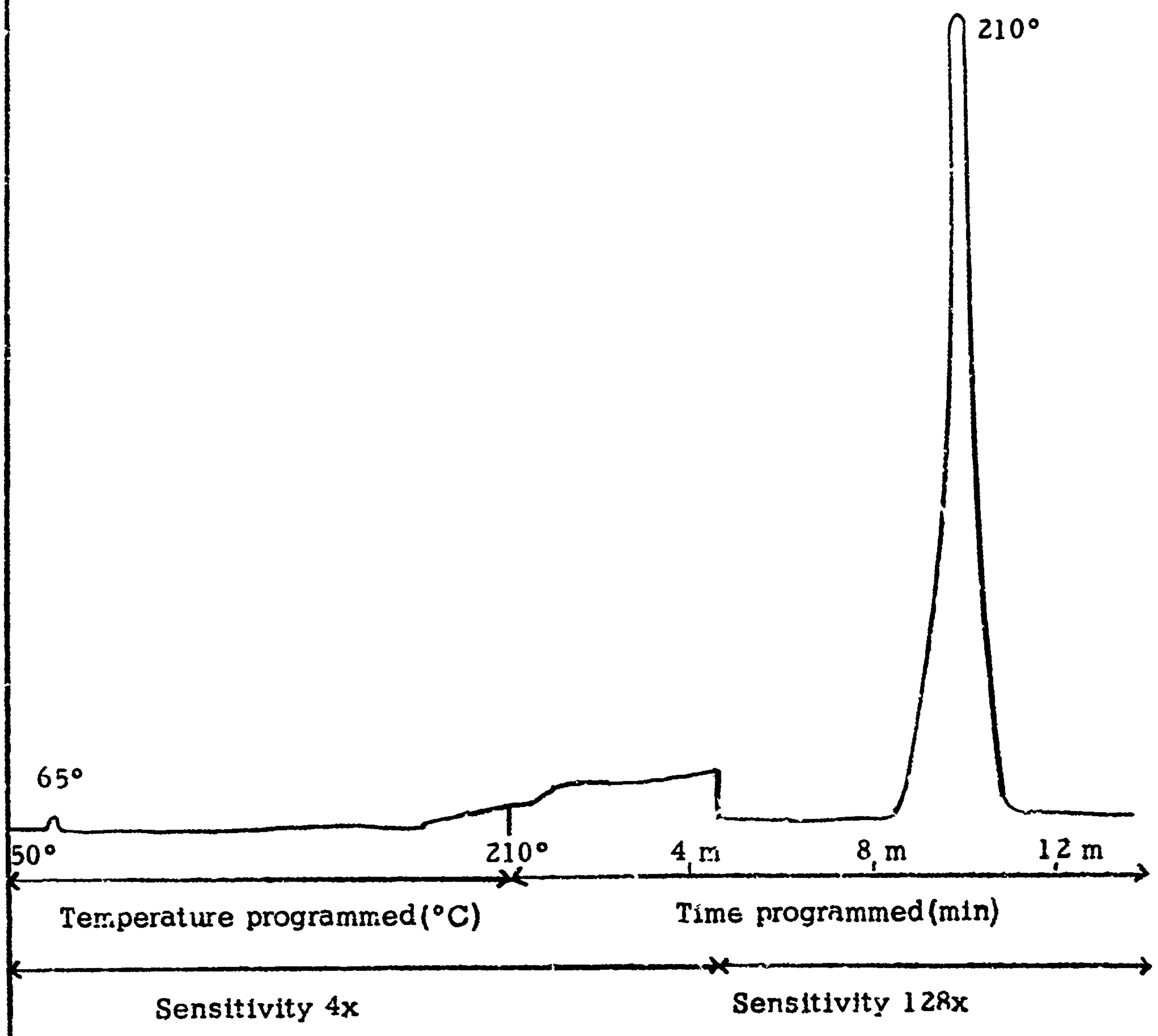
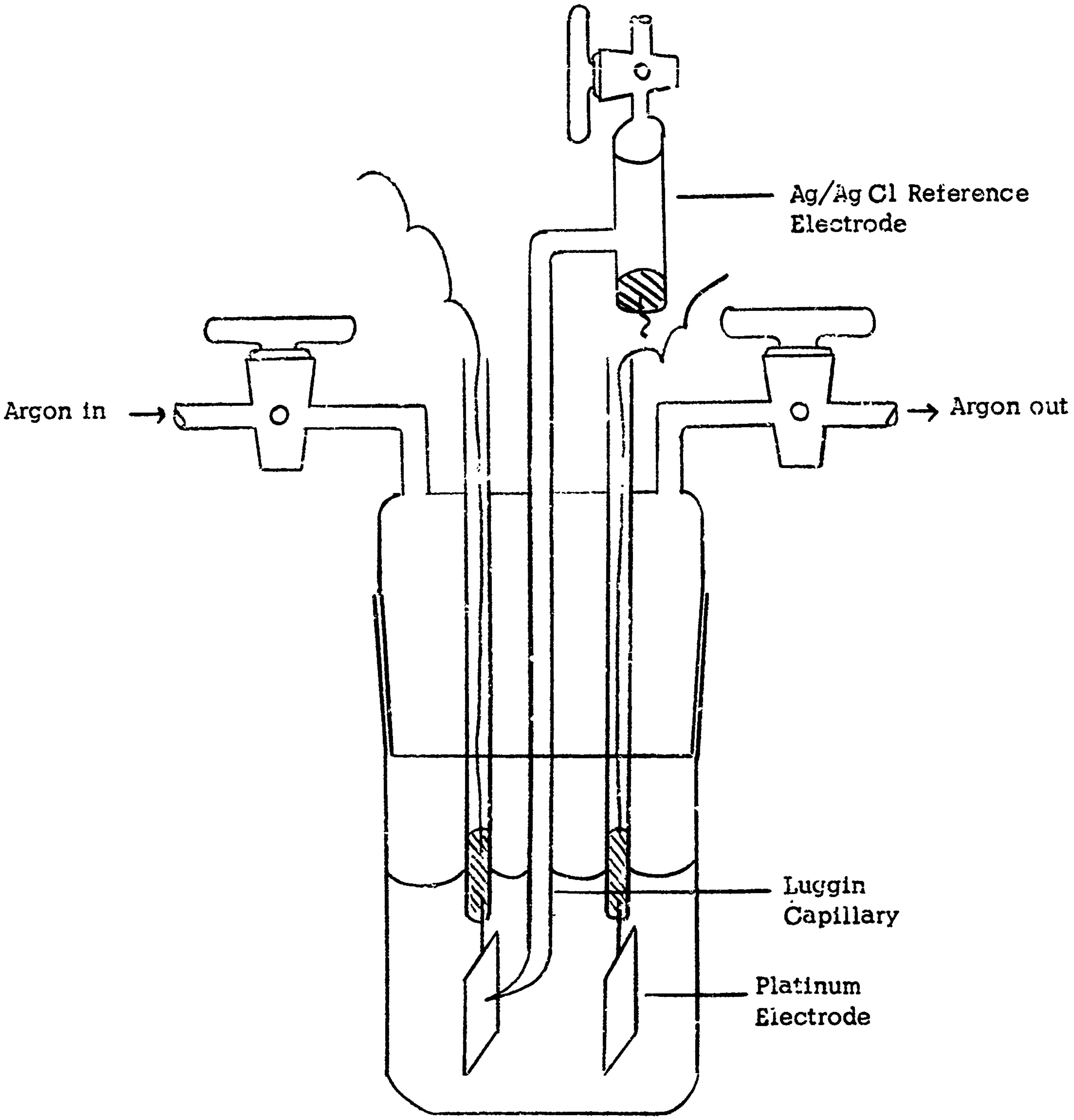


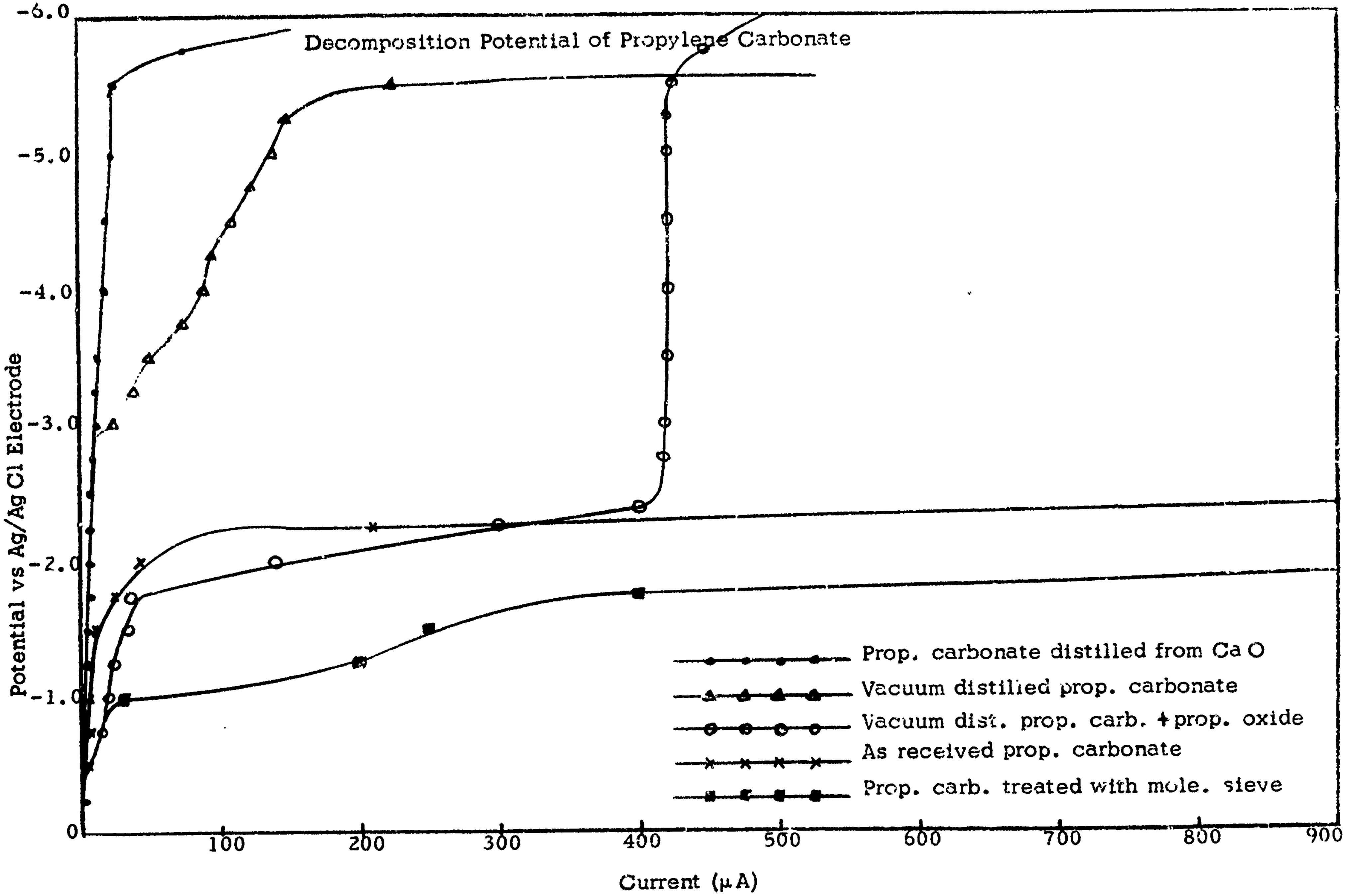
FIGURE 12



Decomposition Potential Cell

FIGURE 13

FIGURE 14


Decomposition Potential of Propylene Carbonate
Potential vs Ag/Ag Cl Electrode
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0
100
200
300
400
500
600
700
800
900
Current (μA)
Prop. carbonate distilled from Ca O
Vacuum distilled prop. carbonate
Vacuum dist. prop. carb. + prop. oxide
As received prop. carbonate
Prop. carb. treated with mole. sieve

Specific Conductance of Li Cl O$_4$ in Organic Solvents

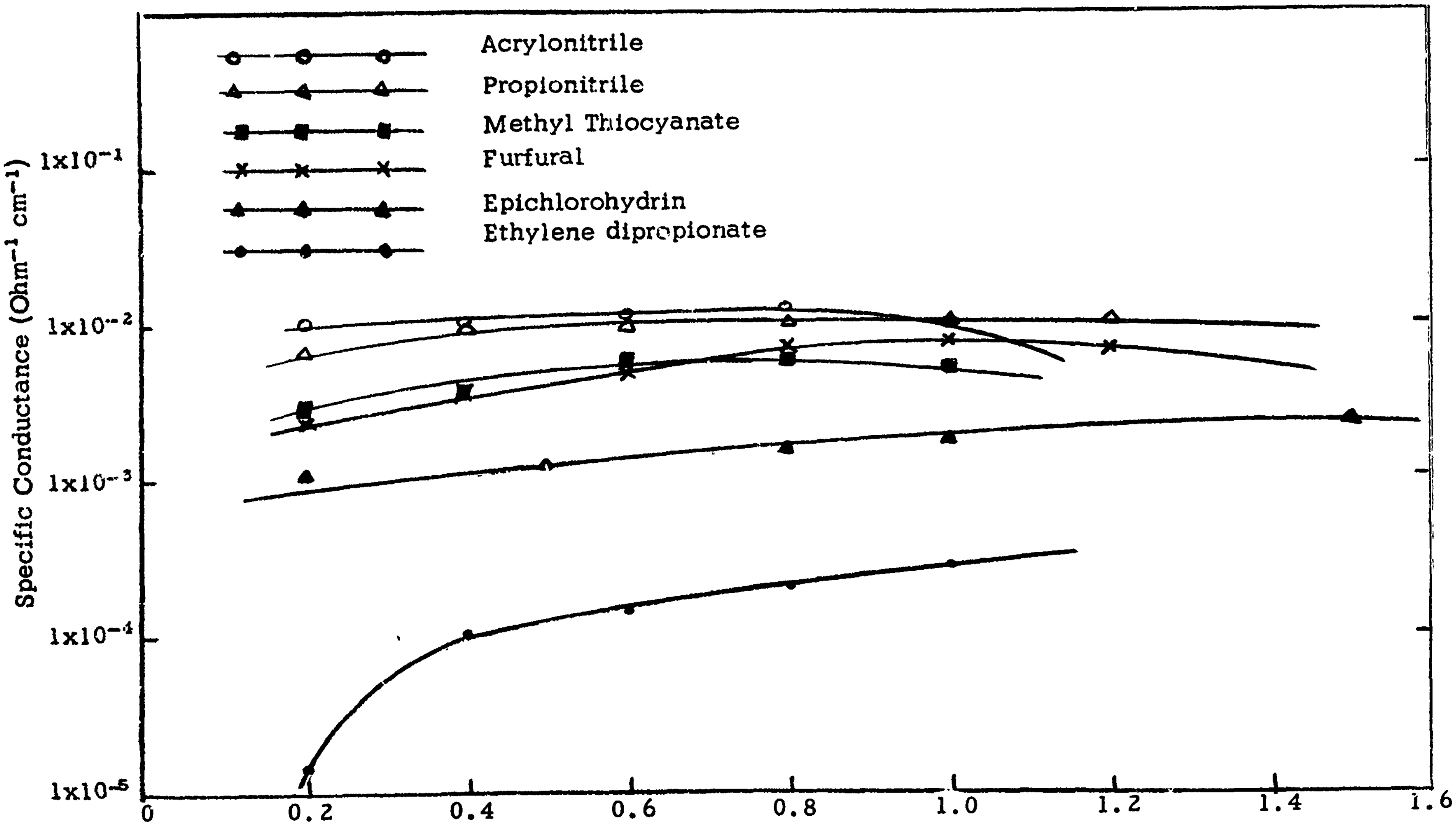


FIGURE 15

Equivalent Conductance of $LiClO_4$ in Organic Solvents

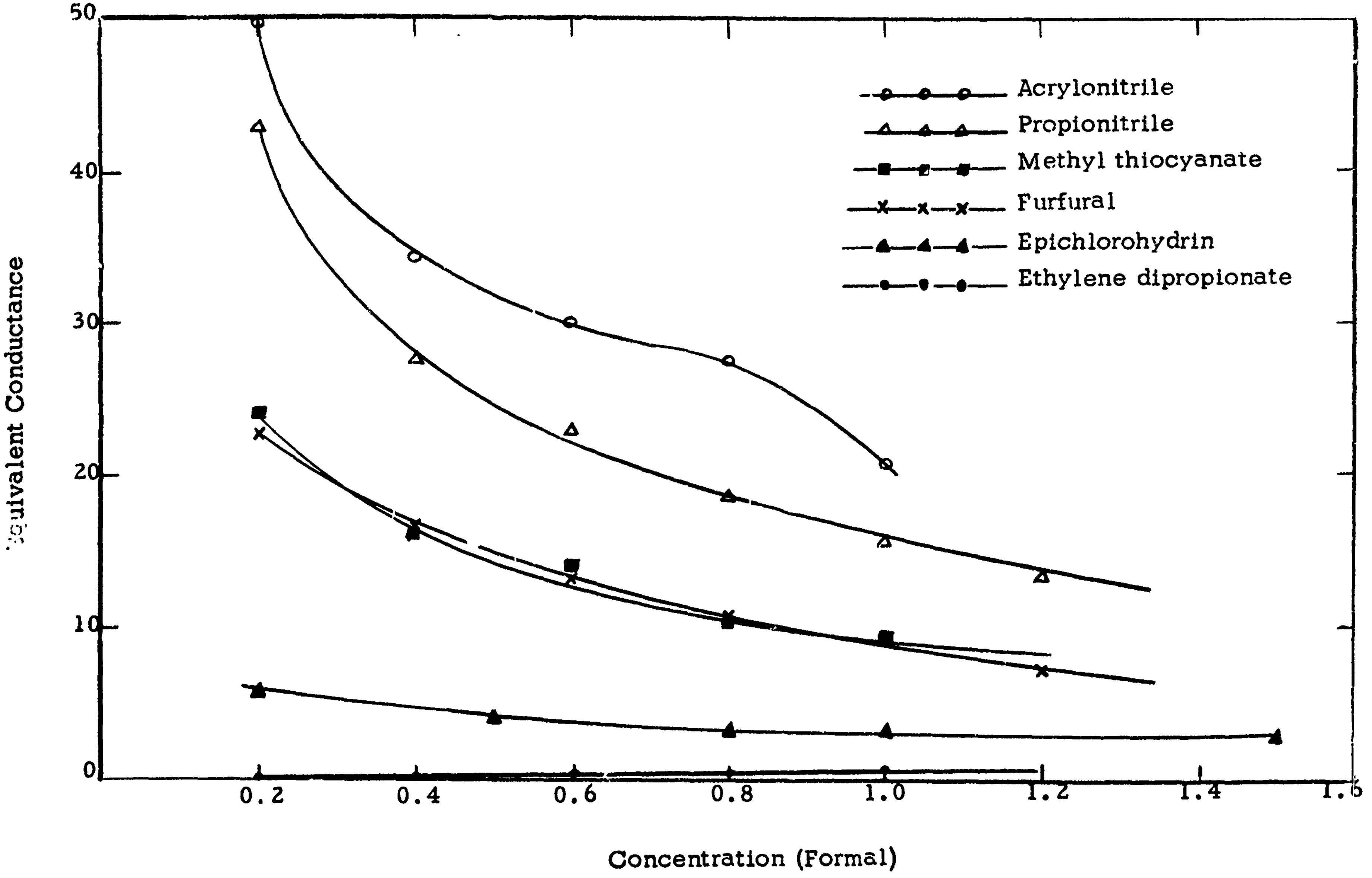


FIGURE 16

Effect of Acrylonitrile and Propionitrile on Performance of CuF_2 Electrode

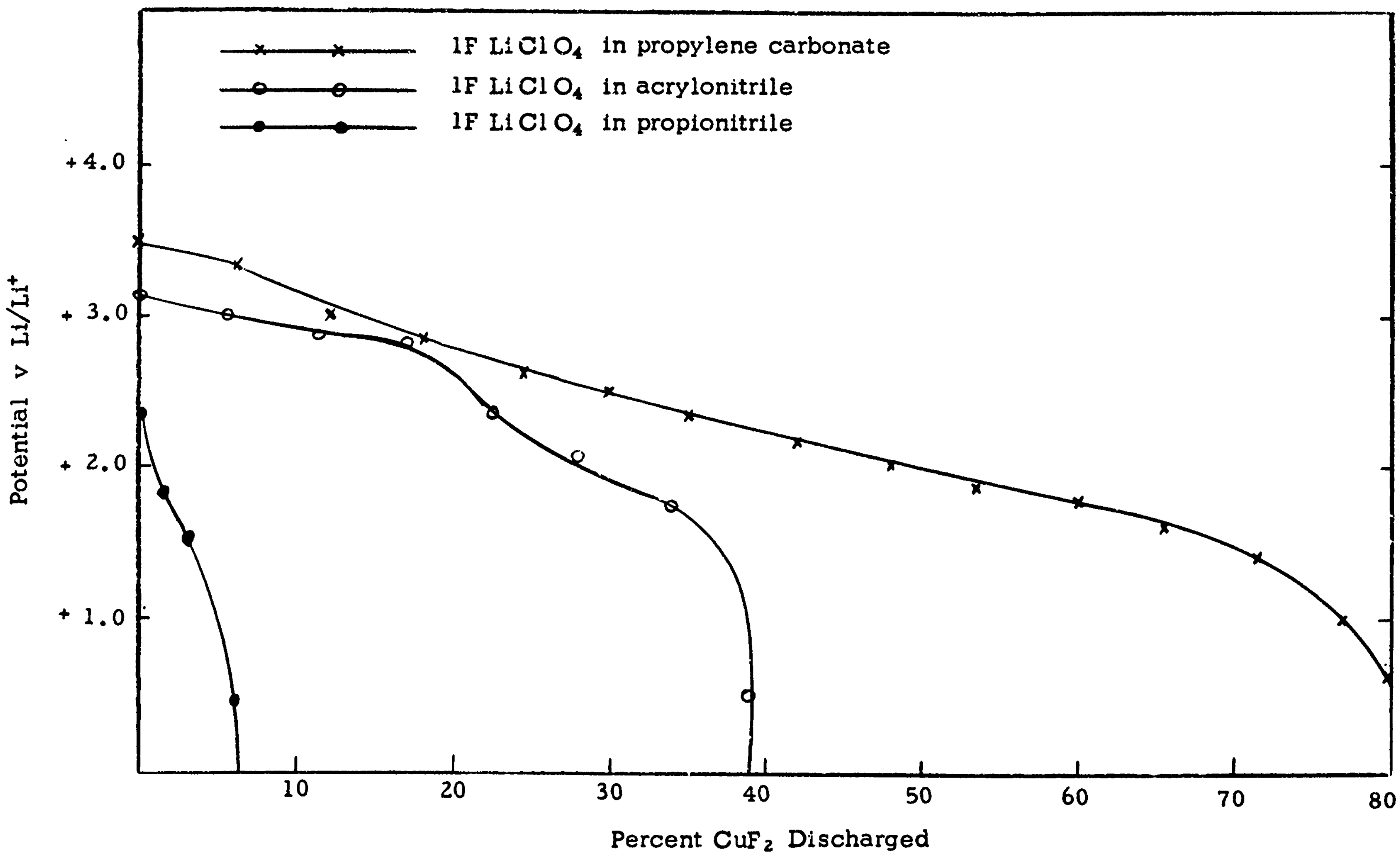


FIGURE 17

Rate of Corrosion of Lithium in Various Solvents and Electrolytes

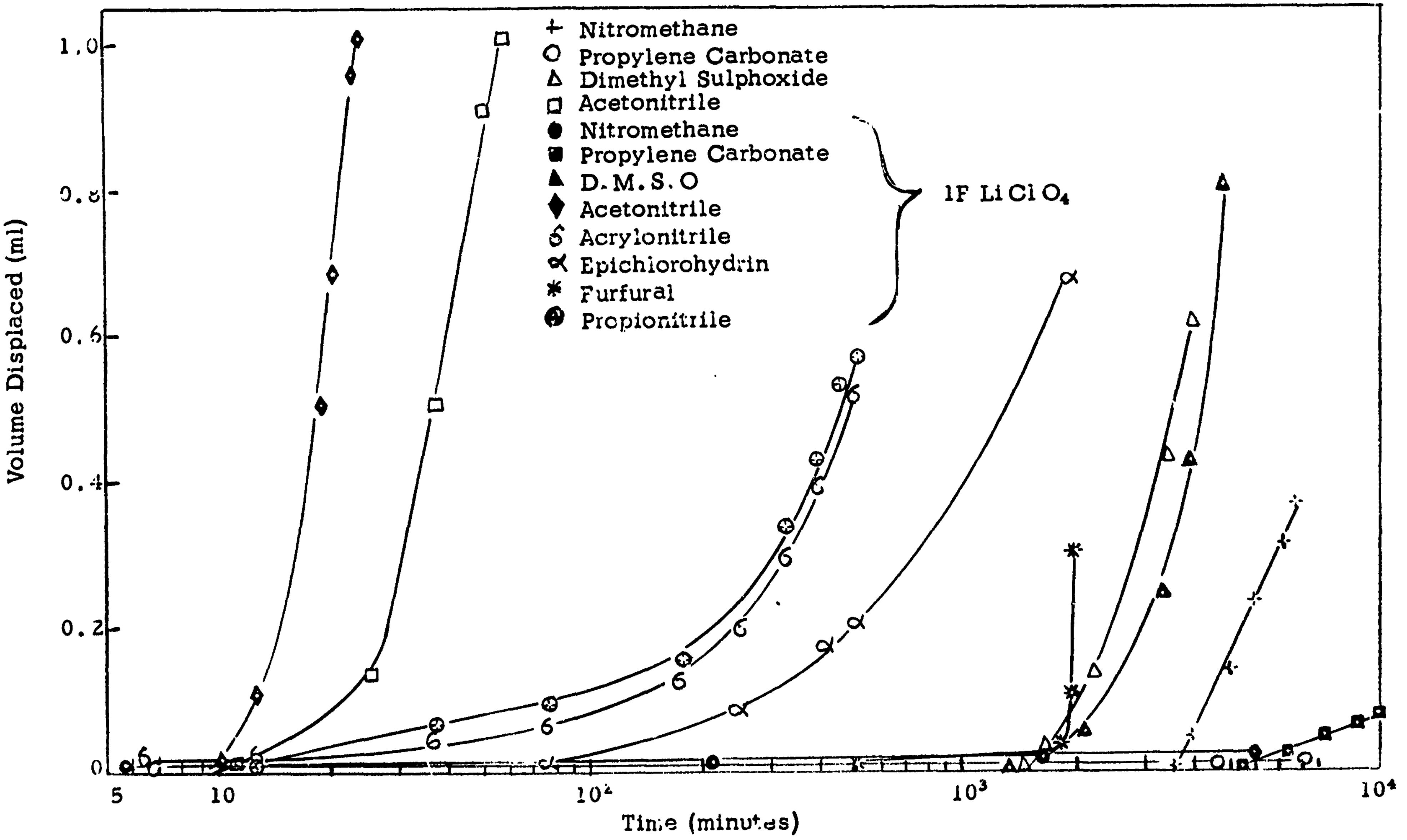


FIGURE 18

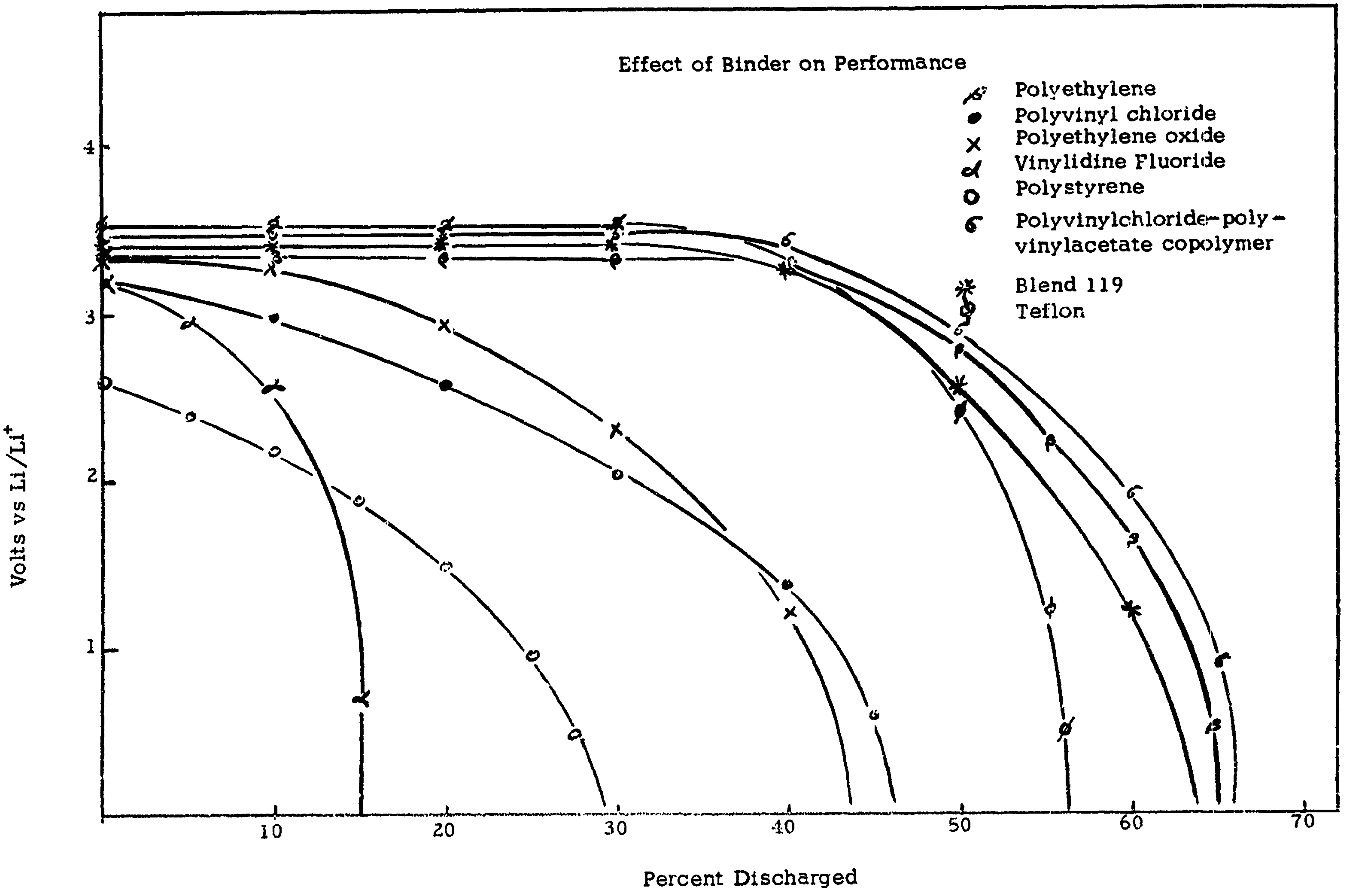

Effect of Binder on Performance
Polyethylene
● Polyvinyl chloride
× Polyethylene oxide
Vinylidine Fluoride
○ Polystyrene
Polyvinylchloride-poly-vinylacetate copolymer
Blend 119
Teflon
Volts vs Li/Li+
4
3
2
1
10
20
30
40
50
60
70
Percent Discharged

FIGURE 19

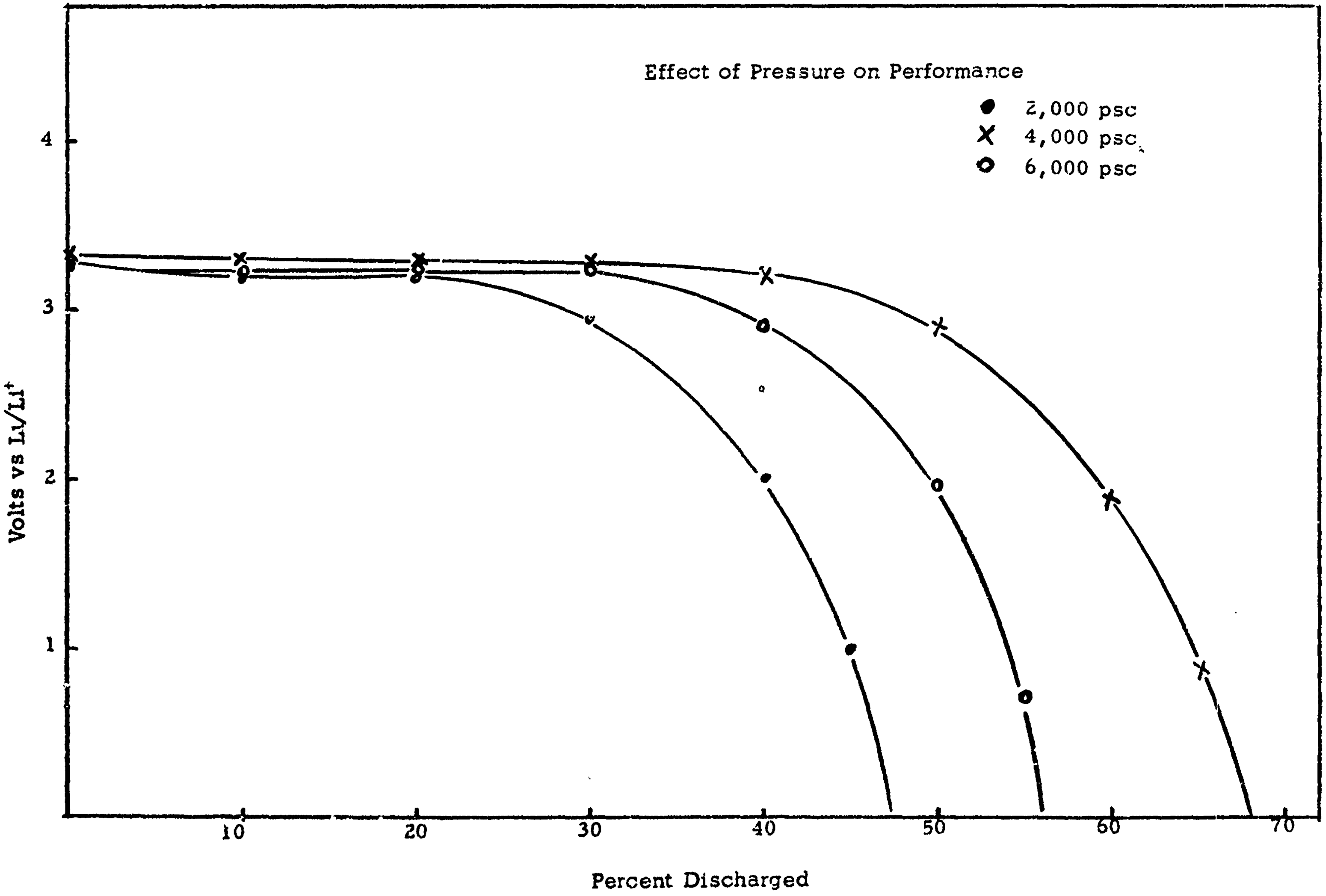

Effect of Pressure on Performance
● 2,000 psc
X 4,000 psc
○ 6,000 psc
Volts vs Li/Li$^+$
4
3
2
1
10
20
30
40
50
60
70
Percent Discharged

FIGURE 20

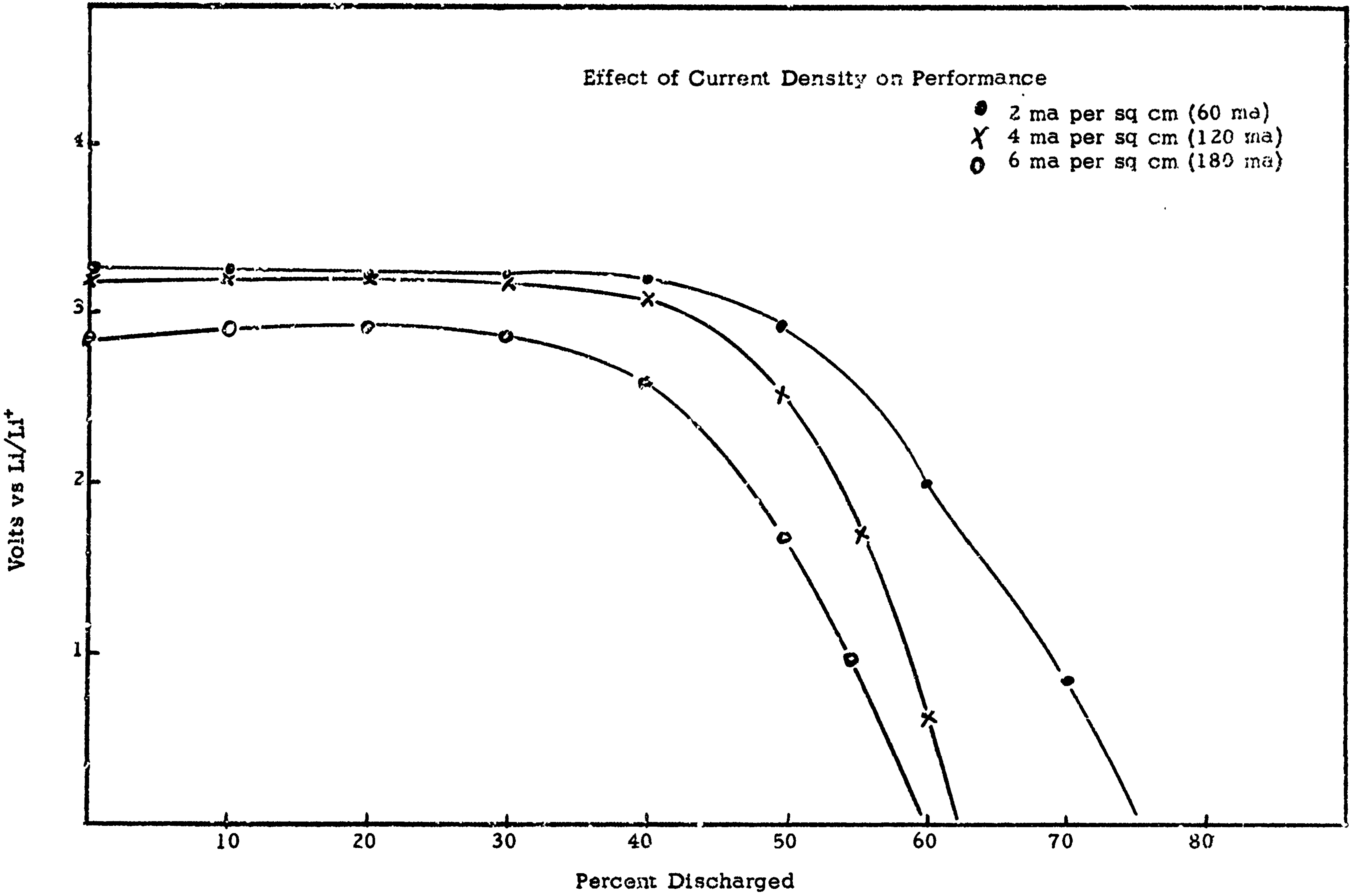

Effect of Current Density on Performance
● 2 ma per sq cm (60 ma)
X 4 ma per sq cm (120 ma)
O 6 ma per sq cm (180 ma)
Volts vs Li/Li+
1
2
3
4
10
20
30
40
50
60
70
80
Percent Discharged

FIGURE 21

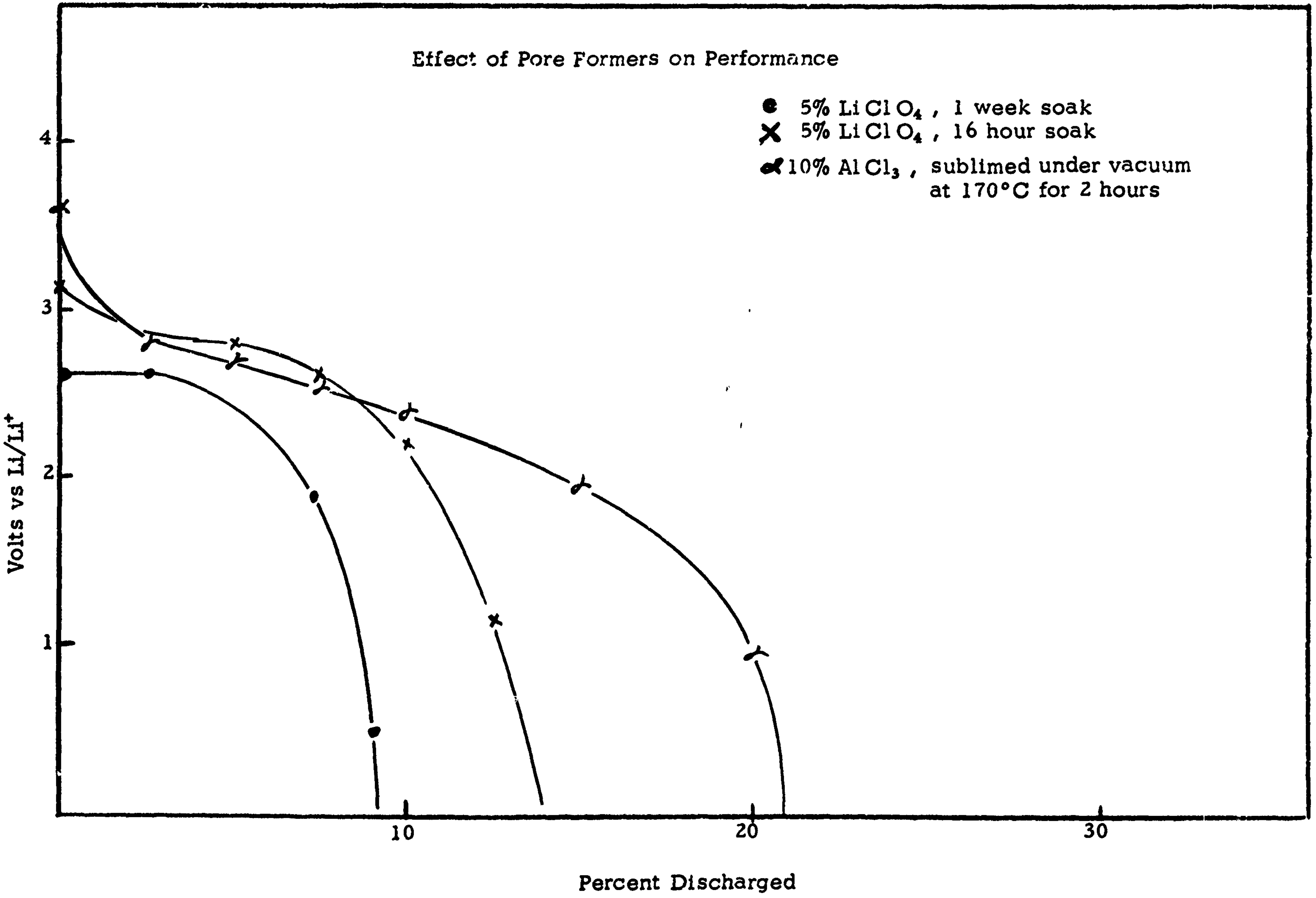

Effect of Pore Formers on Performance
● 5% $LiClO_4$, 1 week soak
✕ 5% $LiClO_4$, 16 hour soak
10% $AlCl_3$, sublimed under vacuum at 170°C for 2 hours
4
3
2
1
Volts vs Li/Li^+
10
20
30
Percent Discharged

FIGURE 22

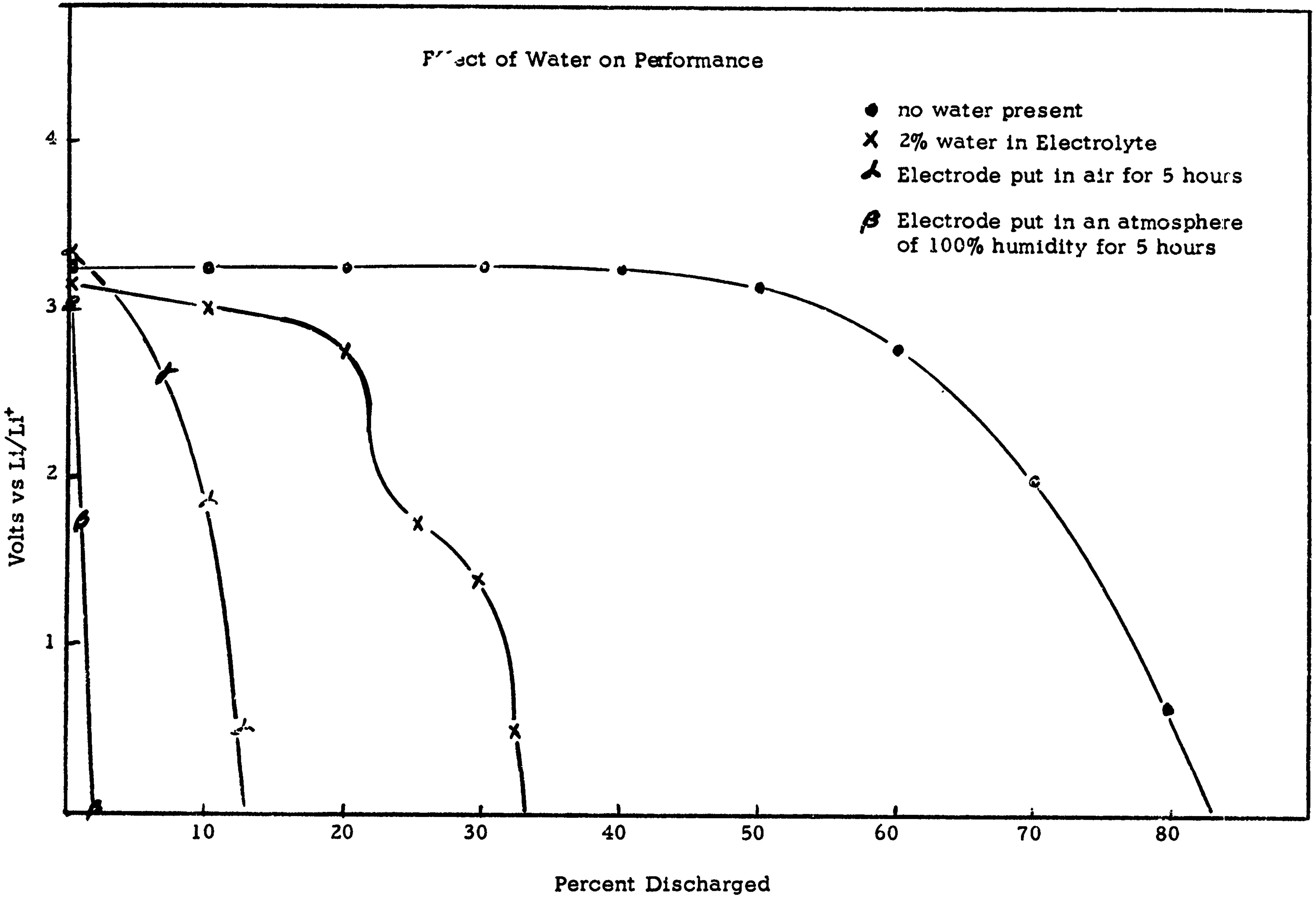

F''ect of Water on Performance
● no water present
X 2% water in Electrolyte
⅄ Electrode put in air for 5 hours
β Electrode put in an atmosphere of 100% humidity for 5 hours
Volts vs Li/Li+
4
3
2
1
10
20
30
40
50
60
70
80
Percent Discharged

FIGURE 23

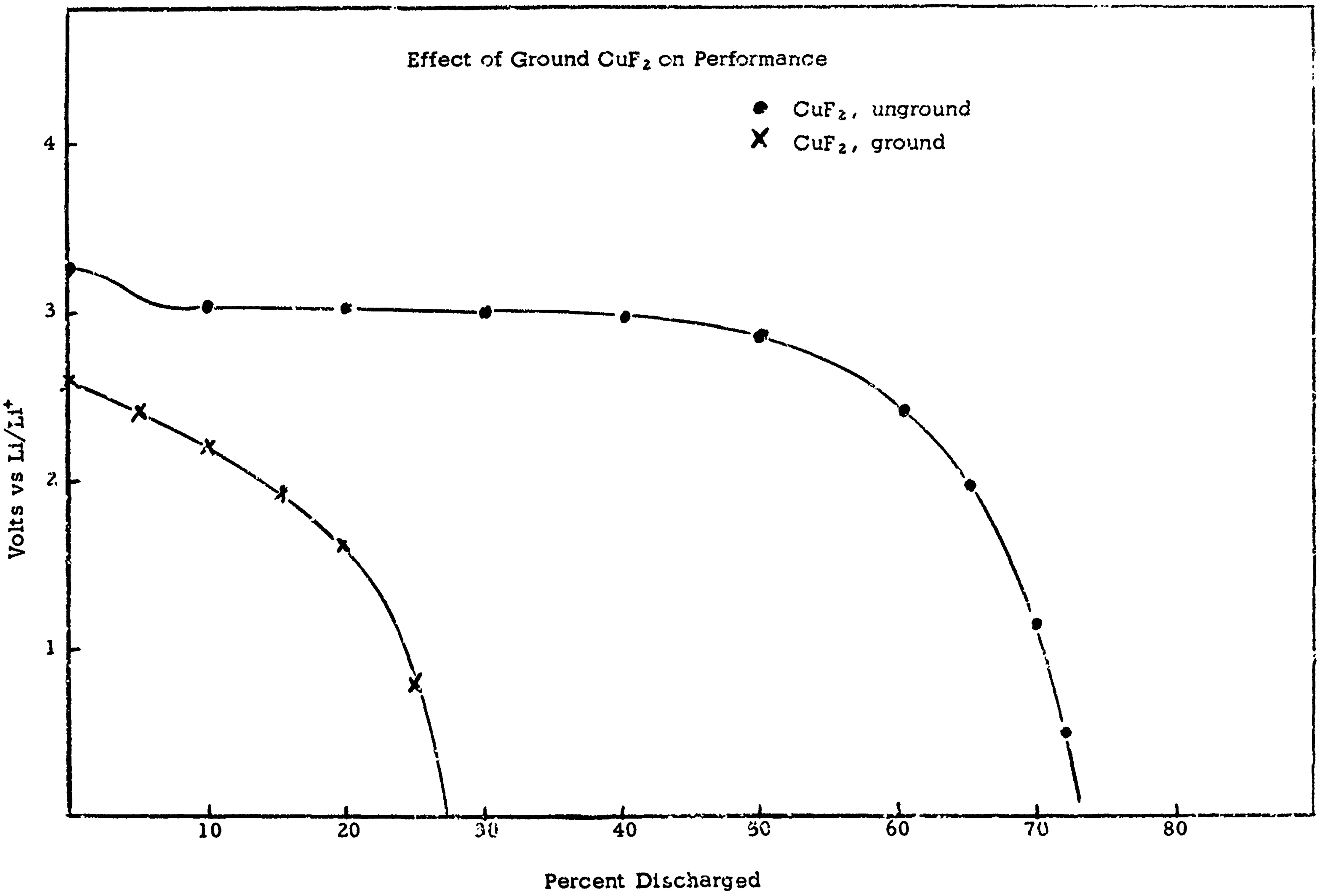
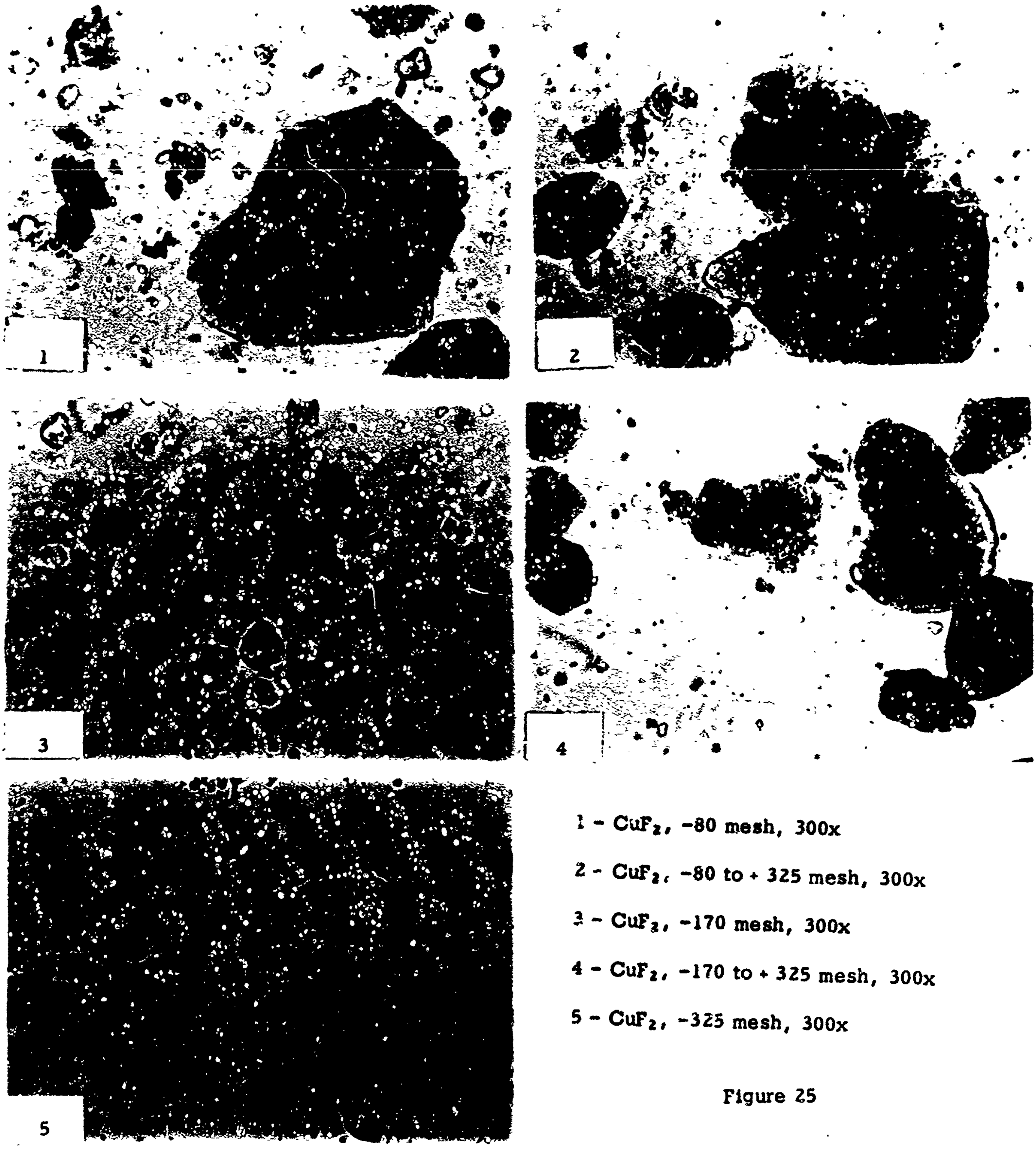

Effect of Ground CuF$_2$ on Performance
● CuF$_2$, unground
X CuF$_2$, ground
Volts vs Li/Li$^+$
4
3
2
1
10
20
30
40
50
60
70
80
Percent Discharged

FIGURE 24



1 - CuF_2, -80 mesh, 300x

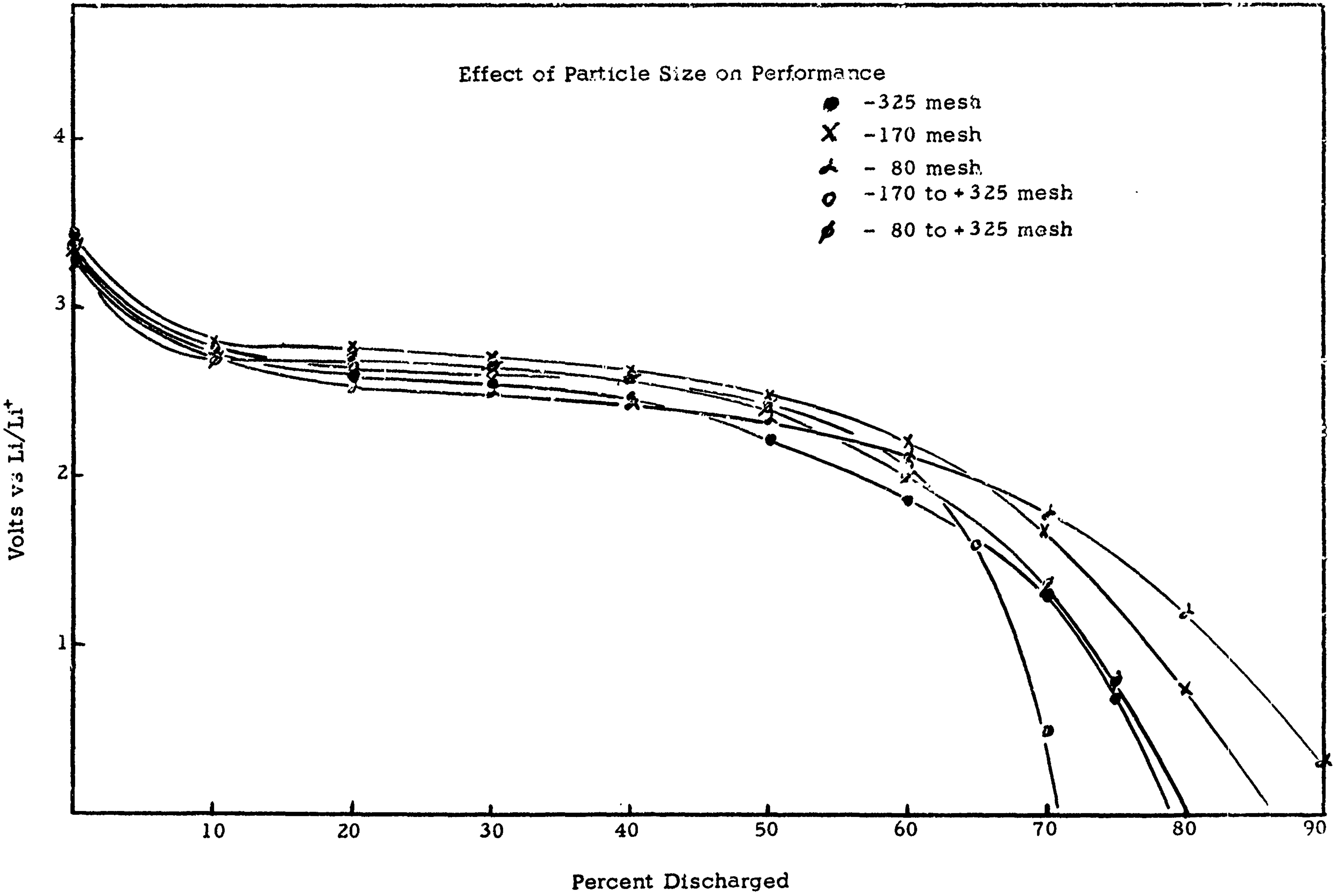
2 - CuF_2, -80 to + 325 mesh, 300x

3 - CuF_2, -170 mesh, 300x

4 - CuF_2, -170 to + 325 mesh, 300x

5 - CuF_2, -325 mesh, 300x

Figure 25



Effect of Particle Size on Performance
● -325 mesh
X -170 mesh
- 80 mesh
o -170 to +325 mesh
ø - 80 to +325 mesh
Volts vs Li/Li+
4
3
2
1
10
20
30
40
50
60
70
80
90
Percent Discharged

FIGURE 26

Effect of Temperature on Performance of CuF_2 Cathodes

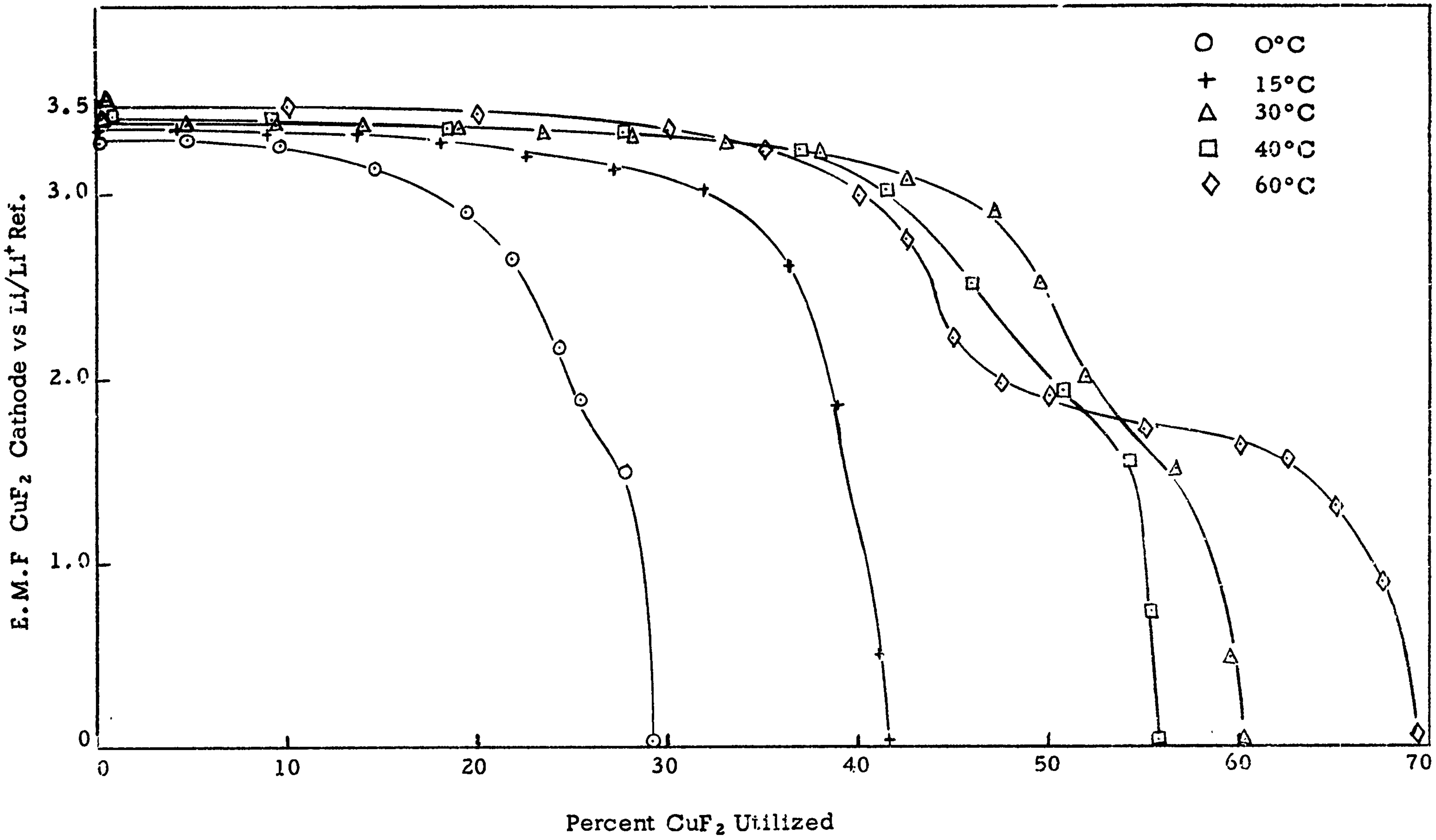


FIGURE 27

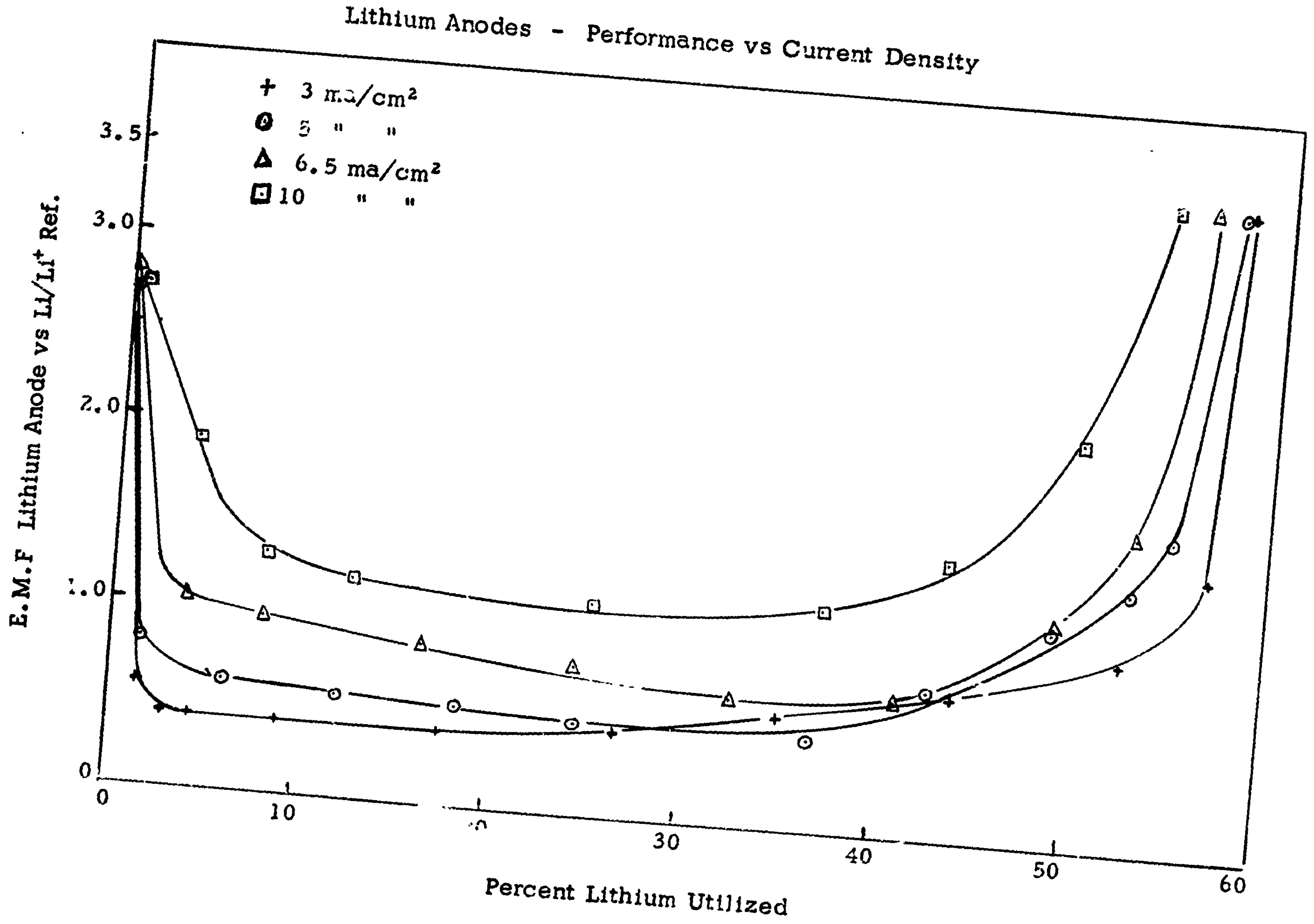

Lithium Anodes - Performance vs Current Density
+ 3 ma/cm²
⊙ 5 " "
△ 6.5 ma/cm²
⊡ 10 " "
E.M.F Lithium Anode vs Li/Li⁺ Ref.
3.5
3.0
2.0
1.0
0
0
10
20
30
40
50
60
Percent Lithium Utilized

FIGURE 28

Performance of Pressed Lithium Ribbon Anodes

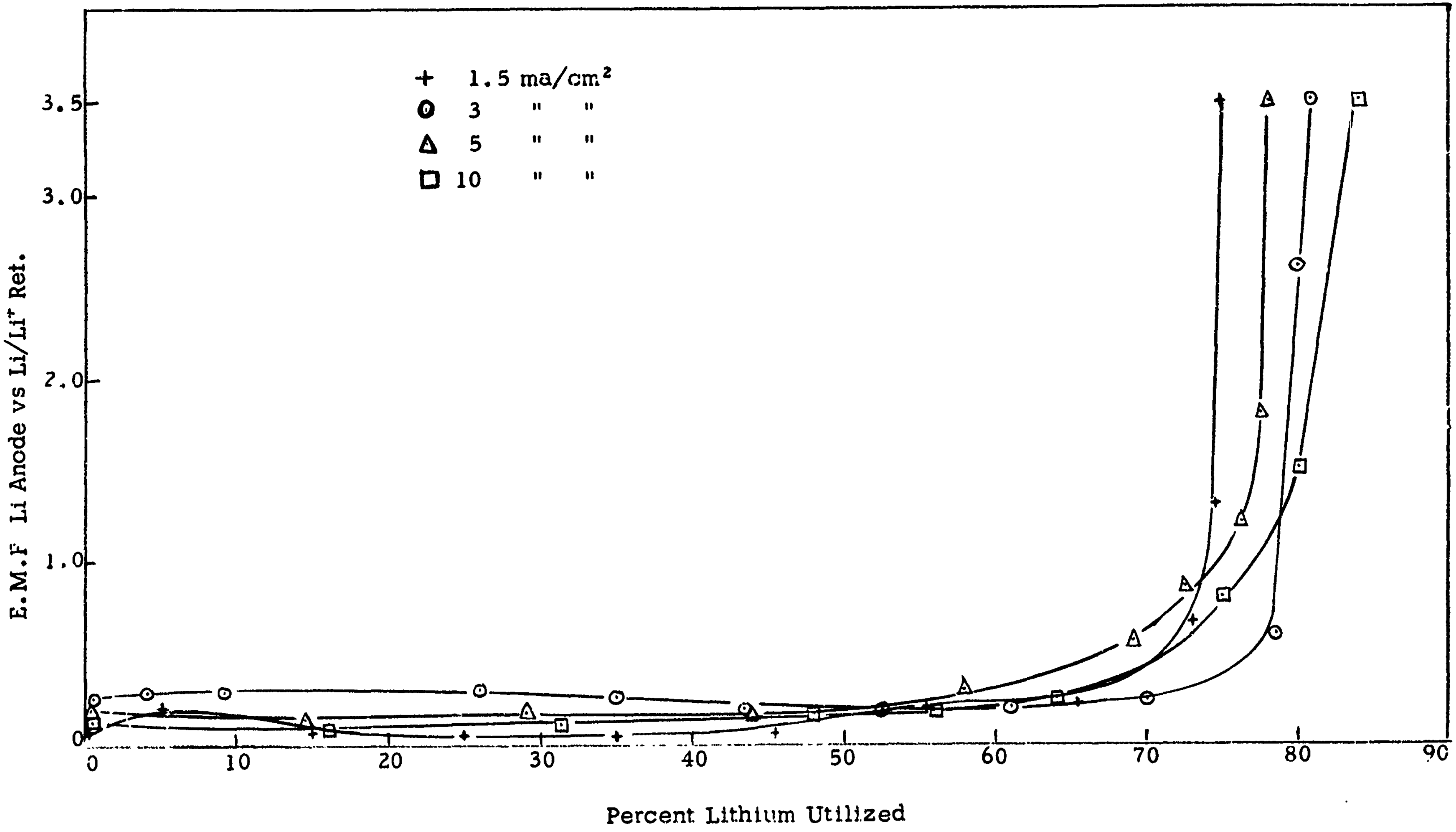


FIGURE 29

Effect of Storage on Performance of Lithium Electrodes

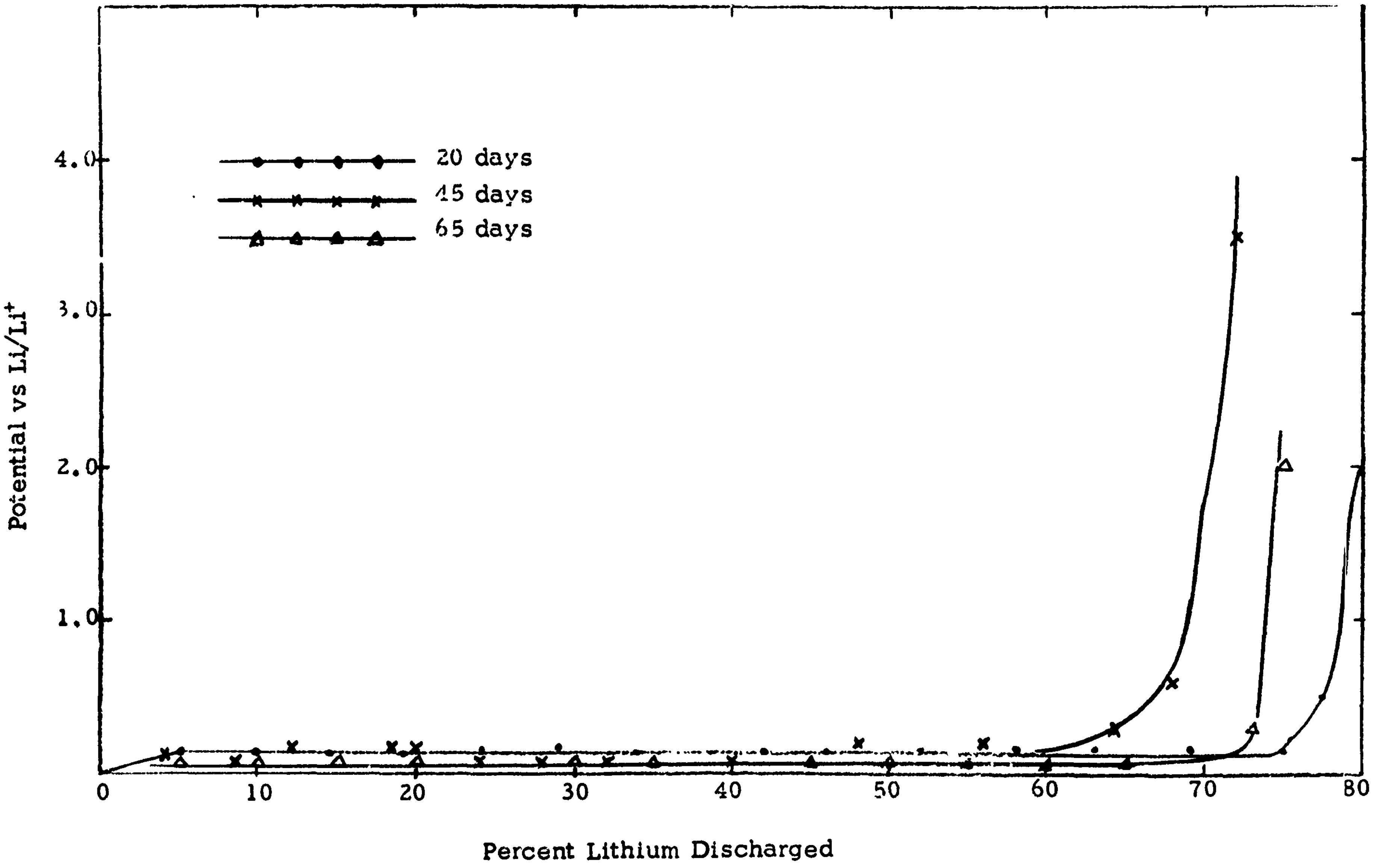


FIGURE 30

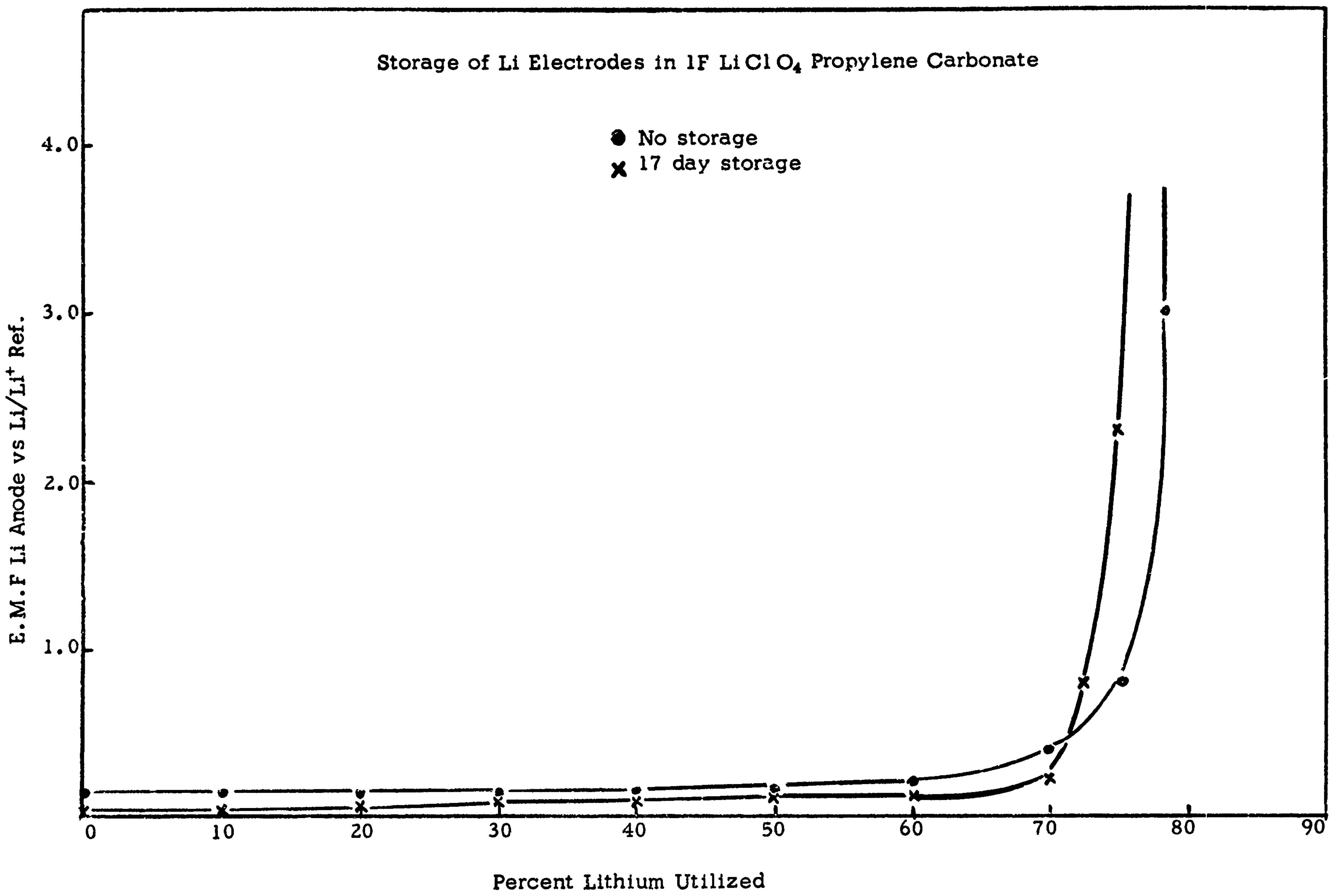

Storage of Li Electrodes in 1F LiClO₄ Propylene Carbonate
● No storage
✕ 17 day storage
E.M.F Li Anode vs Li/Li⁺ Ref.
4.0
3.0
2.0
1.0
0
10
20
30
40
50
60
70
80
90
Percent Lithium Utilized

FIGURE 31

Performance of Pressed Lithium Powder Anodes

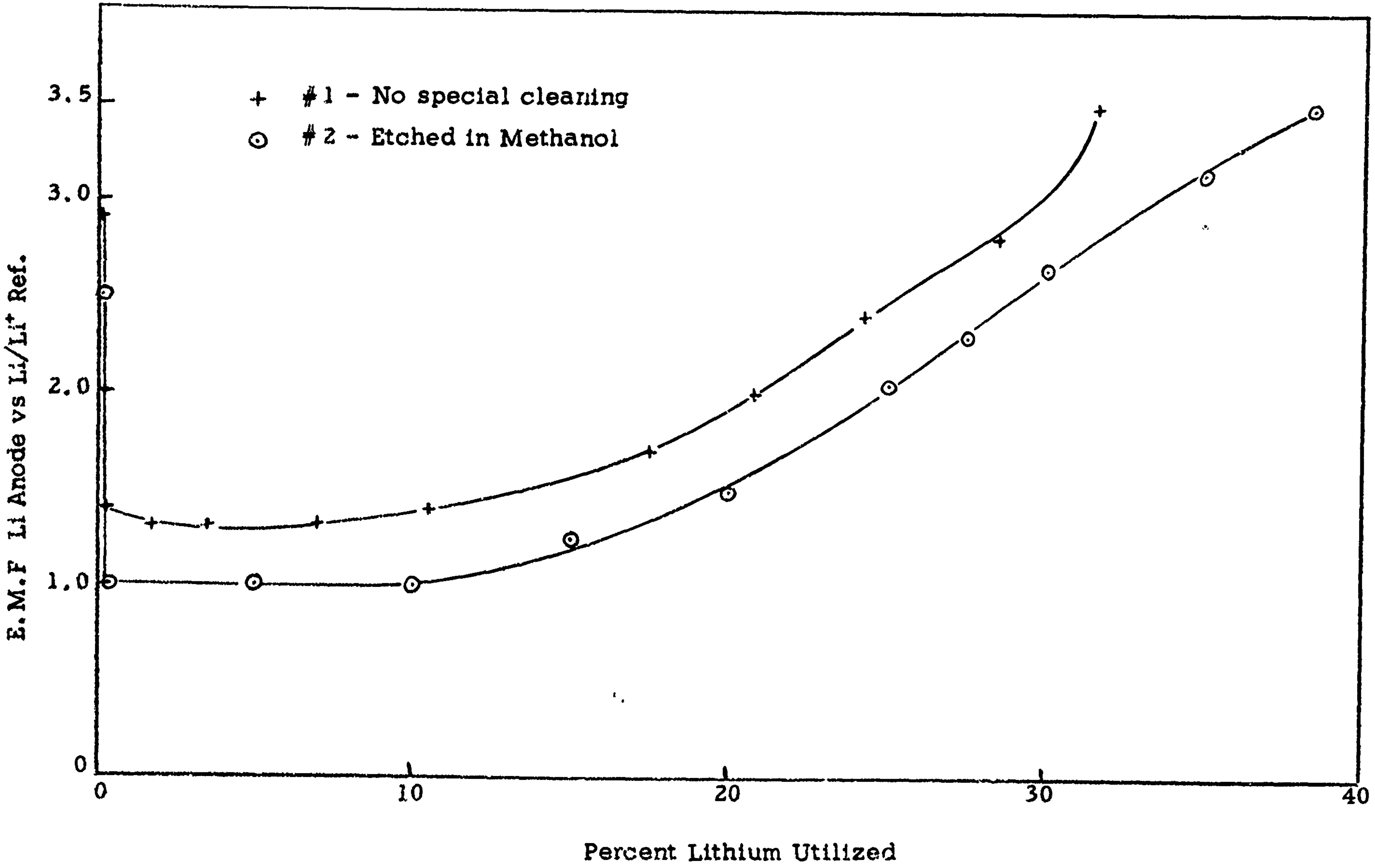


FIGURE 32

Hull Cell

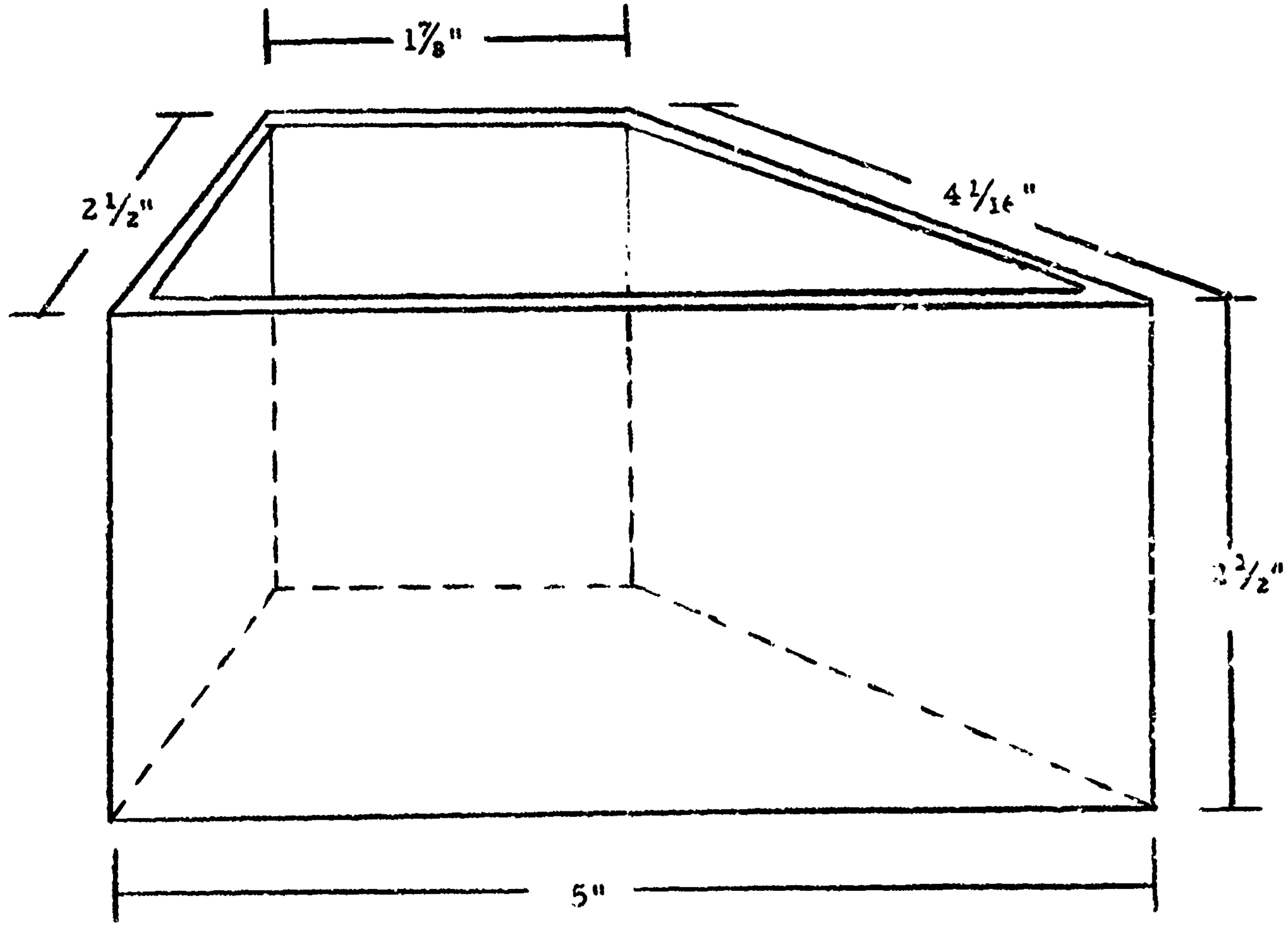
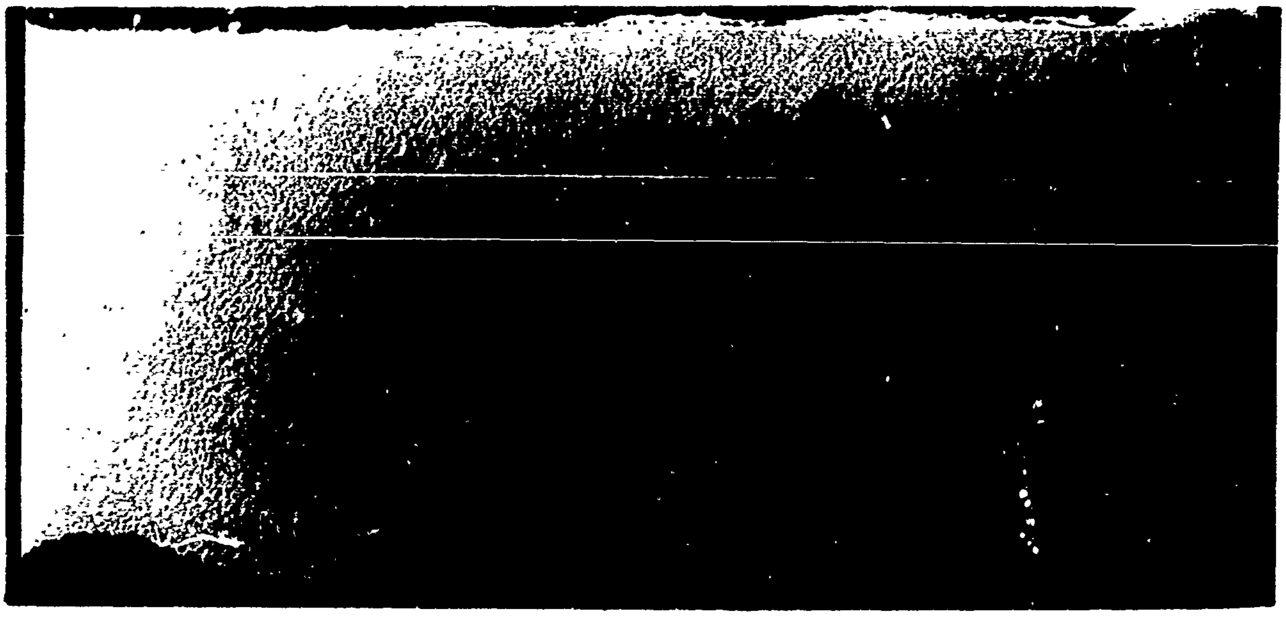


FIGURE 33

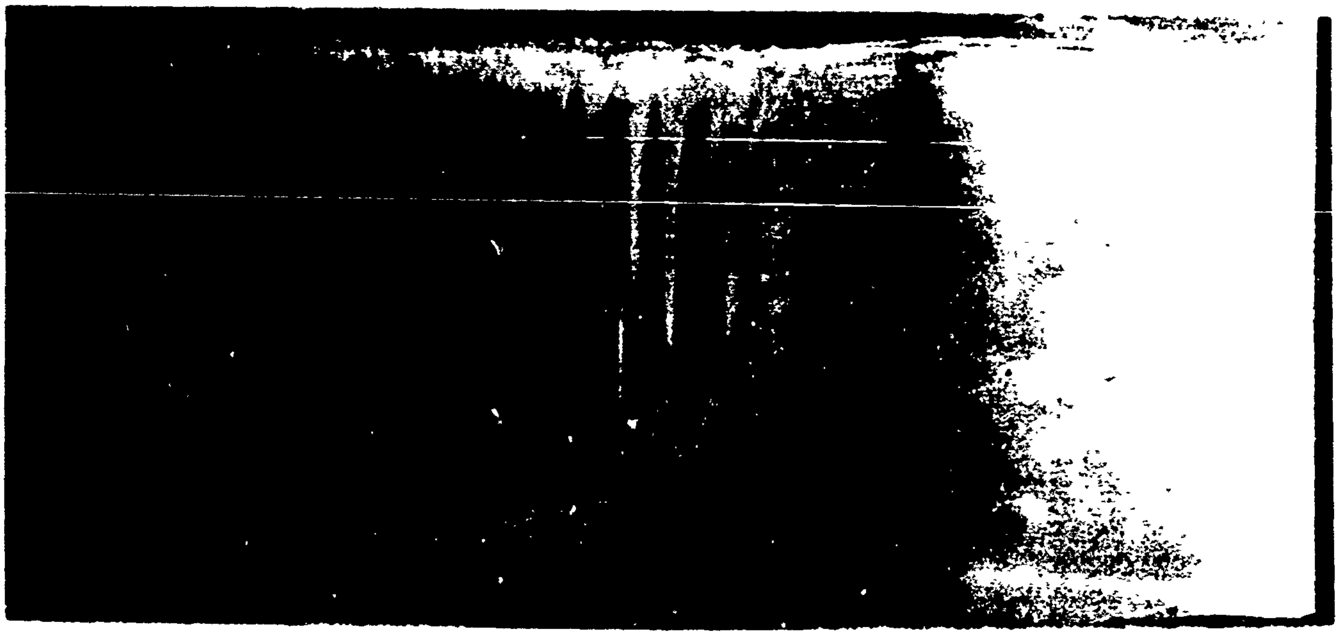


1 M $LiClO_4$ in prop. carb.   Current: 0.5 amp   Duration: 1 hour

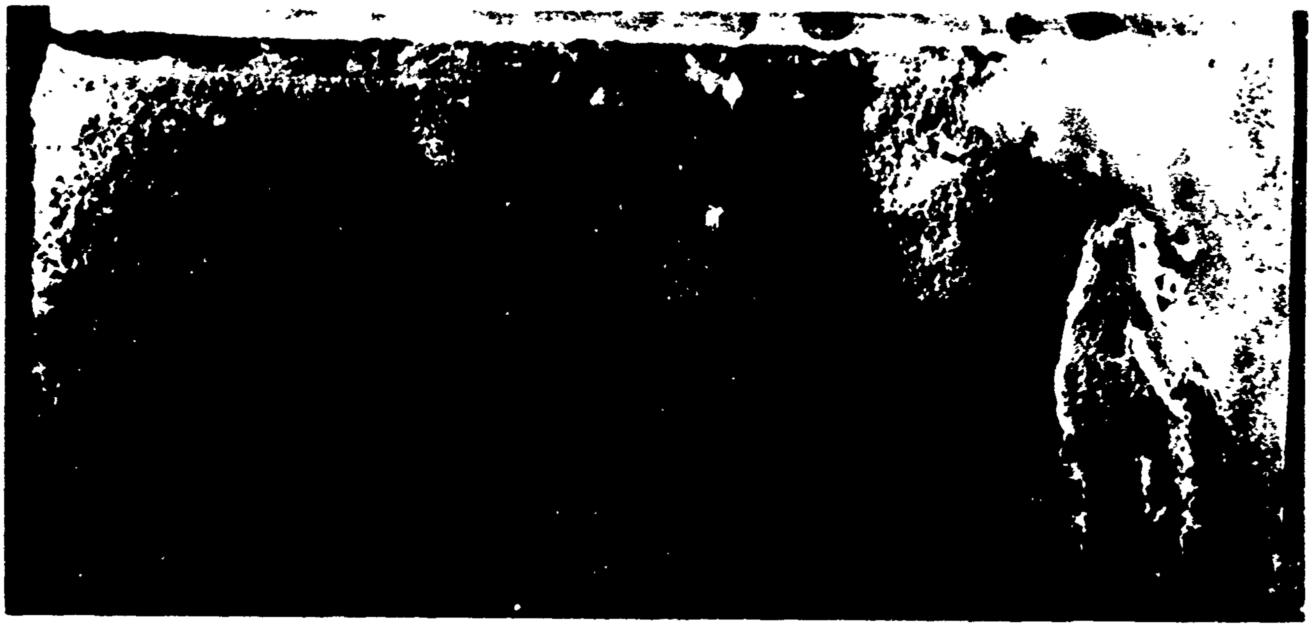
0.1 M $LiClO_4$ in prop. carb.   Current: 0.1 amp   Duration: 20 min

1 M $LiClO_4$ in DMF   Current 0.5 amp   Duration: 1 hour

Hull Cell Panels - Figure 34



Saturated LiCl in prop. carb. Current: 0.05 amp
Duration: 1 hour



1 M $LiClO_4$ in Acetonitrile Current: 0.5 amp Duration: 1 hour

Hull Cell Panels - Figure 35

Discharge of Electrodeposited Lithium Electrode

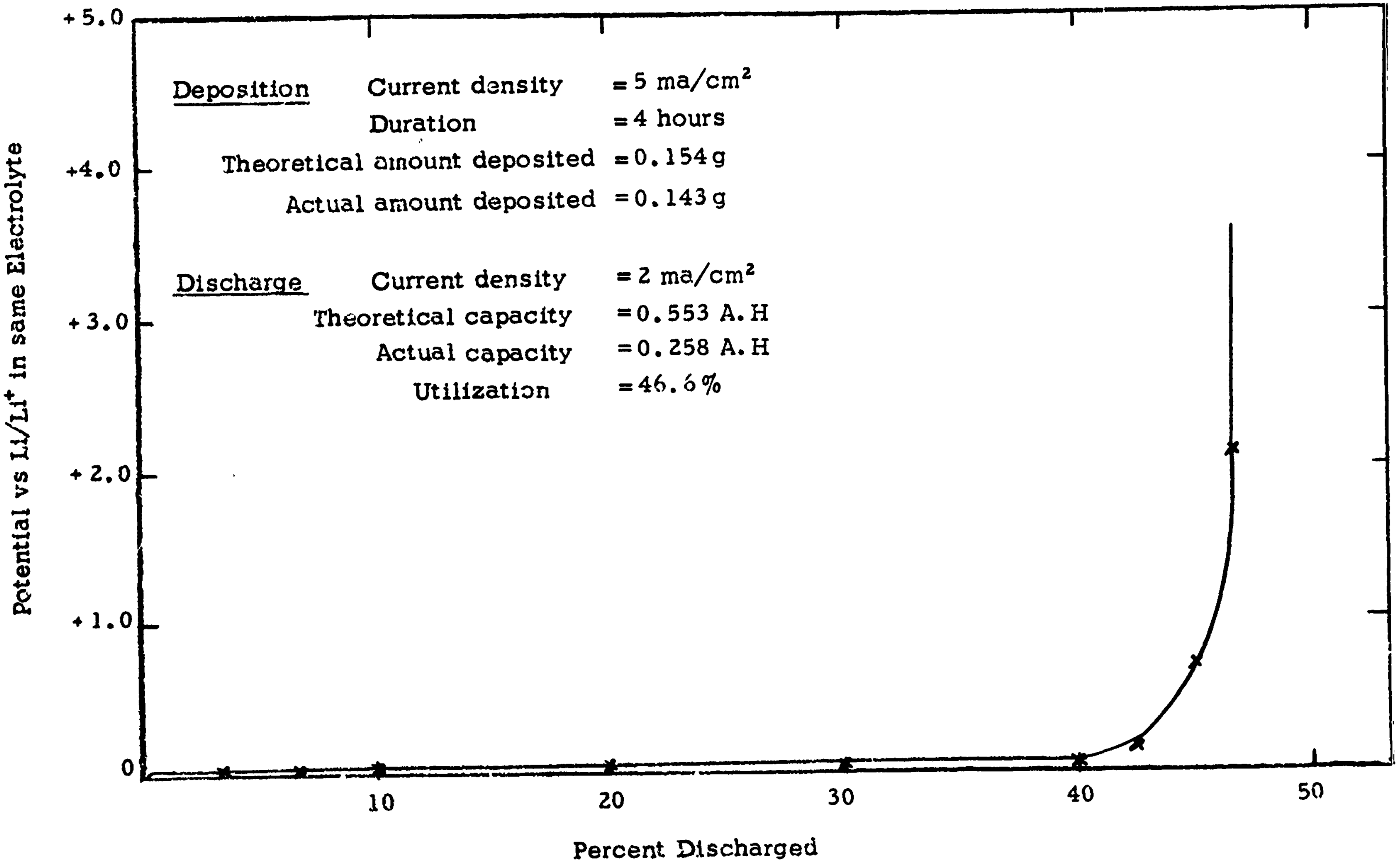
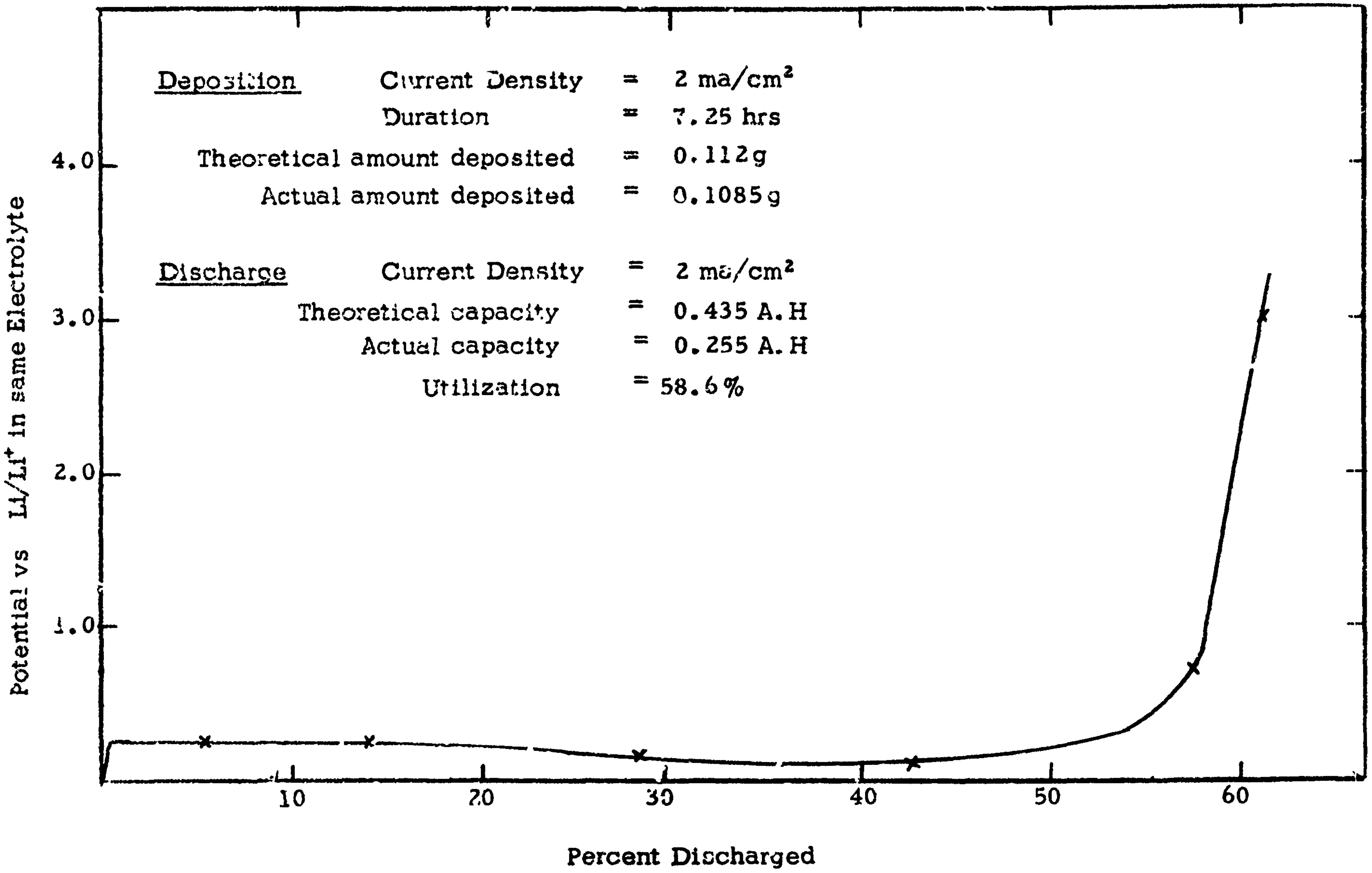


FIGURE 36

Discharge of Electroplated Lithium Electrode



Deposition Current Density = 2 ma/cm²
Duration = 7.25 hrs
Theoretical amount deposited = 0.112g
Actual amount deposited = 0.1085g

Discharge Current Density = 2 ma/cm²
Theoretical capacity = 0.435 A.H
Actual capacity = 0.255 A.H
Utilization = 58.6%

FIGURE 37

TEST CELL

▲ — — — Platinum Wire Electrodes

Material: Polypropylene
Scale: 1:1

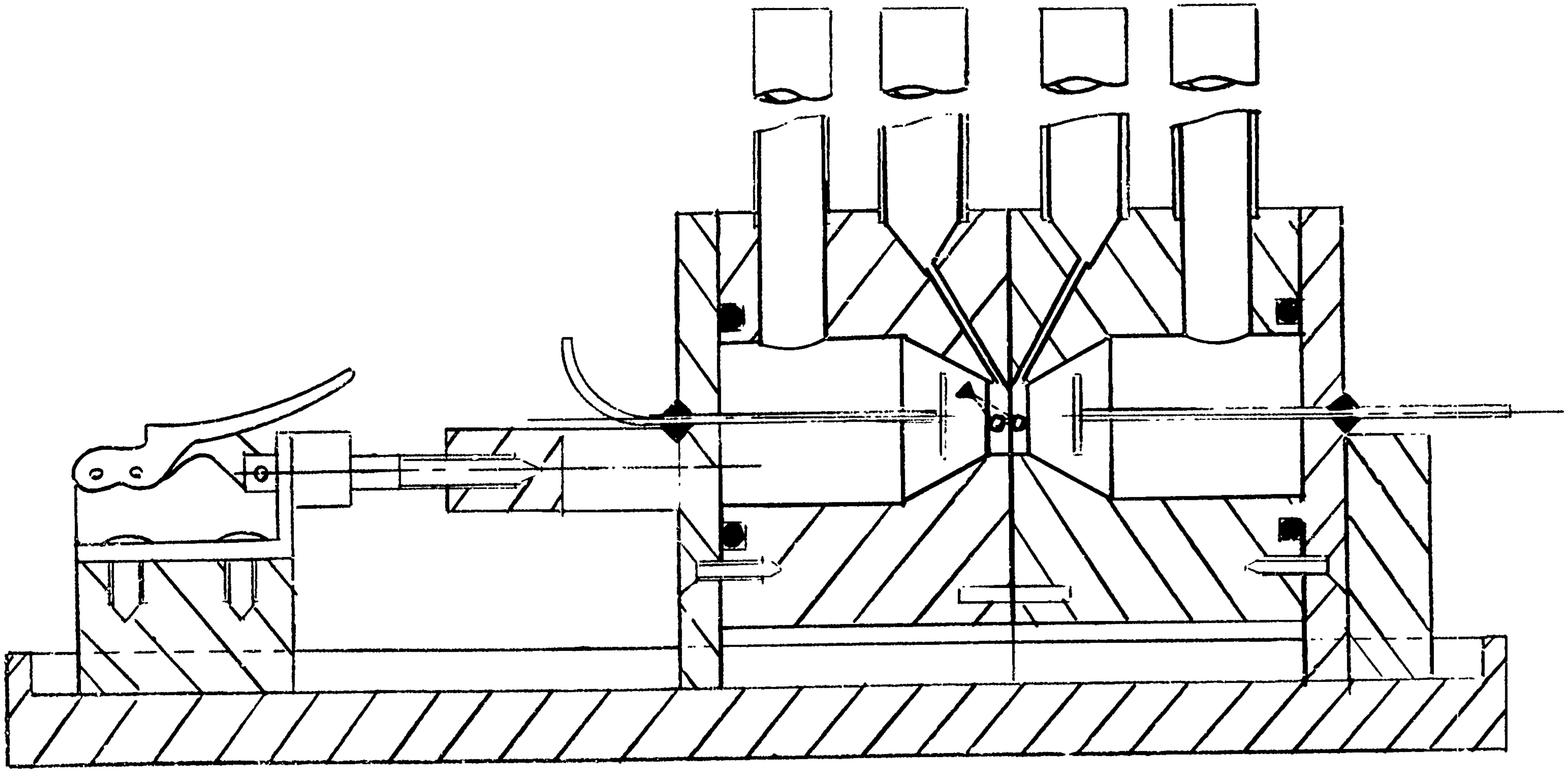


FIGURE 38

Performance of Li-CuF$_2$ Cells

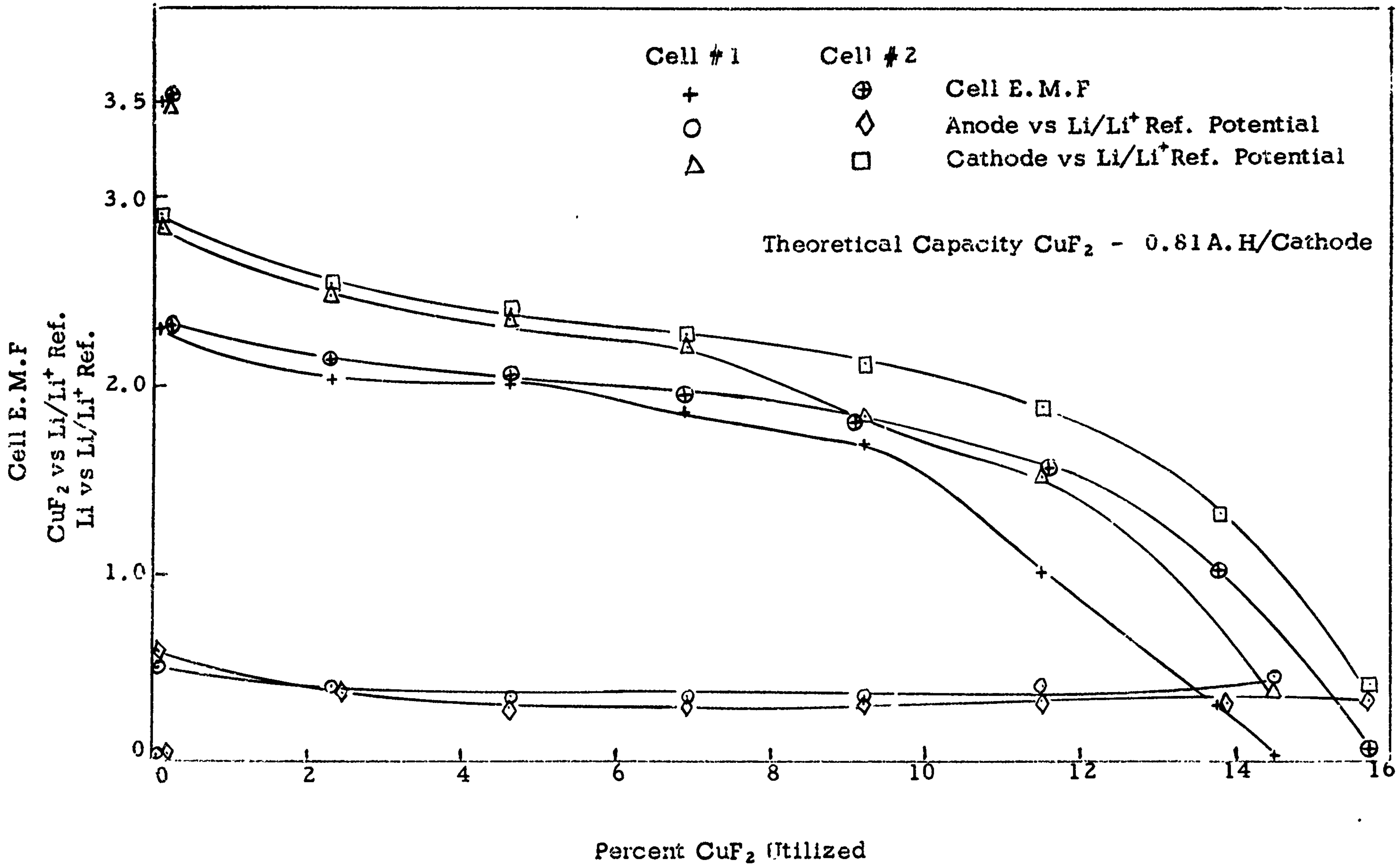


FIGURE 39

Performance Li - CuF$_2$ Cells

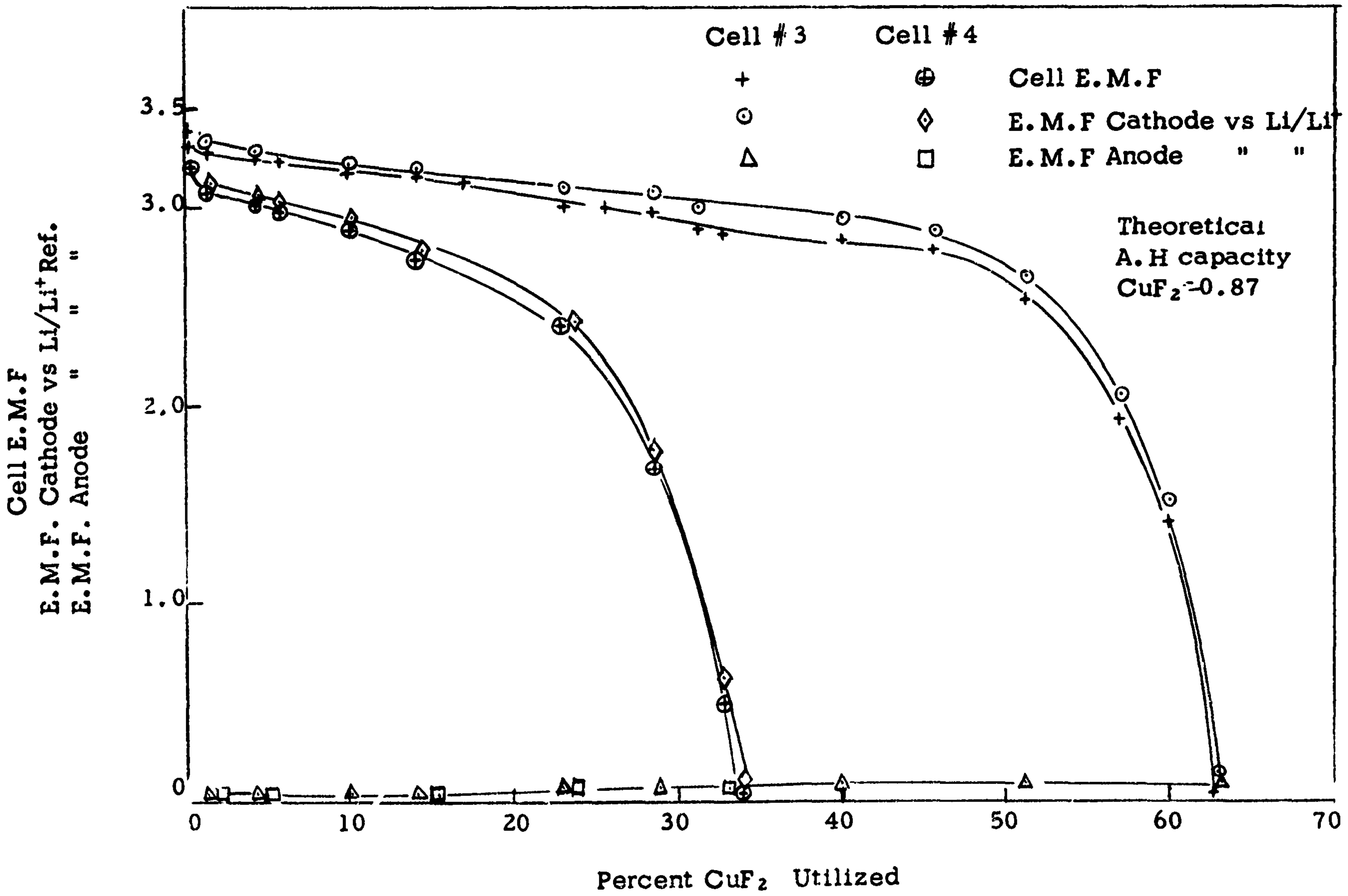


FIGURE 40

Effect of Compacting Pressure on Performance
of CuF_2 Cathodes

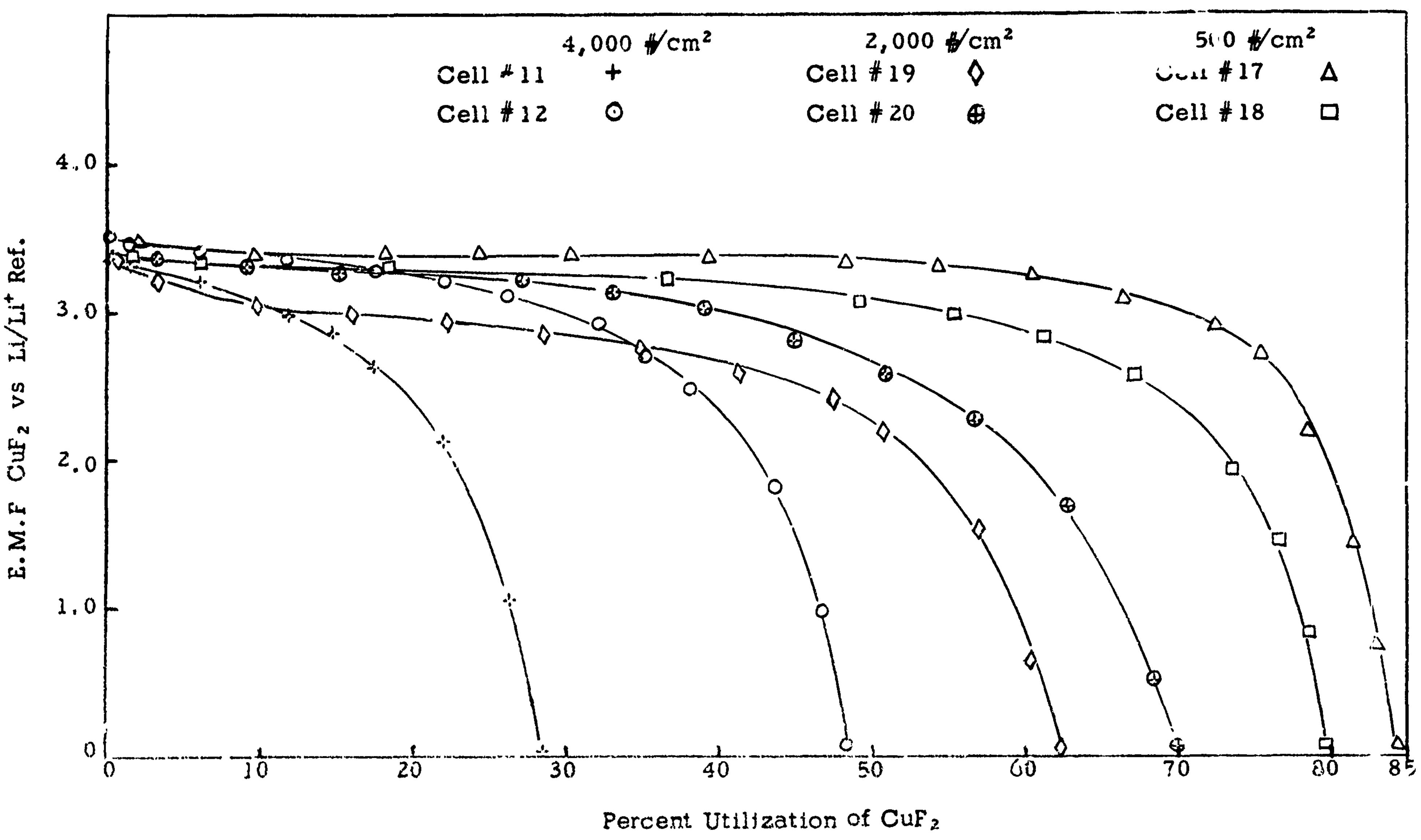
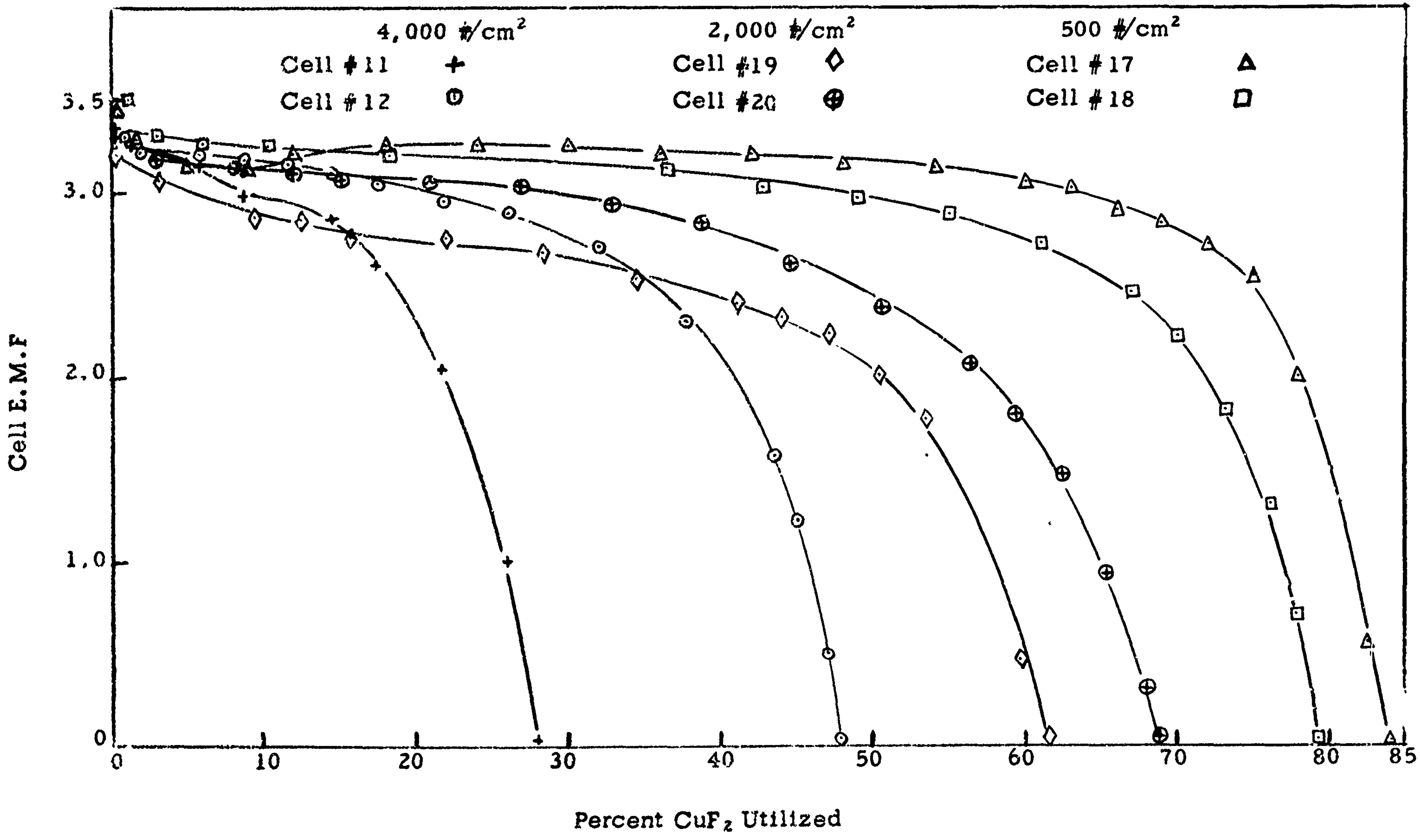


FIGURE 41



Performance of Li - CuF$_2$ Cells

Evaluation of Cathode Compacting Pressure

FIGURE 42

Evaluation of Effect of Sulfur in CuF_2 Cathodes

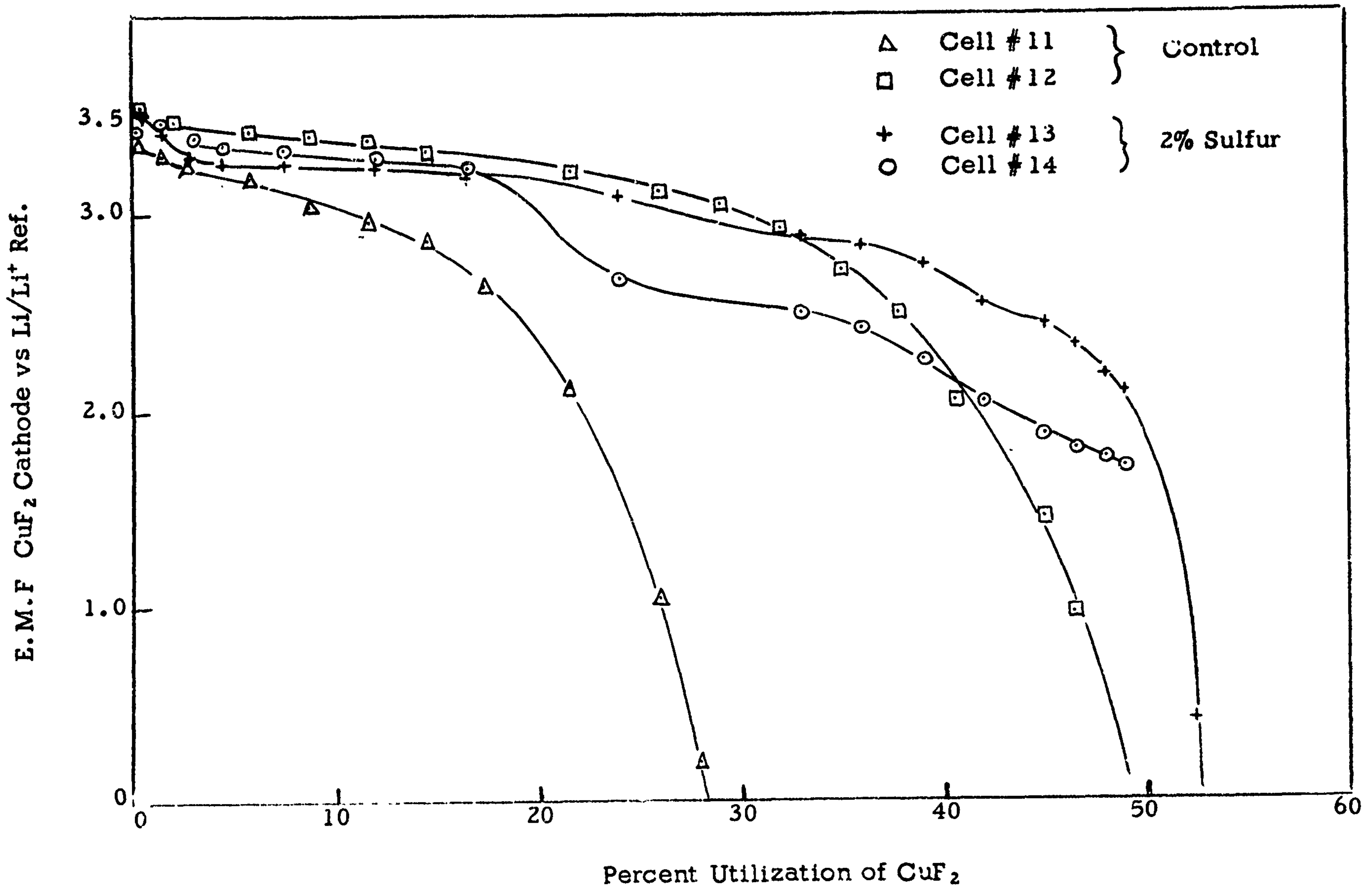


FIGURE 43

Effect of Sulfur on Performance of CuF_2 Cathodes

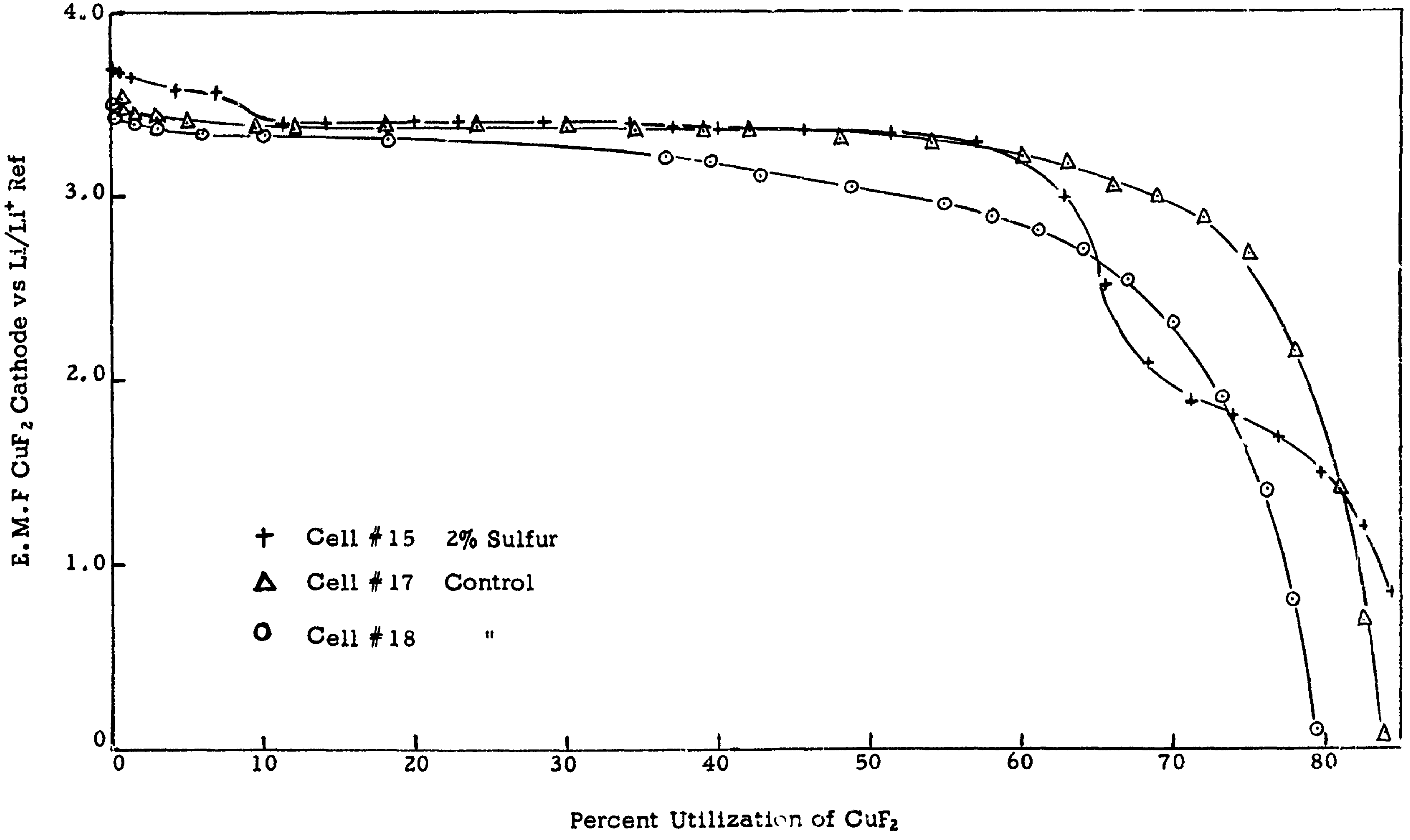


FIGURE 44

Performance of CoF_3 Cathode in a Li - CoF_3 Cell

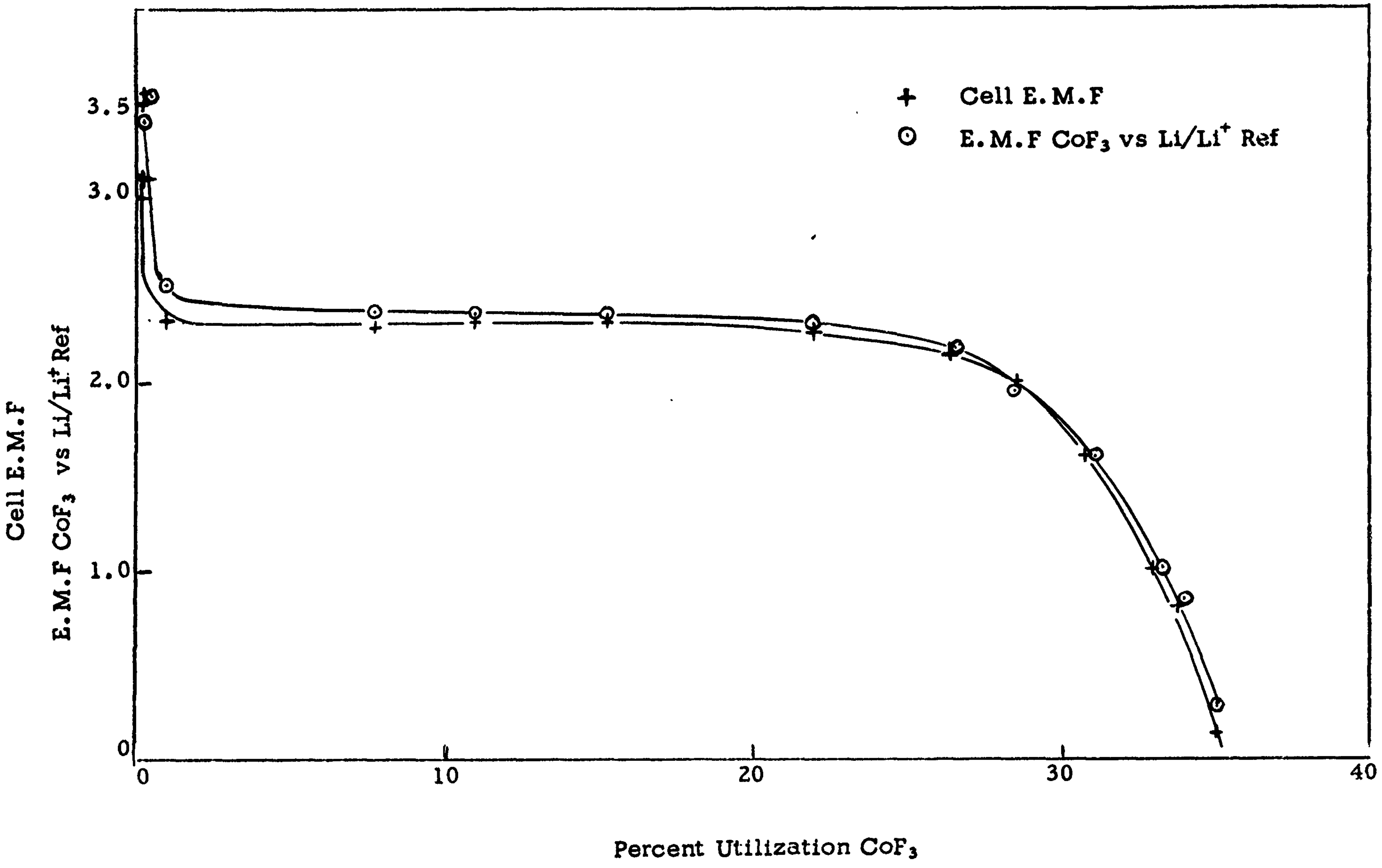


FIGURE 45

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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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13. ABSTRACT

The study of high energy density systems in the second quarter included: investigation of new electrolyte solvents; development of a technique for purifying propylene carbonate and other solvents; continued studies of corrosion and solubility of anode and cathode materials in various electrolytes; investigation of the effect of various fabrication and operating parameters on cathode performance; development of Li anode fabrication methods; and construction and testing of compact Li/CuF_2 cells.

Propylene carbonate of high purity was obtained by vacuum distillation from a basic oxide (CaO) or an alkali metal (Li).

Various new electrolyte solvents were screened to determine their compatibility with the $LiCuF_2$ couple, but none were found to be comparable to propylene carbonate.

A re-evaluation of solubility of CuF_2 in various electrolytes, using purified solvents, revealed generally low solubility, except in $Li\ Cl\ O_4$/acetonitrile, $Li\ Cl\ O_4$/nitromethane, and $AlCl_3$/propylene carbonate. Corrosion rates of Li in these electrolytes were high except for $LiClO_4$/propylene carbonate and $LiClO_4$/nitromethane.

Investigation of new CuF_2 cathode binders revealed that none of those tested was superior to polyethylene.

A re-evaluation of CuF_2 particle size, with regard to its effect on cathode performance, revealed that material of -170 mesh was the best of all fractions tested.

(Continued on Attached Sheet)

13. Abstract (Contd)

Cupric fluoride cathode performance was found to increase with an increase in operating temperature between 0°C and 30°C and decreased with further increase in temperature to 60°C.

Attempts to develop new CuF_2 cathode fabrication techniques, by electroforming copper fluoride in a fluoride containing electrolyte, and by chemical treatment of sintered CuO with BrF_3 were unsuccessful.

A study of various anode fabrication methods, including pressed Li ribbon and powder, and electroformed Li, revealed that the pressed ribbon method was by far the best, with regard to both performance and simplicity of fabrication.

A separator study was initiated to develop a material suitable for use in the Li/CuF_2 system, and having the characteristic of low electrical resistance, resistance to chemical attack, and the capability of acting as a barrier to migration of copper ions to the anode. Thus far, only asbestos filter paper has been used as a separator in cell construction but it is not completely satisfactory.

Li/CuF_2 cells of compact construction, containing two Li anodes and one CuF_2 cathode, and with asbestos filter paper insulation, have been tested. An energy density of 525 watt hours per lb (based on active materials consumed only) has been obtained with a current density of 1.7 ma/cm^2. Charged stand capability is limited to about 16 hours because of migration of copper ions to the anode, with consequent short circuiting of the cells. (Author)

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High Energy Density Systems						
Non-Aqueous Electrolyte Solvents						
Vapor Phase Chromatograms						
Decomposition Potentials						
Equivalent Conductance						
Corrosion Rates						
Electrochemical Behavior						
Cathode Structure Parameters						
Anode Fabrication						
Separator Characteristics						
Charged Stand Capability						

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