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Research and Development of a High Capacity
Nonaqueous Secondary Battery

by

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   The individual processes and phenomena attending secondary
cell operation are discussed and experimental data presented concerning
lithium deposition and cycling, ionic solvation, cathode construction
and discharge efficiency, and solvent purification. Solvents of particular
interest are propylene carbonate, butyrolactone, dimethylformamide,
dimethylsulfoxide, and acetonitrile.

Author

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SUMMARY

The objective of our work is to learn enough about the processes which occur during secondary cell operation to enable us, at the end of the contract period, to make appropriate recommendations concerning the direction in which future development work on secondary, non-aqueous cells should take.

A variety of phenomena and properties will influence cell performance. Some of these are discussed in the remainder of this summary. It is most unlikely that a fortuitous combination of necessary conditions will be found which immediately result in the development of a complete cell with satisfactory characteristics. Thus, we have continued to focus attention on specific phenomena and properties. The purpose of this is to generate enough data to allow some interpretation of the behavior observed with prototype electrodes and cells, and to indicate areas in which further study is required before it is expedient to undertake a serious cell development program.

An important property of the solvent is its ability to solvate ions. One expects significant differences to exist for different solvents. This is reflected in the solubility of salts as well as the oxidation-reduction potentials of redox couples. We have begun an investigation of the latter; and the most significant point is that copper (II) is evidently considerably less strongly solvated in butyrolactone, propylene carbonate, and acetonitrile than in water. This influences the relative stability of copper (I) and copper (II) to the degree that, in these solvents, copper (I) is in fact the species produced in largest quantity

on anodization. The solubility of CuF_2 has also been investigated. Most noteworthy is the enhanced solubility in the presence of lithium salts. Thus, in propylene carbonate we have found the solubility of CuF_2 to be about 0.00016 M, this increases to 0.02 to 0.03 M when the solution is made 0.1 M in $LiClO_4$ or $LiBF_4$. While, this may be the result of impurities we believe it more likely that copper (II) is displaced from its fluoride by lithium ions.

The mode of electrode construction is critical in determining the behavior of cathode salts. We have attempted to improve the performance of CuF_2 electrodes through the incorporation of Teflon powder binders. Efficiency still remained about 40-50% at currents of 0.5 to 5 mA cm^{-2}. These discharges were conducted in excess propylene carbonate - $LiClO_4$ electrolyte. The results may indicate that the reduction proceeds through an intermediate, soluble copper (I) species, which escapes from the electrode before further reduction can occur. We have attempted to improve the electrode structure through the initial incorporation and subsequent sublimation of naphthalene which, we believe, may increase the porosity. Again the maximum efficiency realized was 51% at 4.2 mA cm^{-2}. Considerable time is required to completely remove the naphthalene.

One expects a difference in performance between discharge in excess electrolyte and in starved electrolyte. Cells incorporating CuF_2 and lithium have been subjected to discharge in starved electrolyte. At currents of 1 to 10 mA cm^{-2} the discharge curves were flat, and there was little polarization but the efficiencies varied from 13% to 42% and reflect, we believe, inadequate cell construction and leakage of electrolyte from the cell.

Porous copper electrodes have been cycled in three electrolytes. Each cycle consists of anodic oxidation for a pre-determined period of time, followed by cathodic discharge to a specified cut-off voltage. Cycling was continuous. In a propylene carbonate - $LiAlCl_4$ copper could be cycled for 32 cycles at 10 mA cm^{-2} with 70-76% efficiency· That is, on cathodization 70-76% of the current passed during the preceding anodization could be recovered before polarization occurred. In butyrolactone - LiCl and dimethylformamide -

LiCl no satisfactory cycling could be obtained because, we believe, of the formation of soluble chloride complexes of copper. There is little doubt that copper metal is anodically oxidized with 100% efficiency; that is, there is little likelihood of parasitic reactions such as solvent oxidation. The problem is that of capturing the copper species produced on anodization in such a way that the material can be cathodically reduced.

To _induce_ cycling it may be necessary to incorporate an insoluble salt anion reservoir in the cathode. This has proved successful with the AgCl electrode where it was possible, by incorporating LiCl with silver powder to anodically oxidize the silver to AgCl, and subsequently reduced the AgCl back to silver with essentially 100% efficiency. This was done in a propylene carbonate - $LiClO_4$ electrolyte in which chloride ions were absent. The only source of chloride ions was the insoluble LiCl salt contained in the electrode.

The lithium electrode is somewhat sensitive to the presence of water. Solutions of $LiClO_4$ in propylene carbonate have been analyzed for water by vapor phase chromatography. It appears that water can be determined down to about 0.003% by weight (0.002 M). Preliminary electrochemical studies have been performed. It is seen, for example, that the chronopotentiograms in a solution 0.11 M in water do not sensibly differ from those in a solution 0.02 M in water. Efficiencies for lithium deposition of up to 83% can be realized in the 0.11 M water solution. While the presence of water is doubtless deleterious, its presence is evidently not manifested in any straightforward fashion. It is likely that smaller amounts of water are preferentially bounded by the ClO_4^- or, perhaps, the Li^+ ions and that the water so bound is not electrochemically active to such a degree as to profoundly affect the lithium deposition.

Bulk lithium electrodes have been used in several experiments. The results indicate that the Li^0/Li^+ couple is electrokinetically "reversible", that is, there is no evidence for serious activation overvoltage. There is evidence that the lithium metal rapidly becomes coated with a passivating film

which inhibits chemical reaction with the electrolyte and also results in a significant iR drop.

The primary problem with the lithium electrode is that of inducing more efficient deposition and decreasing the rate of chemical reaction. We believe this will turn out to be a much more complex problem than is generally understood. It has seemed desirable to develop a broader phenomenological description of cathodic behavior in various electrolytes. The results are described for various acetonitrile and propylene carbonate solutions. These results will not be further discussed in this summary other than to note that the results in acetonitrile are not, generally, qualitatively different from those in propylene carbonate and primarily reflect the greater rate of mass transport in acetonitrile because of its lower viscosity.

The purification of solvents is expected to be important. Work has continued and results are reported on the purification and subsequent gas chromatographic analysis of propylene carbonate, butyrolactone, dimethylformamide, acetonitrile, n-butyl formate, N-nitrosodimethylamine and dimethylsulfoxide. The results cannot be conveniently summarized other than to note that vacuum distillation does not effect as clean a separation as might be desired and that water, which is but one of a number of impurities in most of the solvents, has not been reduced to levels of less than 0.002 M, even after prolonged standing over molecular sieves.

I. INTRODUCTION

The answers to two questions of primary importance are sought with respect to secondary cell electrodes:

What properties must an environment have to allow one to induce cyclability of cathode materials?

What properties must an environment have to allow one to efficiently cycle the lithium electrode?

We believe much of the confusion that exists in the study of non-aqueous systems arises from an unsatisfactory differentiation between the inherent properties of materials -- anodes, cathodes, solvents, solutes, etc., -- and the nature of the interactions between materials.

A further problem in this area arises from the lack of established criteria by which systems or environments shall be evaluated. It is, therefore, as much an objective of our work to attempt to determine the best criteria by which systems should be evaluated with respect to further development as it is to determine what these systems are. In our work to date we have considered various individual phenomena and interactions which, we believe, are likely to be relevant to secondary cell operation. The criteria by which systems will be evaluated will be a composite of the degree to which systems show satisfactory behavior with respect to the various specific conditions required for cyclable cells.

A. Cathodes

For reasons discussed previously (3rd Quarterly Report, p.1), we still consider the CuF_2 electrode the best cathode candidate. The question of whether the CuF_2 electrode is cyclable is probably meaningless, so stated. The proper question is, what can be done to effect an environment in which one may expect to induce cyclability of CuF_2. We now consider the conditions

requisite for cyclability in describing the work of the past quarter.

1. The environment in which cyclability may be induced should be one in which the electrochemically active cathode material is trapped in the electrode region. This is to prevent direct chemical reaction with the anode material and to have the active material available for subsequent cathodic discharge.

The most desirable cathode material is probably an insoluble salt. During the past quarter we have investigated the solubility of CuF_2 and CoF_3 in four solvents (p.2): propylene carbonate (PC); butyrolactone (BL); dimethylformamide (DMF); and, acetonitrile (AN). The apparent solubilities are satisfactorily low, but these results should be considered tentative in view of solubilization through impurities in the salt or solvent.

The composition of the two salts was therefore analyzed (p.1,3-4). CoF_3, as received from the vendor, was found to be grossly impure. CuF_2 was found to be satisfactorily pure.

2. The environment in which cyclability may be induced should be one in which the electrochemically active cathode material may be efficiently discharged.

We have previously reported (3rd Quarterly Report, pp.68-79), the results of a large number of experiments concerned with the cathodic discharge of CuF_2. Efficiencies of 25-50% were generally realized. It is of interest to investigate what may be done to enhance efficiency.

During the past quarter, attempts were made to improve the physical stability of the CuF_2 electrode through incorporation of a Teflon binder (p.18). The results were unsatisfactory in that improved efficiency at low currents was not realized.

During the past quarter, we have attempted to improve the performance of the CuF_2 electrode through inducing porosity by incorporation of naphthalene. in the electrode mix, followed by subsequent sublimation (p.19). The results

were no better than those obtained by incorporating a salt in the mix which, by solubilization, may result in a porous electrode or a more concentrated electrolyte.

It is a possibility that inefficiency might be inherent in the operation of cathodes in poorly conducting, non-aqueous media. We have studied the discharge of seven other cathode materials (p. 20-23). Efficiencies were sufficiently satisfactory to indicate that the nature of the medium is not inherently limiting to cathodic discharge.

It is a possibility that inefficiency might be inherent in the nature of the reduction of CuF_2. We have attempted to use X-ray diffraction as a means of studying the reaction (p. 1-2). The results are not yet satisfactory because of a number of experimental problems.

3. The environment in which cyclability may be induced should be one in which the reduction product of the electrochemically active cathode material may be subsequently re-charged, anodically, to its original form.

For an insoluble salt cathode material, this environment must be one in which exists a reservoir of anions available for re-precipitation of the cathode salt on charge. Two types of reservoirs are considered; one in which the anions are soluble; the other in which the anions are present in an insoluble salt. We have considered both types of situations.

The cycling of copper electrodes in three soluble chloride media has been investigated (pp. 26-32). In only one situation could the copper be anodically oxidized to an insoluble salt. In the other, the copper ions were not rendered immobile on anodic oxidation but simply went into solution. Satisfactory cycling behavior up to thirty-two cycles was obtained in the first electrolyte.

The use of an insoluble anion reservoir has been investigated with AgCl electrodes (p. 25-26). The results indicate that the principle is valid

and can be used for secondary cell cathode cycling.

We do not yet have enough information to indicate what types of electrolytes may be required for similar operation of the CuF_2 electrode and are attempting to acquire such information through such measurements as oxidation potentials, which reflect important differences between solvents with respect to solvation energies.

B. Anodes

We know the lithium electrode is cyclable in various media. The problem remains one of inducing more efficient cycling. In the past our approach has been to consider what type of electrochemical behavior would be observed if the reduction of lithium were a simple, reversible, one-electron process and compare this with the type of behavior actually observed (2nd Quarterly Report, pp. 7-26). The results have consistently shown that the process of reduction to the metal is, in fact, not simple.

To learn more about the general nature of cathodic reduction in non-aqueous electrolytes we have continued to investigate other systems (p. 49-50, 56-63) and hope, by the end of the contract period, to have established a fairly clear phenomenological description of a sufficient variety of systems to allow a reasonable assessment of the expected relative utility of the systems.

We have examined the behavior of bulk lithium electrodes (pp. 43-48). This has been of interest primarily in indicating the existence of resistive films formed on the electrode surface through reaction with the electrolyte which then inhibit further reaction.

The cycling of the lithium electrode has been studied over several cycles (pp. 42-43). In the systems chosen for study the results did not indicate a catastrophic or serious cumulative failure.

The role of impurities on the lithium electrode remains unsolved. We have further investigated the effect of water and found (pp. 33-41) in the conditions studied, no catastrophic effect on lithium deposition.

C. Solvents

Solvents have been examined with respect to purification through vapor phase chromatography (pp. 51-56).

II. CATHODES

II-A. Characterization of CuF_2 and CoF_3

II-A-1. X-ray examination

X-ray diffraction has been used as an auxiliary technique for studying electrode behavior. Our initial objective was simply to examine the electrode both before and after discharge to see what insoluble materials form as a result of discharge.

A major problem involved the pick-up of water both by the CuF_2 and by the $LiClO_4$ incorporated in the electrode mix. The pick-up of water by CuF_2 is shown by the data given below. Samples of CuF_2 taken from the bottle were treated as indicated. The subsequent X-ray spectra were well-defined. All of the lines could be identified as belonging either to CuF_2 or to $CuF_2 \cdot 2H_2O$. The relative intensities of the lines agreed satisfactorily with those given in the literature. For convenience we compare the relative intensities of the two strongest lines; for CuF_2 at 3.219Å, and for $CuF_2 \cdot 2H_2O$ at 4.72 Å.

Sample Treatment	Relative Maximum Intensity CuF_2 : $CuF_2 \cdot 2H_2O$	
Powder, directly from bottle	3.3	0.7
Powder, dried in vacuum oven at 150°C for 1/2 hr.	7.4	ca. 0.3
Powder pressed at 6000 lb.		
after 1 hr.	5.8	2.0
after 6 hrs.	4.5	3.0
after 23 hrs.	3.0	4.3
after 47 hrs.	2.0	4.8
Powder, placed in desiccator with water	0.0	3.7

It would appear that the sample used is largely anhydrous CuF_2.

Next, several mixes of CuF_2, $LiClO_4$, and acetylene black were prepared and subjected to X-ray examination. The results were quite variable. In the "best" mix the relative intensity of the major CuF_2 line to the $CuF_2 \cdot 2H_2O$ line was 2.5 to 1.0. However, in another mix no CuF_2 lines were observed at all, indicating extensive hydration. The $LiClO_4 \cdot 3H_2O$ spectrum was evident in varying degree in all mixes. In addition a number of unknown lines were observed at the following spacings: 6.32, 5.71, 5.27, 4.35, 4.06, 3.92, and 3.83Å. We do not know the source of these lines. We have no information on the X-ray spectrum of anhydrous $LiClO_4$, but certainly such wide spacings as 6.32Å cannot derive from this material.

Finally, two of the mixes were discharged to 30% of theoretical capacity and the spectra examined. Two materials were evidenced in the discharged mixes, CuF_2 and $CuF_2 \cdot 2H_2O$. No lines for $LiClO_4 \cdot 3H_2O$ were observed. All of the previously described unknown lines disappeared except that line at 5.27Å; which was quite pronounced in both discharged specimens. In addition the first line for metallic copper, at 2.088Å, was observed, though the intensity was weak. Since this line is sufficiently widely separated from the nearest lines for CuF_2 or $CuF_2 \cdot 2H_2O$, it is probable that metallic copper had, in fact, been formed. We had also sought evidence for the formation of insoluble LiF; however, the three strongest lines for this material overlap those for $CuF_2 \cdot 2H_2O$ and it was not possible to obtain information on the presence of LiF.

II-A-2. Solubility of CuF_2 and CoF_3

To a 50 ml. sample of solvent was added enough solid CuF_2 or CoF_3 such that, if totally soluble, the solution would be 0.1 M in the salt. The samples were allowed to stand, with frequent agitation, in plastic stoppered flasks for one month. The specific conductance of the solutions was measured and in addition the concentration of soluble copper or cobalt species

measured as follows. Ten ml. of solution were added to a 100 ml. volumetric flask. To this was added fifteen ml. of a 1 M NH_3/1 M NH_4 Cl buffer and the solution diluted to 100 ml. The solution was examined polarographically, and from the diffusion current the concentration in the initial samples was determined by comparison with the diffusion currents obtained with standard copper or cobalt solutions. In an ammonia buffer the reduction of copper (II), polarographically, proceeds in two steps. $E_{1/2}$ for the first reduction is at about -0.1V, and for the second at about -0.35 V. The height of the second wave should be double that of the first and this was observed for all four copper samples. The polarographic reduction of cobalt in the ammonia buffer is more complex. $E_{1/2}$ for the first wave occurs at such potentials that it cannot be separated from the anodic dissolution wave of mercury. This reduction is of cobalt (III) to cobalt (II). The second wave, with $E_{1/2}$ about -1.05 V, is for cobalt (II) to cobalt (0). Since two electrons are involved in the second reduction, the total height of the second wave is triple that of the first. In propylene carbonate, butyrolactone, and acetonitrile it was observed that the first wave was absent, indicating that only cobalt (II) was actually present in solution. In dimethylformamide the double wave was obtained indicating the material in solution to be cobalt (III), this, however, may have resulted from some oxidative attack of cobalt (II) to form the cobalt (III) dimethylformamide complex.

Table 1

SOLUBILITY OF CuF_2 AND CoF_3 IN ORGANIC SOLVENTS

Solvent	CuF_2 Conc. (M l^{-1})	Specific Conductance (ohm^{-1} cm^{-1})	CoF_3 Conc. (M l^{-1})	Specific Conductance (ohm^{-1} cm^{-1})
Propylene Carbonate	0.00016(Cu^{+2})	3.5×10^{-6}	0.0011 (Co^{+2})	6.0×10^{-5}
Butyrolactone	0.00022(Cu^{+2})	5.1×10^{-6}	0.00126(Co^{+2})	7.4×10^{-5}
Acetonitrile	0.00075(Cu^{+2})	2.3×10^{-4}	0.00053(Co^{+2})	1.7×10^{-4}
Dimethyl-formamide	0.00034(Cu^{+2})	1.4×10^{-5}	0.0017(Co^{+3})	2.2×10^{-4}

We do not consider such data necessarily valid since they may reflect the presence of solubilizing impurities in the solvent and in the salt. We were particularly suspicious that the CoF_3 was rather grossly impure since the brown material contained pieces of both metallic looking and fibrous material. This material was examined in two ways. The total cobalt content was determined by weighing out a sample of the "CoF_3" and dissolving by warming with concentrated HCl. Water was added and an excess of concentrated ammonia to convert the solution to a 1:1 NH_3/NH_4Cl buffer. A few drops of 30% H_2O_2 were added and the solution warmed until gas evolution ceased. Finally more of an ammonia buffer was added and the solution examined polarographically. The polarogram was excellent, corresponding to that expected for a cobalt (III) – ammonia system, indicating complete oxidation of cobalt (II) by the hydrogen peroxide. The results indicated the salt to contain 8.89 millimoles of total cobalt per gram of salt. The actual amount of cobalt (III) in the salt was assayed by adding an amount of salt to a hydrochloric acid – potassium iodide solution. The iodine generated through oxidation by cobalt (III) was backtitrated with sodium thiosulfate. The results indicated the salt to contain 4.25 millimoles of cobalt (III) per gram of salt. Assuming both cobalt (II) and cobalt (III) to be present as the anhydrous fluorides one calculates the initial salt to contain 49% by weight CoF_3 and 45% by weight of CoF_2, the remaining 6% being impurities.

II-B. <u>Formal Reduction Potentials in Nonaqueous Solvents</u>

The procedure used by us for determining the formal reduction potentials of various metals in non-aqueous solvents involved the <u>in-situ</u> generation of the metal ions. Specifically, the metal of interest is anodically oxidized in quiet solution for a given period of time; the open circuit potential immediately after the current is turned off is the quantity of interest.

A conventional H-cell was used. The large compartment contained about 200 ml. of electrolyte and in this compartment the usual lollipop

electrode assembly was used for the working electrode. A platinum helix in the same compartment was the counter electrode. In the smaller compartment, containing about 25 ml. of electrolyte and separated from the larger compartment by a fritted glass disc, was immersed a silver wire.

The electrolyte in both compartments was a 0.5 M $LiClO_4$ solution in the solvent of interest. In addition, to the solution in the smaller compartment (containing the silver wire) was added an amount of solid $AgClO_4$ such that the concentration of this salt was 0.01 M. Thus the smaller compartment comprised the reference electrode, the Ag/Ag^+ (0.01 M) couple.

The purpose of using the $LiClO_4$ solutions was three fold: to inhibit the development of density gradients during electrolysis and subsequent convective effects, to maintain the activity coefficients constant, and to prevent ionic migration. These are, of course, the reasons supporting electrolytes are normally used in electrochemical experiments.

The metal in question was anodically oxidized, in quiet solution, at various currents for exactly 25 sec. The potential during anodization and the open circuit potential after anodization were recorded. In Figure 1 are shown a series of runs performed on silver in propylene carbonate, 0.5 M in $LiClO_4$.

Since there is a recorder time lag of about 0.5 sec. for full scale deflection, we have arbitrarily used the potential observed exactly 0.5 sec. after the cessation of anodization as the potential of interest. The appearance of the anodization curves varied from metal to metal and from solution to solution. Typical curves are shown in Figure 2 for the other three metals studied, copper, cadmium, and lead. Although the appearance of the anodization curves was not very reproducible, the subsequent open circuit potential traces were reproducible.

In Figure 3 are shown results obtained in propylene carbonate and acetonitrile solutions. In Figure 4 are shown the results obtained in the butyrolactone solution. Each point in the two figures gives the potential

5
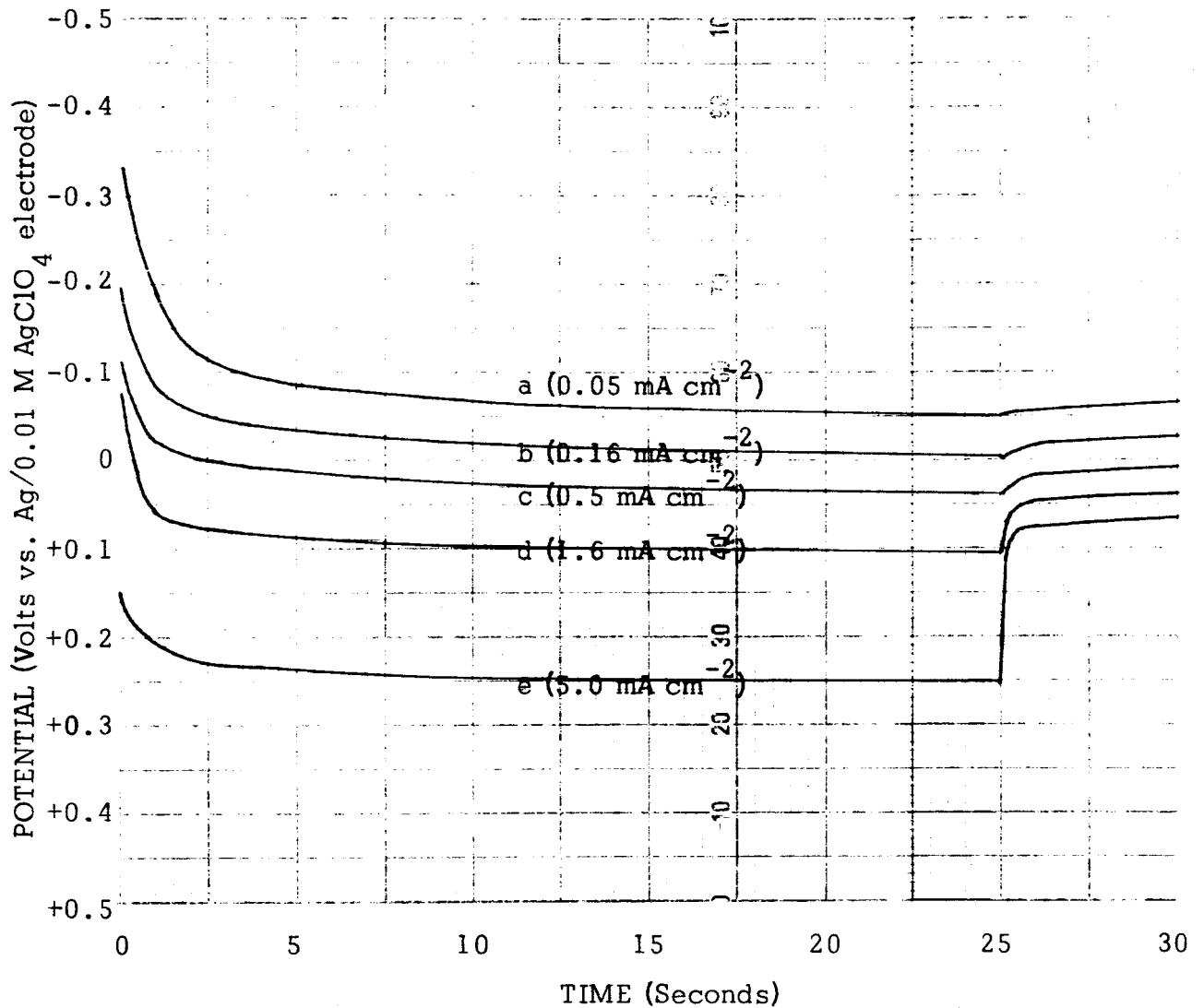
Figure 1: ANODIC DISSOLUTION OF SILVER IN PROPYLENE CARBONATE

Measurements performed in propylene carbonate, 0.5 M in $LiClO_4$. A silver metal disc was anodized at the current density indicated in quiet solution for 25 sec. The potential during anodization and the open circuit potential following anodization were recorded as shown in the above figure.
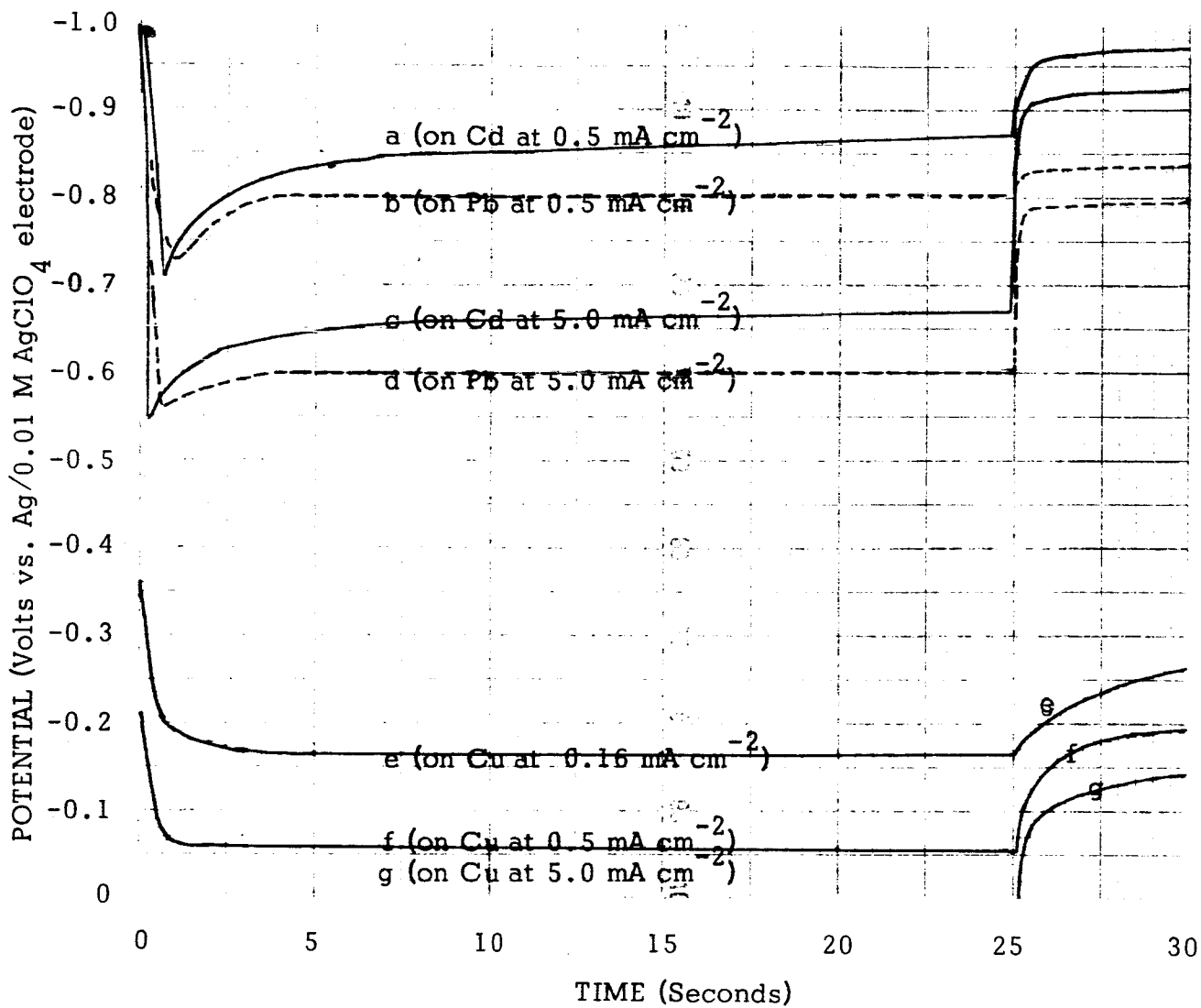
Figure 2: ANODIC DISSOLUTION OF CADMIUM, LEAD AND COPPER IN PROPYLENE CARBONATE

Experiments performed in identical fashion to those described in figure 1.
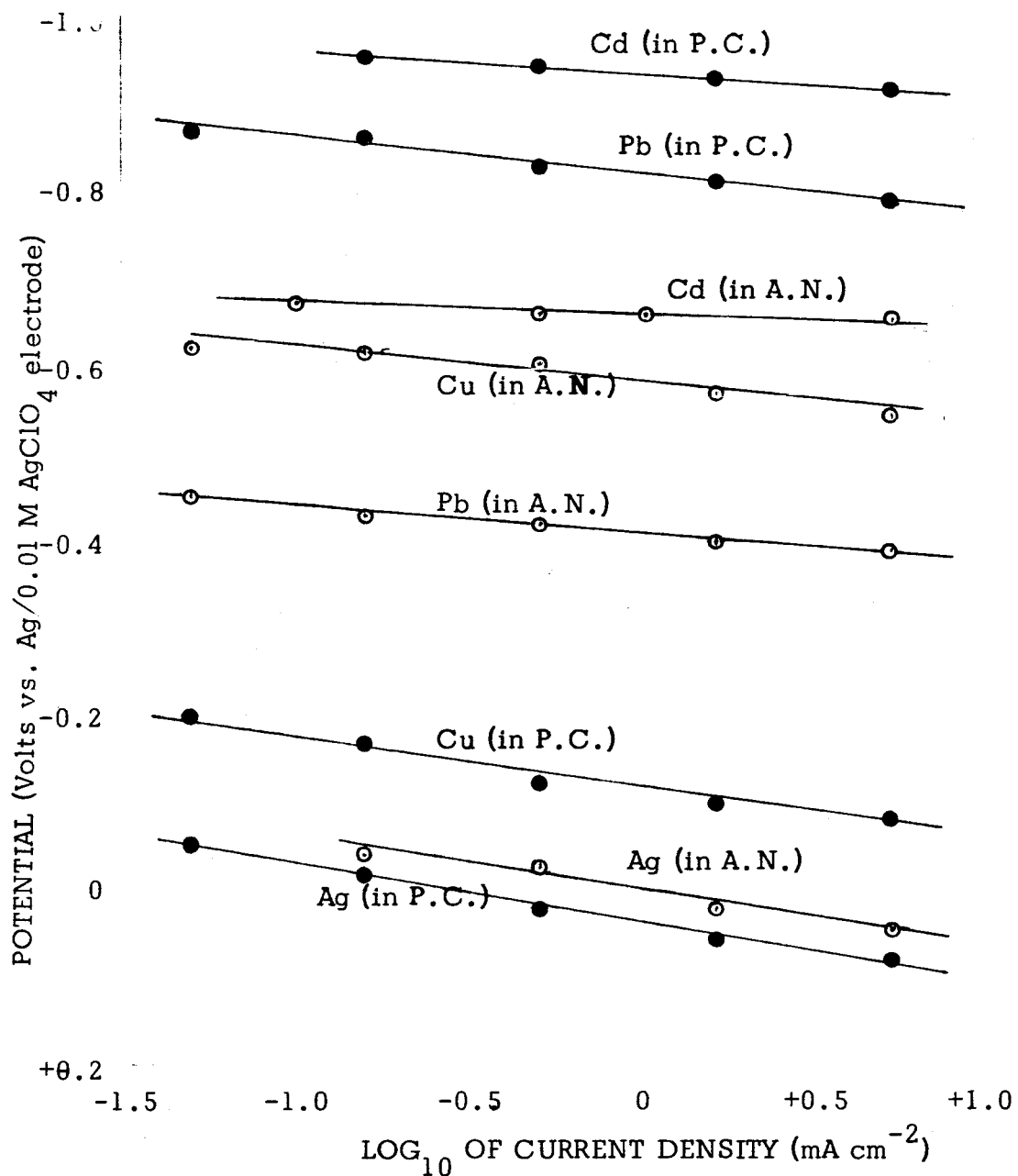
Figure 3: REDUCTION POTENTIALS OF METAL/METAL ION COUPLES

Measurements obtained, as described in text, in propylene carbonate (P.C.) and acetonitrile (A.N.).
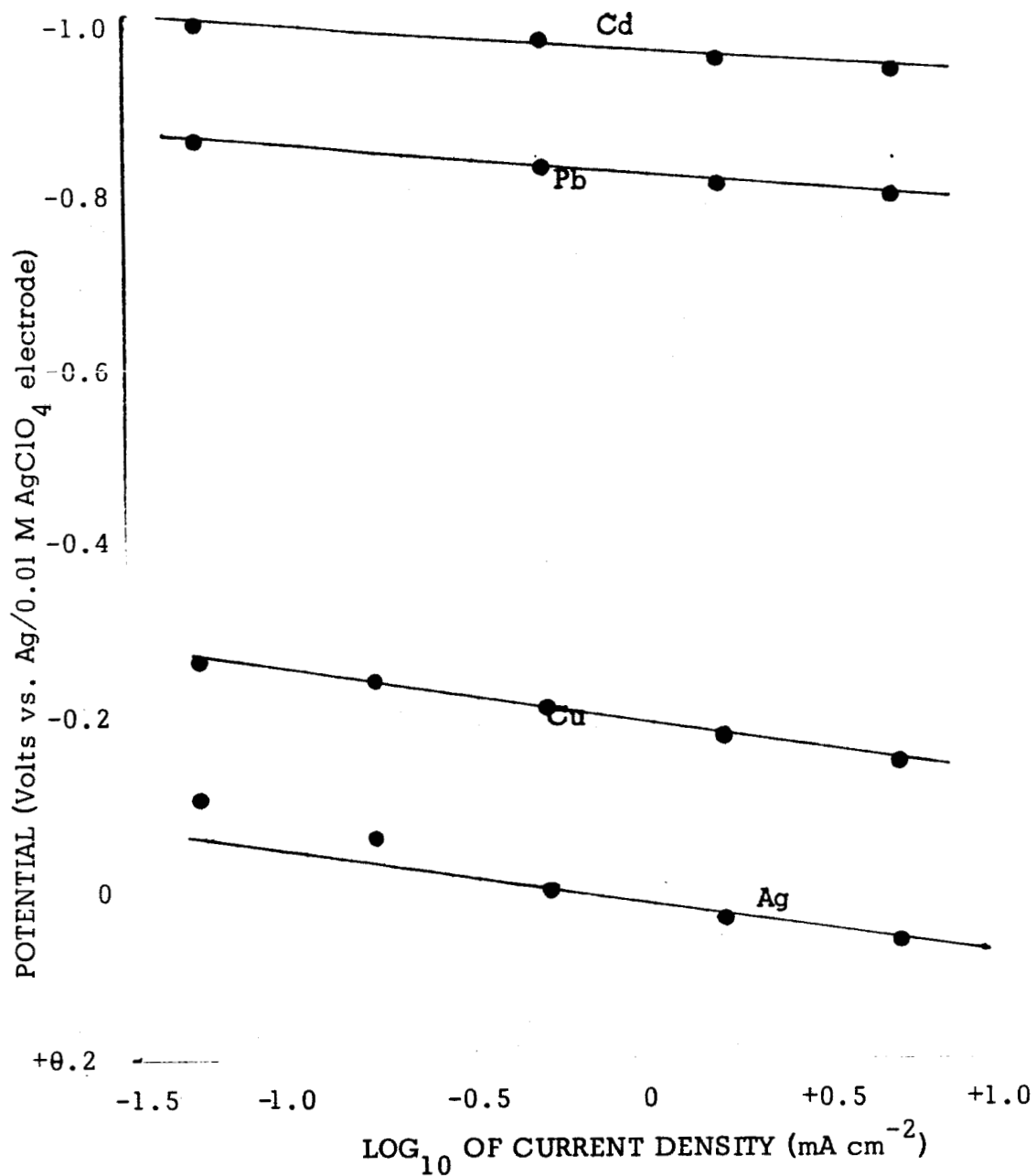
Figure 4: REDUCTION POTENTIALS OF METAL/METAL ION COUPLES

Measurements obtained, as described in text, in butyrolactone.

measured 0.5 sec. after the cessation of anodization (performed on the metal indicated) at the current indicated.

We are interested in comparing the potentials of 0.01 M solutions of the metal ion in the 0.5 M $LiClO_4$ solution. To make this comparison we use the silver electrode behavior as a reference system. As an example, we note, from Figure 3, that the potential observed on the silver electrode was zero versus the reference electrode at log i = -0.5, or i = 0.28 mA cm^{-2}. Since the reference electrode is an Ag/0.01 M Ag^+ system, when the potential of the working silver electrode is equal to that of the reference electrode, the concentration of silver ions at the working electrode surface must then be 0.01 M. Thus we may say that, in the propylene carbonate, 0.5 M $LiClO_4$, solution anodization of silver metal at 0.28 mA cm^{-2} for 25 sec. in quiet solution will produce, 0.5 sec. after cessation of anodization, a concentration of silver ions at the electrode surface of 0.01 M.

To determine the formal potentials of the other couples we first assume the diffusion coefficients are similar to that of the silver ion. We also assume that the equilibrium potential is rapidly established, that is, we assume the exchange currents for copper, lead, and cadmium to be sufficiently large that the rate of establishment of the true equilibrium potential is more rapid than the recorder response.

To continue the example, we consider copper which, for reasons later discussed in this section, we assume to be anodized to copper (I). If the assumptions discussed in the preceding paragraph are valid then, as with silver, a current of 0.28 mA cm^{-2} for 25 sec. in quiet solution should result in a concentration of copper (I) at the electrode surface of 0.01 M, 0.5 sec. after cessation of anodization. The potential corresponding to this current on Figure 4 (log i = -0.5) is -0.15 V. We take this to be the formal potential of the 0.01 M copper (I)/copper metal redox couple versus the silver reference system.

Since lead and cadmium are oxidized to the divalent species, it is clear that twice the current, i.e., $0.56 \, mA \, cm^{-2}$, is required under the same conditions to produce a 0.01 M concentration at the electrode surface. From Figure 3 one sees that the potentials corresponding to this current (log i = -0.2) are -0.94 for cadmium and -0.83 for lead.

Finally, it was desired to measure the potential of the lithium/lithium ion couple in the same solution. This was done by depositing lithium metal on the copper disc working electrode. The subsequent open circuit potential was then measured and was constant for a sufficiently long period of time (e.g. for 57 min. in acetonitrile, longer in P.C. and B.L.) to allow meaningful measurements.

In Table 2 below are shown the results obtained to date and are compared with those calculated for aqueous solutions which have been calculated from the Nernst equation.

Table 2

FORMAL REDUCTION POTENTIALS

Measured potential of metal/metal ion couple versus silver/silver ion (0.01 M) couple in solvent indicated, made 0.5 M in $LiClO_4$

Couple	Potential (Volts) in			
	PC	BL	AN	H_2O
Cu(I), 0.01 M/Cu	-0.15	-0.21	-0.58	-0.28
Pb(II), 0.01 M/Pb	-0.83	-0.82	-0.42	-0.87
Cd(II), 0.01 M/Cd	-0.94	-0.96	-0.66	-1.12
Li(I), 0.5 M/Li	-3.67	-3.60	-3.20	-3.74

Major shifts in potentials doubtless largely reflect the shift, to a varying degree, of the solvation energy in the different solvents. This is

especially pronounced in acetonitrile and most likely reflects the much stronger solvation of copper (I) and silver (I) in this solvent through specific interactions (e.g. covalent bonding with the acetonitrile). In P.C. and B.L. we do not believe the data indicates substantial differences in the solvating power of these two solvents as compared with water and the shifts may reflect only variations in activity coefficients or solvation entropy.

Although one may be quite certain that cadmium and lead go into solution as the +2 ions, there remains some question about the oxidation state of the soluble copper species. The following procedure was used to obtain some indication of the preferred oxidation state of copper. Copper was deposited on polished platinum electrodes at 25 mA cm^{-2} for 100 sec. from an acidified aqueous copper sulfate solution. Subsequent discharges of the copper deposit in aqueous solution gave 95-100% efficiencies.

Deposits similarly formed were discharged in the same nonaqueous electrolytes in which the previously described studies were performed. If the copper goes into solution as the +2 ion, 100% efficiency should ideally be realized; if copper goes into solution as the +1 ion, however, only 50% efficiency should be realized since, on deposition two electrons were required per copper atom deposit whereas, on discharge, only one electron would be required. The results are shown below. The anodic discharge curves were flat in all cases, and the visible disappearance of copper was also attended by marked polarization. The efficiencies are calculated by dividing the number of coulombs passed during anodic dissolution by the number of coulombs passed during the preceding deposition:

Anodization Current	Stripping Efficiency in		
	P.C.	B.L.	A.N.
1.0 mA cm^{-2}	79%	59.5%	--
2.5 mA cm^{-2}	--	61%	45.4%
5 mA cm^{-2}	70%	64%	46.0%
10 mA cm^{-2}	68%	--	46.4%
25 mA cm^{-2}	62%	61.4%	--

We believe the results in acetonitrile indicate that copper goes into solution exclusively as the +1 ion. The results in butyrolactone suggest copper goes into solution in both the +1 and the +2 oxidation states, but, predominately, the +1 state, whereas in propylene carbonate approximately equal amounts of copper (I) and copper (II) are formed.

II-C. Discharge of CuF_2

II-C-1. Discharge in Acetonitrile

As described in the Third Quarterly Report, the best discharge efficiencies for CuF_2 were obtained in acetonitrile – $LiClO_4$ electrolytes where, for the 6:3:1 ($Ag:CuF_2:LiClO_4$) mixes, efficiencies of between 45-49% were obtained at currents of from 2.1 to 17 mA cm^{-2}. Discharges of CuF_2 were further investigated to test the effect of varying the mix ratio. The results are shown in Table 3 below and in Figure 5.

Table 3

DISCHARGE OF CuF_2 IN ACETONITRILE

Mix Ratio $Ag:CuF_2:LiClO_4$	Theoretical Capacity (mA-hr cm^{-2})	Discharge Current (mA cm^{-2})	Potential of discharge plateau (See Fig. 5)	Efficiency
In 0.5 M $LiClO_4$				
6:3:1 (Fig. 5)	8.5	4.3	-0.60	48%
2:7:1 (Fig. 5)	8.5	4.3	-0.65	32%
6:3:1 (repeat)	8.5	4.3	-0.52	46%
6:3:0	8.5	4.3	-0.58 Electrode fell off after 1 hr.	
6:3:0 (Fig. 5)	8.5	4.3	-0.40	42%
1:1:0 (Fig. 5)	8.5	4.3	-0.55	50%
3:6:1	17	4.3	-0.60 Electrode fell off after 65 min.	
1:1:0	17	1.1	-0.55 to -0.63	*
8:1:1	4.3	4.3	-0.35	39%
8:0:5:1	2.1	4.3	-0.42	30%
8:0.25:1	1.1	4.3	-0.58	13%

* Discharge continued overnight, for 17 hr. No potential break was observed, and the discharge was discontinued.

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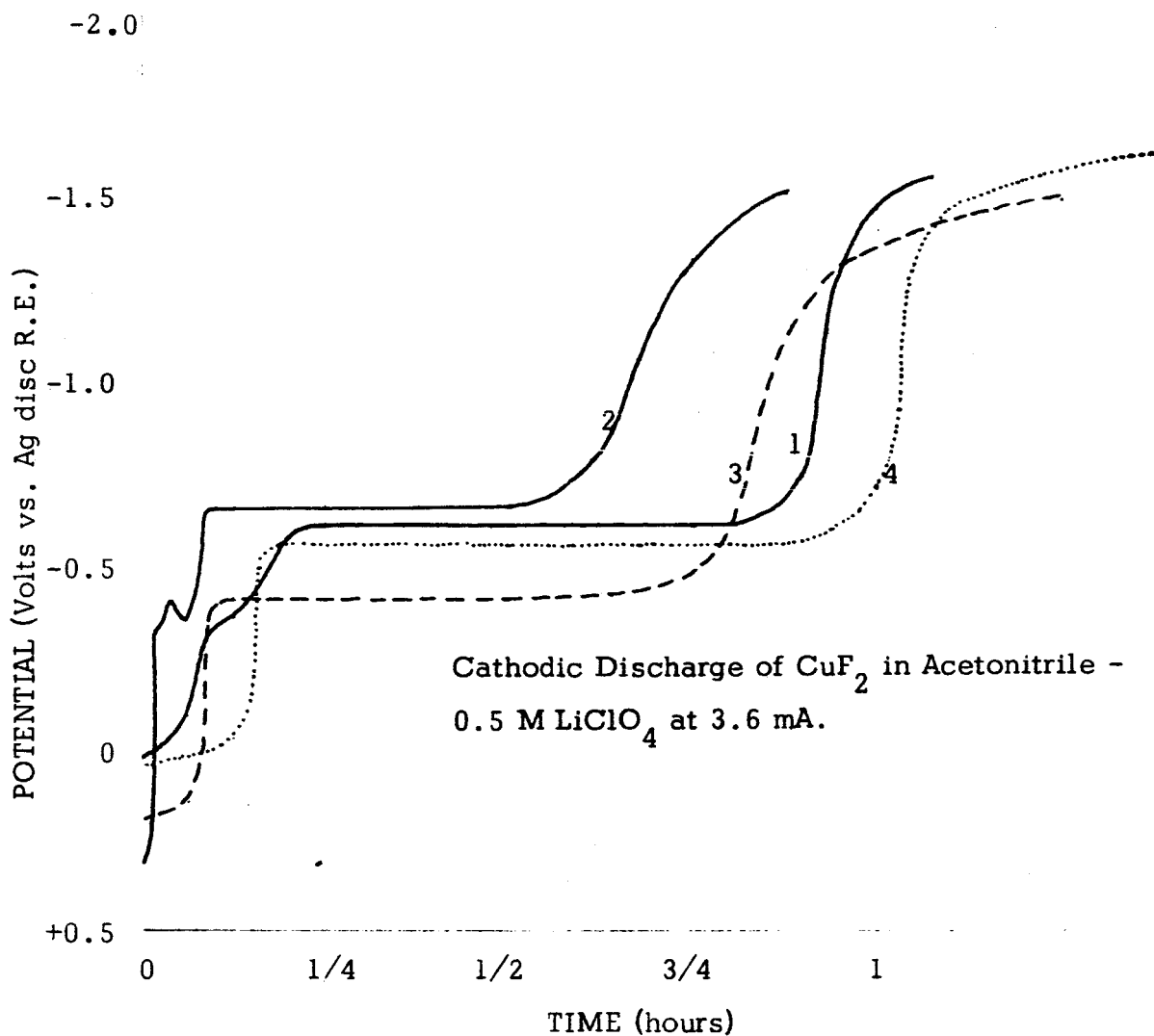
Figure 5: CATHODIC DISCHARGE OF CuF$_2$ IN ACETONITRILE

All discharge performed on 0.85 cm^2 electrodes with mix ratio of

Ag:CuF$_2$:LiClO$_4$ as follows:

1   6:3:1

2   2:7:1

3   6:3:0

4   1:1:0

All electrodes had theoretical capacities of 7.2 mA-hr, based on a two-electron

reduction of CuF$_2$

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Table 3 (Continued)

Mix Ratio $Ag:CuF_2:LiClO_4$	Theoretical Capacity (mA-hr-cm^{-2})	Discharge Current (mA cm^{-2})	Potential of discharge plateau (see Fig. 5)	Efficiency
In 0.5 M $Mg(ClO_4)_2$				
6:3:1	8.5	8.5	-0.15	**
6:3:1	8.5	2.1	-0.3	**

** At about -0.6 V the discharge curves were so ill-defined, with a slow, steady rise to potentials more negative than -0.0 V, that it was difficult to determine the efficiency. Using a cut-off potential of -0.7 V, efficiencies were about 14% for both runs.

To date, the variability of the potentials along the reduction plateau has not been of great concern to us, since we were primarily interested in the efficiency of discharge. The calculated iR drop correction for reductions at 3.6 mA (0.85 cm^2 electrode) is 0.08 V in this solution. We do not believe this is in error by more than 0.01 V. If this is so, then the varying potential of reduction may reflect real processes within the electrode or the varying potential of the silver disc reference electrode. Although, in acetonitrile, we do not know what the potential of the silver disc reference electrode is, versus some reference electrode (e.g. the Li/Li$^+$ electrode), it has been our past experience that the silver disc does assume a surprisingly constant and reproducible potential. Thus, in propylene carbonate, the potential of the silver disc is always +3.1 ± 0.1 V vs. a lithium deposited electrode. As can be seen from Table 3, the variation in the discharge potential for reductions at 3.6 mA (4.3 mA cm^{-2}) is -0.35 to -0.65 V. If the variations were erratic within these limits, one would expect to see this reflected in erratic potential wanderings during the discharge. It may be that the treatment of the silver electrode surface between each run may account for the varying potentials of discharge, and greater attention will be given to this in the future.

The apparent approach toward 50% efficiency is most interesting

since varying the Ag:CuF_2 ratio does not seem to change this as markedly as might be predicted. Various mechanisms may be invoked explaining 50% efficiency, the most obvious is that copper (II) undergoes a one-electron reduction to copper (I) as occurs in chloride media and in aqueous ammoniacal media.

II-C-2. Discharge in Butyrolactone

As described in the Third Quarterly Report, it has been found that the 6:3:1 electrodes could be discharged in butyrolactone, 1 M in $LiBF_4$ with efficiencies of 22-26% at currents of 4.3 to 17 mA cm^{-2}. Using acetylene black instead of silver, efficiencies as large as 49% were obtained at 4.3 mA cm^{-2}. The potential along the discharge plateau at 4.3 mA cm^{-2} was -0.35 V for discharge of the silver mix electrode, and -0.3 V for discharge of the acetylene black mix. This indicated, we believe, that there was not much likelihood of the reaction of CuF_2 with the silver powder (Note: This reaction is not favored, thermodynamically.)

Further work was done using $LiClO_4$ instead of $LiBF_4$ as the electrolyte. Furthermore, no vacuum distilled butyrolactone was available at the time this work was done, and we used the "as-received" material which, as discussed in Section IV, contains about 0.04% by weight of water. This is a concentration of about 0.02 M, corresponding to a limiting current in quiet solution of about 1 mA cm^{-2}. The results are shown in Table 4 below, and in Figure 6. It will be noted that the efficiencies are only about half those obtained and reported during the Third Quarter.
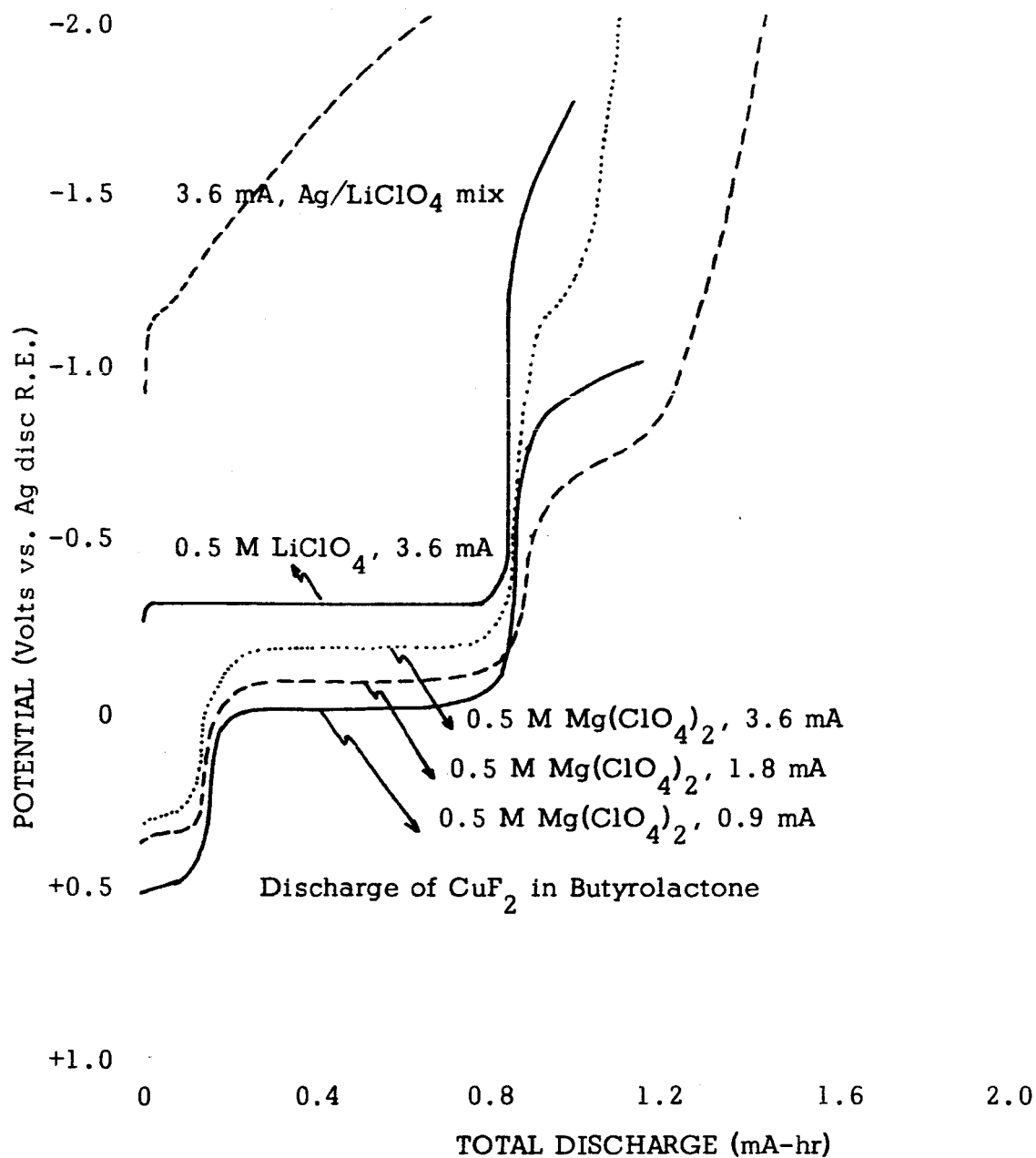
Figure 6: DISCHARGE OF CuF_2 IN BUTYROLACTONE

Except where indicated, all electrodes (0.85 cm^2) of 6:3:1 mix ratio

($Ag:CuF_2:LiClO_4$) with theoretical capacity of 7.2 mA-hr

Table 4

DISCHARGE OF CuF_2 IN BUTYROLACTONE

Solution	Mix Ratio $Ag:CuF_2:LiClO_4$	Theoretical Capacity (mA-hr cm^{-2})	Discharge Current	Efficiency
0.5 M $LiClO_4$ (Fig. 6)	6:3:1	8.5	4.3	13%
0.1 M $MgCl_2$	6:3:1	8.5	4.3	9%
0.1 M $Mg(ClO_4)_2$	6:3:1	8.5	4.3	8%
0.1 M $Mg(ClO_4)_2$	6:3:1	8.5	2.1	8%
0.1 M $Mg(ClO_4)_2$	6:3:1	8.5	1.1	13%
0.5 M $Mg(ClO_4)_2$ (Fig. 6)	6:3:1	8.5	4.3	12%
0.5 M $Mg(ClO_4)_2$ (Fig. 6)	6:3:1	8.5	2.1	12%
0.5 M $Mg(ClO_4)_2$ (Fig. 6)	6:3:1	8.5	1.1	12%

Here three points are, we believe, of particular interest. First is noted the appearance of an initial reduction plateau in the magnesium perchlorate solutions, as was observed in acetonitrile. Second, one would expect, were concentration polarization the limitation to CuF_2 utilization, the efficiency to significantly increase as the current is decreased. This is not observed, as can be seen in Figure 6, and suggests inherent structural limitations. Finally, the potential of reduction is different in the $LiClO_4$ vs. the $Mg(ClO_4)_2$ solution. The calculated correction for iR drop is, in the $LiClO_4$ solution, 0.24 V, giving a corrected reduction potential of -0.06 V. In the $Mg(ClO_4)_2$ solution the iR drop correction and the corrected reduction potentials are, respectively, at 3.6 mA (0.32 V), E = +0.14; at 1.8 mA (0.16 V), E = +0.08; at 0.9 mA (0.08 V), E = +0.09 V. Again, more experimental work is required before these differences can be said to be real.

CuF_2 ELECTRODES

II-C-3. Discharge of Teflon Containing Mixes

Attempts were made to improve the discharge efficiency

of CuF_2 electrodes through the incorporation of Teflon powder as a binder. The electrode mixes were prepared in the weight ratio given below, and pressed into the lollipop electrode structure described in previous reports at 3000 lb. The theoretical capacity is based on the complete reduction of CuF_2 to the metal. The discharge curves were sufficiently well-defined to give unambiguous efficiency values. The discharges were conducted in propylene carbonate, 0.5 M in $LiClO_4$.

Table 5

DISCHARGE OF CuF_2 MIXES WITH TEFLON BINDER

Mix	Capacity (mA-hr cm^{-2})	Discharge Current (mA cm^{-2})	Efficiency	
1	8.5	4.2	51%	
1	8.5	4.2	50%	
1	8.5	4.2	28%	Pellet soaked in electrolyte 1 hr. prior to discharge
1	8.5	0.56	22%	
1	8.5	0.56	37%	With copper support screen
1	4.2	4.2	42%	With copper support screen
1	4.2	4.2	43%	"
1	4.2	2.1	40%	"
2	4.2	4.2	43%	"

$1 = 9{:}1{:}1{:}0.5$ $Cu{:}CuF_2{:}LiClO_4{:}$Teflon by weight
$2 = 9{:}1{:}1{:}1$

The failure to obtain increased efficiency with lower discharge currents is again noted. This may result from the slow dissolution of the CuF_2 into the bulk of the electrolyte which, if so, is quite serious. Whether the possible slow dissolution is through impurities in the electrolyte or is inherent

in the system is a matter for further study.

II-C-4. Discharge of Naphthalene Containing Mixes

Attempts were made to improve the porosity of the CuF_2 electrode through the incorporation of naphthalene in the mix and subsequent removal by sublimation. The results are shown in Table 6 below. All electrodes had a theoretical capacity of 8.5 mA-hr cm^{-2}. The mix ratio was 9:1:1, Cu: CuF_2:Naphthalene. The electrodes were discharged in propylene carbonate, 0.5 M in $LiClO_4$, to provide a comparison with the results shown in Table 5.

Table 6

DISCHARGE OF CuF_2 MIXES WITH NAPHTHALENE

Treatment of Mix	Discharge of Current Efficiency (mA cm^{-2})	
Pressed at 7000 lb. heated at 750°C for 1/2 hr.	4.2	0%
Pressed at 7000 lb. no heat applied	4.2	0%
Pressed at 7000 lb. heated in vacuum oven at 60°C for 1 hr.	4.2	4%
Pressed at 3000 lb. heated in vacuum oven at 150°C for 1/2 hr.	4.2	4%
Pressed at 7000 lb. heated in vacuum oven at 150°C for 1/2 hr.	4.2	3%
Pressed at 3000 lb. heated in vacuum oven at 150°C for 1 1/2 hr.	4.2	15%
Pressed at 3000 lb. heated in vacuum oven at 150°C for 1 1/2 hr.	0.56	22%
Pressed at 7000 lb. heated in vacuum oven at 150°C for 1 1/2 hr.	4.2	23%
Pressed at 3000 lb. heated in vacuum oven at 150°C for 16 hr.	4.2	51%

The results at the top of the table doubtless reflect the incomplete removal of naphthalene. The maximum efficiency of 51%, obtained following prolonged heating, is about the same as that previously observed when porosity is increased through the incorporation of $LiClO_4$ in the mix, as shown in Table 5.

II-D. Discharge of Other Materials

The marked variations observed for the discharge of CuF_2 and, as discussed in the Third Quarterly Report, of AgCl in different electrolytes suggested the desirability of briefly examining the discharge behavior of other materials using the same mode of electrode construction. In Figure 7 are shown the results obtained. In addition, the discharge of a 6:3:1 mix of Ag_2O (7.2 mA-hr) was studied at 3.6 mA; the results were identical to those shown for AgO.

The entire question of the potential at which discharge occurs will be examined at a later date. It is important to note that oxide electrodes may be discharged at quite reasonable currents (4.3 mA cm^{-2}).

It was not surprising that $CuCl_2$ gave only 50% efficiency, since one expects a one-electron reduction in chloride media to copper (I). It was surprising that CuCl gave only 50% efficiency and discharges were conducted under other conditions as indicated below. Again, all discharges were conducted in 1.0 M $LiClO_4$/propylene carbonate.

Table 7

DISCHARGE OF CuCl IN PROPYLENE CARBONATE

Mix Ratio Ag:CuCl:LiClO$_4$	Theoretical Capacity (mA - hr cm^{-2})	Discharge Current (mA cm^{-2})	Efficiency
6:3:1	8.5	4.3	48%
1:4:0	17.0	1.1	56%
1:4:0	17.0	8.5	47%
2:8:1	17	8.5	50%
6:6:1	8.5	4.3	47%
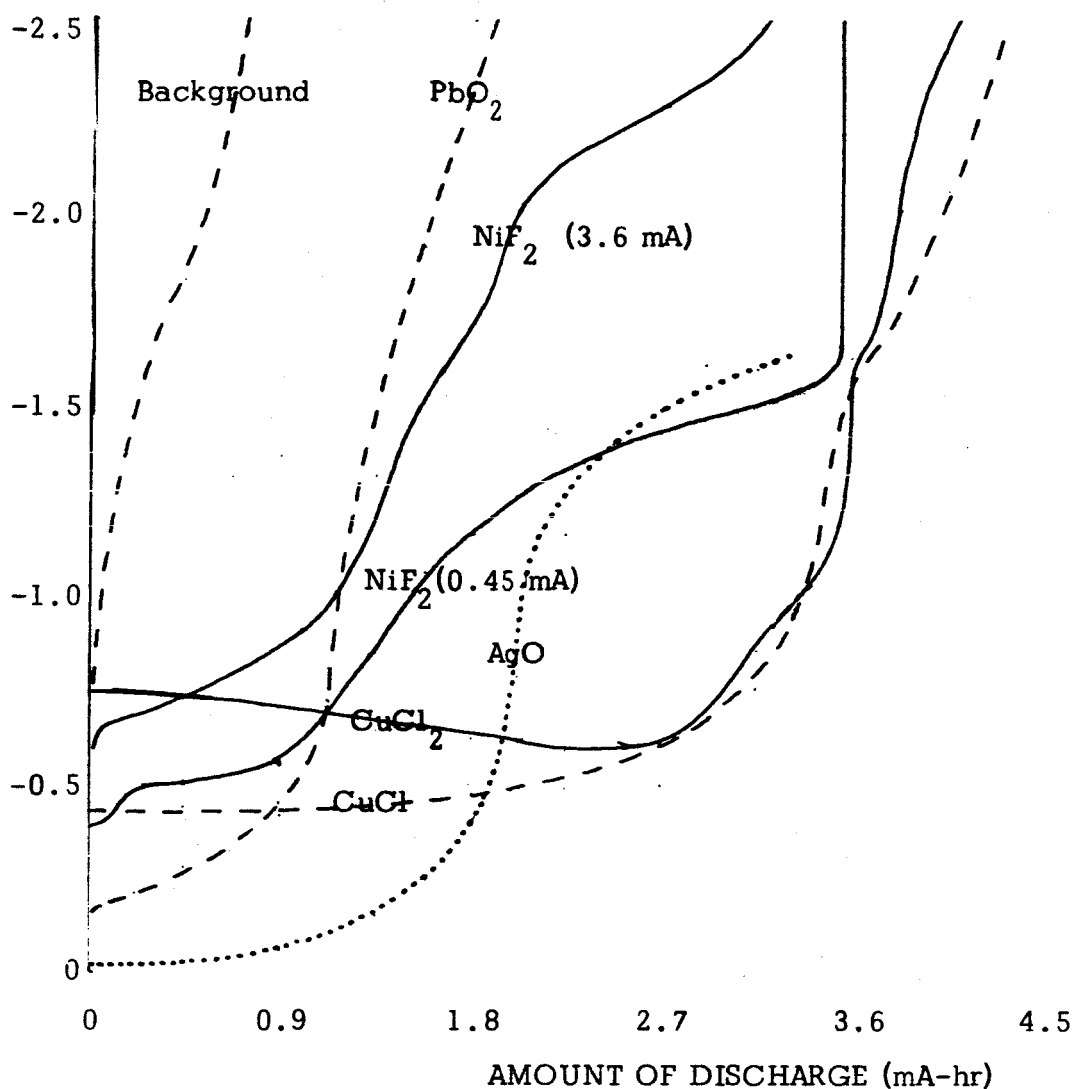
Figure 7: CATHODIC DISCHARGE OF VARIOUS MATERIALS

Discharge of 0.85 cm^2 electrodes. Mixes were in weight ratio 6:3:1
Ag:Cathode Salt:LiClO$_4$. Theoretical capacities were 7.2 mA-hr. Except
where indicated, all discharges were done at 3.6 mA. Potentials
are given with respect to a silver disc R.E. against which the potential
of a lithium electrode in the same solution is about -3.1 V. Discharges
were performed in propylene carbonate, 1 M in LiClO$_4$. Under the conditions
prevailing in these experiments, the iR drop for reductions at 3.6 mA is about
0.5 V.

The results suggest, we believe, that the 50% efficiency is inherent in the system. As was discussed in the Second Quarterly Report, CuCl is solubilized in chloride media, apparently with the formation of $CuCl_2^-$. If this were true in the systems here employed one would expect reduction to proceed: $2CuCl + e^- = Cu^O + CuCl_2^-$. If the complex escapes from the electrode, 50% efficiency will occur. A similar mechanism may prevail in the discharge of CuF_2.

The AgCl electrode was also used to further investigate the ability to discharge cathodes in dilute electrolytes. Two solutions with approximate equal conductivities were investigated, a 0.2 M $LiClO_4$/propylene carbonate solution (Specific Resistance = 333 ohm-cm), and a 0.1 M $LiClO_4$/Butyrolactone Solution (Specific Resistance = 370 ohm-cm). All electrodes had a theoretical capacity of 8.5 mA-hr cm^{-2} and contained 10% by weight of silver powder and, as indicated in certain cases, $LiClO_4$. The results are shown in Table 8 below.

Table 8

DISCHARGE OF AgCl IN $LiClO_4$ SOLUTIONS

Solution	Weight % $LiClO_4$	Discharge Current (mA cm^{-2})	Efficiency
Propylene Carbonate	none	8.5	8%
Propylene Carbonate	none	2.1	8%
Propylene Carbonate	none	4.3	8%
Butyrolactone	none	4.3	67%
Butyrolactone	none	2.1	60%
Butyrolactone	none	0.5	78%
Butyrolactone	12%	8.5	65%
Butyrolactone	25%	8.5	68%
Butyrolactone	25%	17	67%
Butyrolactone	25%	4.3	73%
Butyrolactone	25%	1.1	67%

The results obtained in butyrolactone are similar to those described in the Third Quarterly Report for $LiBF_4$/Butyrolactone solutions. The results obtained in propylene carbonate are significantly lower than those observed in the $LiBF_4$/Propylene carbonate solutions, reported in the Third Quarterly Report, where efficiencies of 10% at 8.5 mA cm^{-2}, 27% at 4.2 mA cm^{-2}, and 25% at 2.1 mA cm^{-2} obtained.

II-E.   Discharge in Starved Electrolyte

Cells were constructed with a design essentially that shown in Figure 8. This cell consists of a hollow teflon sleeve, 2 cm in internal diameter. The inside of the sleeve was milled to form a shoulder to separate and space the two electrodes. This shoulder was 0.2 cm thick and projected 0.2 cm into the inside of the sleeve. In earlier experiments a teflon spacer ring, 0.2 cm thick was used to separate the electrodes rather than the milled shoulder.

Two electrode "plugs", milled to fit tightly inside the sleeve were used. In the work described in this section these plugs were made of epoxy. In the face of each plug were sealed stainless steel cups to provide the cavities in which were placed the electrode material.

In the work here described bulk lithium metal was pressed into one cavity. In the other cavity was pressed a mix of silver, copper fluoride, and lithium perchlorate in the weight ratio 9:1:1 ($Ag:CuF_2:LiClO_4$).

The two plugs were then pushed part way into the teflon sleeve and a small amount of electrolyte injected into the space between the two electrodes. They were then pushed together against the separating shoulder or teflon ring, and excess electrolyte was expelled. The electrolyte was butyrolactone, 1 M in $LiBF_4$.

The main problem appeared to be leakage of electrolyte during discharge, thus the efficiencies were low. However, the discharge curves were

ELECTROLYTE

ANODE

CATHODE

ANODE LEAD

CATHODE LEAD

SEAL

SEAL

REFERENCE ELECTRODE
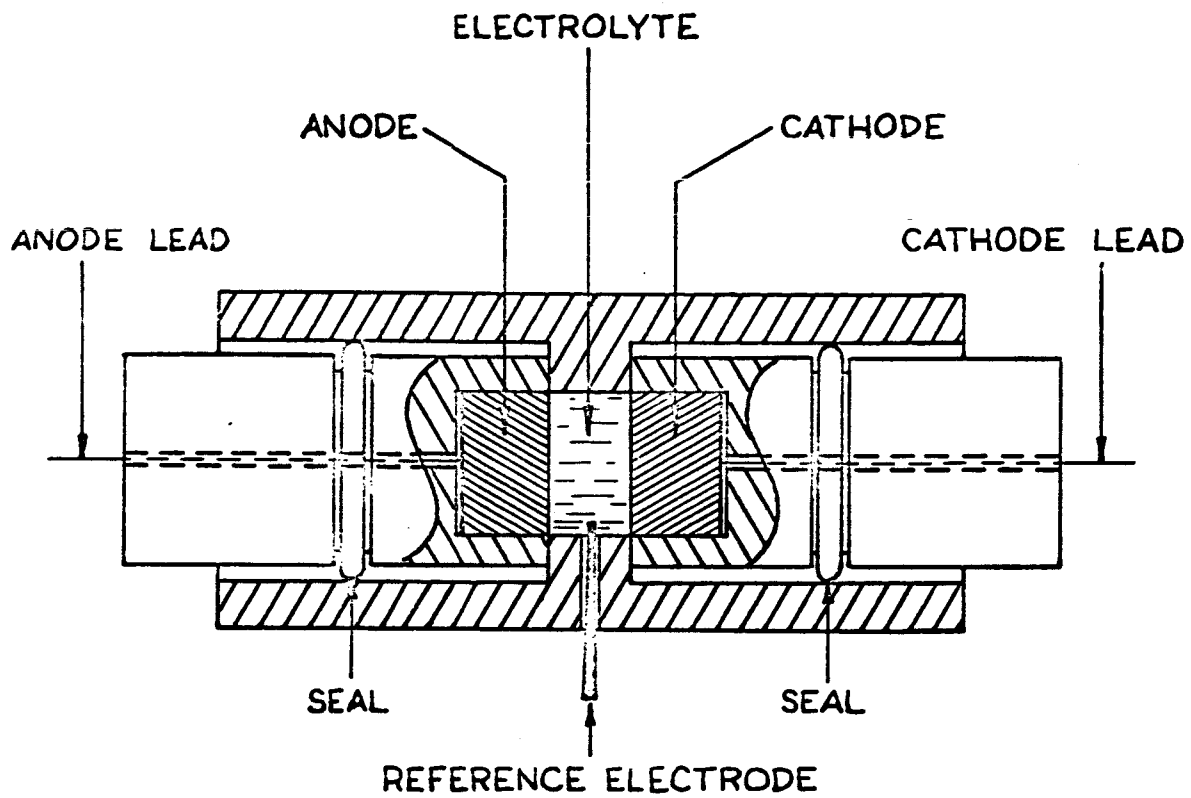
Figure 8: Cell for Starved Electrolyte Studies

flat with the exception of the discharge at 20 mA. The results are shown below. Each cathode had a capacity of 7.2 mA-hr and the area was about 0.85 cm^2.

Current	Potential during discharge	Discharge efficiency
1.0 mA	3.12 V	23%
3.6 mA	3.1 V	42%
3.6 mA	2.8 V	23%
3.6 mA	2.8 V	13%
7.9 mA	2.4 V	19%
20.0 mA	ill-defined	ca. 19%

Attempts were made in most cases to recharge the cell by reversing the current after discharge. This was unsuccessful. The cathode polarized by several volts during charge. On reversing the current again (discharge) satisfactory discharge plateaus were not observed.

If initial discharge efficiency was limited by loss of electrolyte through leakage or by gas formation, one would not expect satisfactory charging. The results indicate one type of difficulty expected in attempting to learn more about the cyclability of the CuF_2 electrode if one cannot first develop a system which first discharges with reasonable ease.

II-F. Cycling of Silver Chloride Electrodes

If LiF is an insoluble product of the cathodic education of CuF_2, it should then serve as a reservoir for fluoride ions for subsequent anodic oxidation of copper to CuF_2. The validity of this principle was tested with the AgCl electrode.

A mix comprising equimolar amounts of silver (0.0290 g.) and lithium chloride (0.0114 g.) was pressed at 1500 lbs. This was 8.5 mA-hr cm^{-2} for a one electron change. The electrode was placed in propylene carbonate, 0.5 M in $LiClO_4$, and subjected to anodization at 8.5 mA cm^{-2} for 1/4 hr. The current was reversed and 93% of the previous anodization was recovered before polarization. A second anodization for 1/4 hr. gave 98% recovery on cathodization, and a third anodization, continued until polarization occurred after 23 min., gave 100% recovery on discharge. The electrode remained compact

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and firmly adherent to the platinum substrate. This indicates that the LiCl contained in the mix did serve as a reservoir for chloride ions.

A second electrode was similarly prepared and anodized at 4.2 mA cm^{-2} for 30 min. Subsequent current reversal at 4.2 mA cm^{-2} gave 100% efficiency. A third electrode incorporating $LiClO_4$ instead of LiCl was subjected to anodization at 8.5 mA cm^{-2} for 15 min. On current reversal the efficiency was only 7%. Thus, we believe, the ability of insoluble LiCl incorporated within the electrode to serve as a reservoir of chloride ions for anodic formation of insoluble AgCl is proved, and we see no reason why the process should not have general validity.

II-G. Cycling of Copper Chloride Systems

Preliminary studies of the cycling behavior of copper electrodes in chloride media have been conducted. These studies were performed using porous copper electrodes, 1 cm^2 in projected area. The electrodes were 0.076 cm thick and were designated by the manufacturer (Clevite Corporation) to have a porosity of 62%. Thus the electrodes contained a total of 0.0041 moles of copper, or 410 coulombs for one-electron change. This is in considerable excess of the amount of current passed during a cycle.

The electrolyses were conducted in small H-cells, and each compartment held about 4 ml. of electrolyte. Both the counter and working electrodes were porous copper. The reference electrode simply consisted of a silver wire immersed in the same solution as the working electrode. Three electrolytes were examined as described below:

a. Propylene Carbonate, 0.5 M in LiAlCl_4

The working electrode was anodized at 10 mA for 1000 sec. on each cycle. Cathodization was then performed at the same current until polarization was observed. The first 32 cycles were almost identical and in Figure 9 is shown the charge and discharge for the 25th cycle. Cathodic
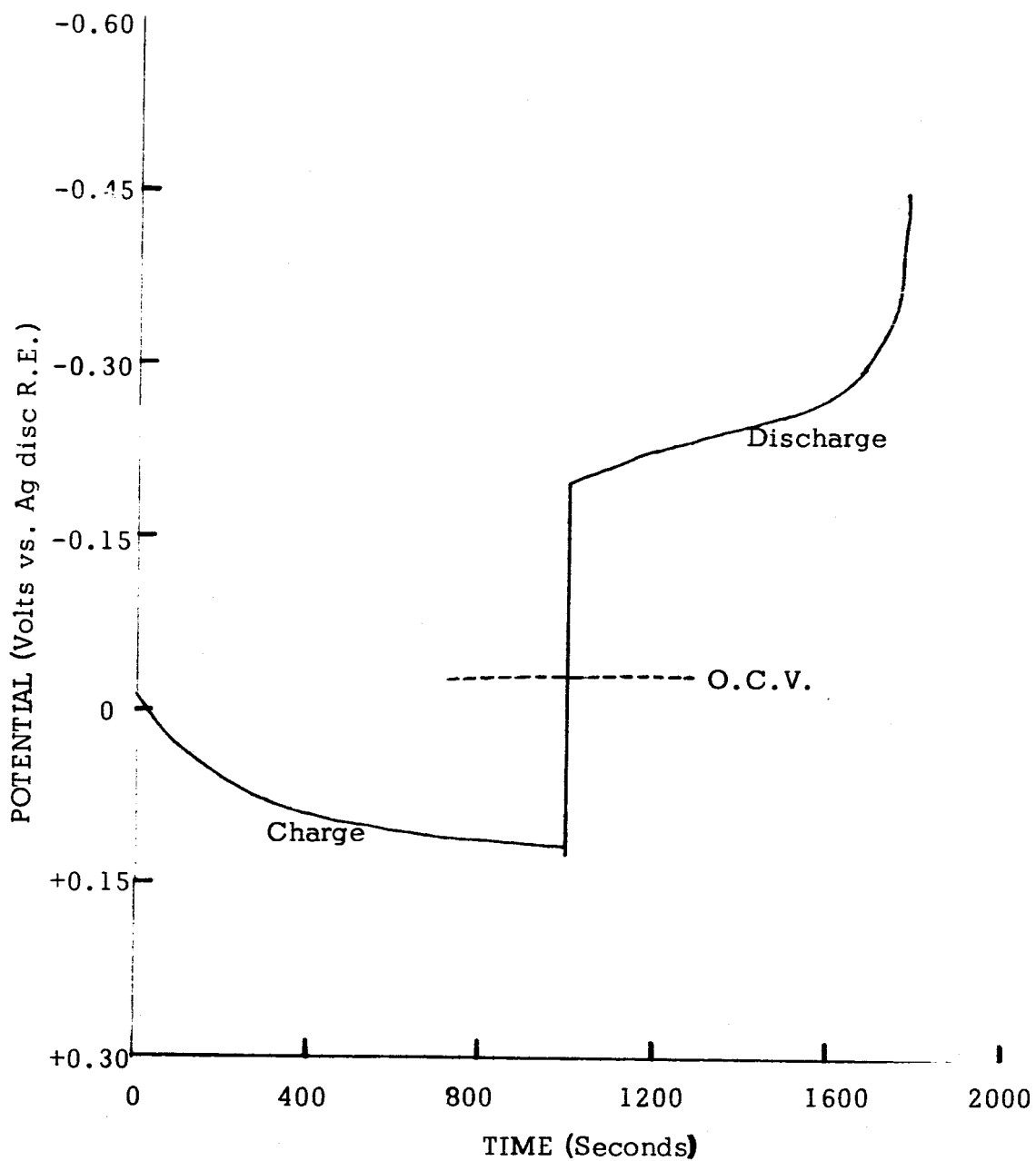
Figure 9: CYCLING OF COPPER ELECTRODE IN PROPYLENE CARBONATE

Figure shows the 25th cycle of a series of cycles performed on a porous copper electrode in propylene carbonate, 0.5 M in $LiAlCl_4$. Cycling was performed by charging the 1 cm^2 electrode at 10 mA for 1000 seconds, followed by current reversal to the point of rapid polarizqtion.

recoveries (the amount of current passed during cathodization, before polarization, divided by the amount of current passed during the preceding anodization) were from 70-76% for each cycle. The conditions of cycling were then varied as shown below:

Cycle No.	Anodic Current	Cathodic Current	Cathodic Recovery
33	10	20	73
34	10	20	75
35	10	50	59
36	10	50	71
37	10	50	67
38	10	1	106
39	10	1	70
40	50	10	69
41	50	10	69
42	20	10	74
43	20	10	75
44	5	10	71
45	5	10	73

Thereafter the capacity was varied for cycles 46-64. The current was maintained at 10 mA for both charge and discharge. The results are shown in Figure 10.

Finally, on cycles 65 through 81, the electrode was allowed to stand on open circuit for varying periods of time following charge to see what effect this would have on subsequent cathodic recovery. Recoveries did not vary markedly with the time of open circuit stand. An electrode which had stood in solution for 63 hours after charge still gave 61% cathodic recovery.

Although the solution became badly discolored after these cycling experiments, it is remarkable that so little change was observed in the cycling behavior.

b. Butyrolactone, 0.5 M in LiCl

The results in this solution were totally unsatisfactory. The
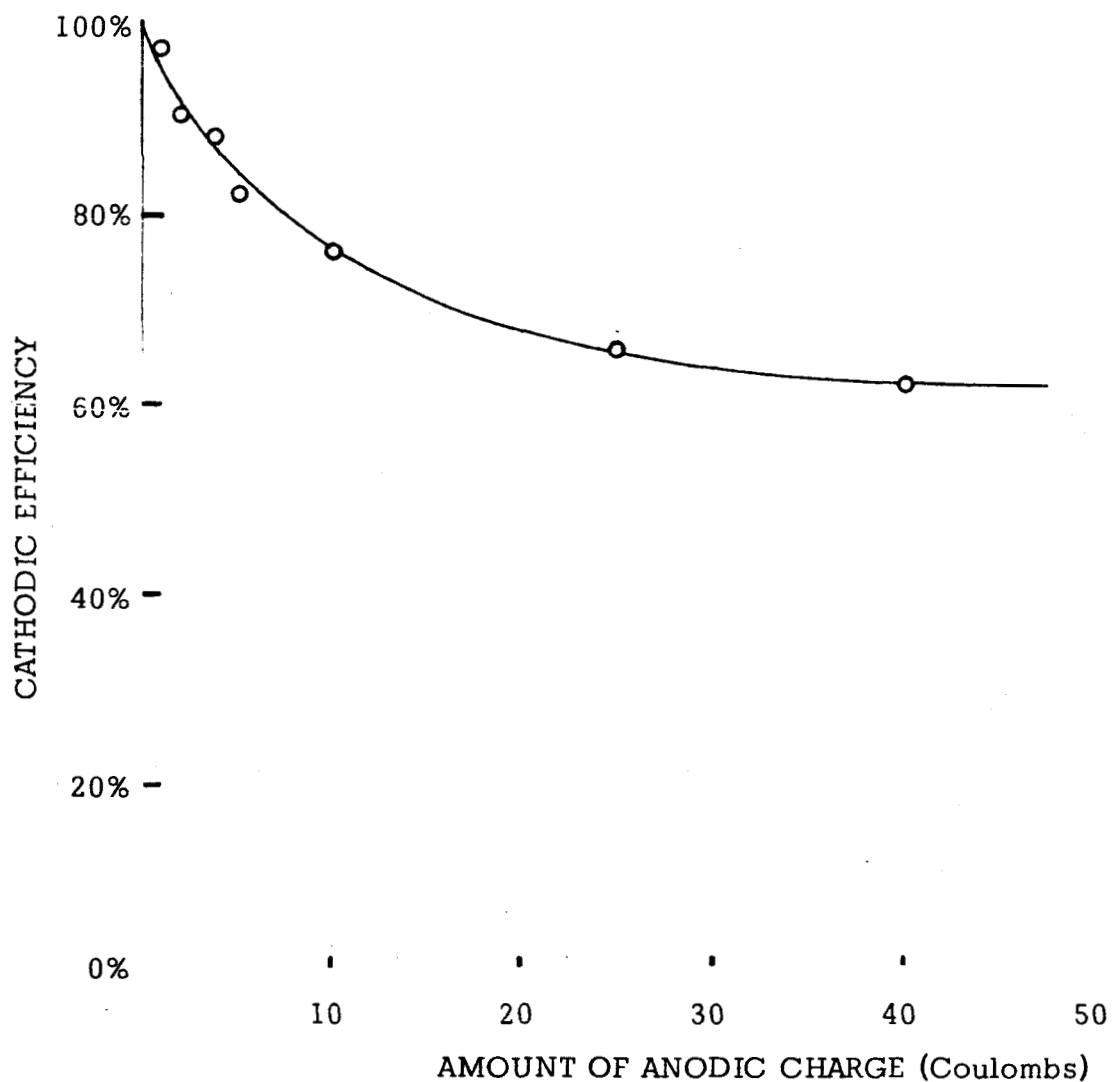
Figure 10: CATHODIC EFFICIENCY ON CYCLING OF COPPER IN PROPYLENE CARBONATE

Experiments performed on porous copper electrode (1 cm^2) in propylene carbonate, 0.5 M in LiAlCl$_4$. Anodic charging was performed at 10 mA to give total amount of charge indicated. Subsequent cathodization was also performed at 10 mA to the point of rapid polarization. Efficiencies calculated by dividing the total amount of cathodic discharge by the amount of the previous anodic charge.

first few cycles were conducted by anodizing the electrode at 10 mA for 1000 sec. followed by cathodic discharge. The cathodic discharge was interrupted after severe polarization was observed. The solid line in Figure 11 shows the results obtained on the second cycle. The dashed line shows the results obtained after the ninth cycle. Subsequent cycling was then performed automatically. Anodization was continued for 1 hr. and cathodization for 15 min. These experiments were discontinued after the 22nd cycle when it was noted that the resistance across the glass frit separating the two compartments had become so large that the electronic constant current supply could not deliver the desired 10 mA. It had not been known how long this condition had existed, thus invalidating the results for cycles 10-22.

c. Dimethylformamide, 0.5 M in LiCl

Preliminary cycling was done by anodizing the electrode at 10 mA for 1000 sec. Cathodization was performed at 10 mA until the electrode polarized to an arbitrary cut-off voltage of -0.9 V. In Figure 12, the solid line shows the 14th and 15th cycles. From cycle 17 on cycling was performed automatically. Anodization was continued for about 800 sec. and subsequent cathodization for a third this time, 270 sec. In Figure 12, the dashed line shows the results for the 23rd and 24th cycle. As cycling continued the curves gradually changed in character and this is shown by comparing the results for cycles 23 and 24 with those for cycles 37 and 38 also shown in Figure 12.

The changing character of the cycling curves indicates, we believe, that significant changes in electrolyte composition are occurring and further study is necessary before this system is satisfactorily characterized.
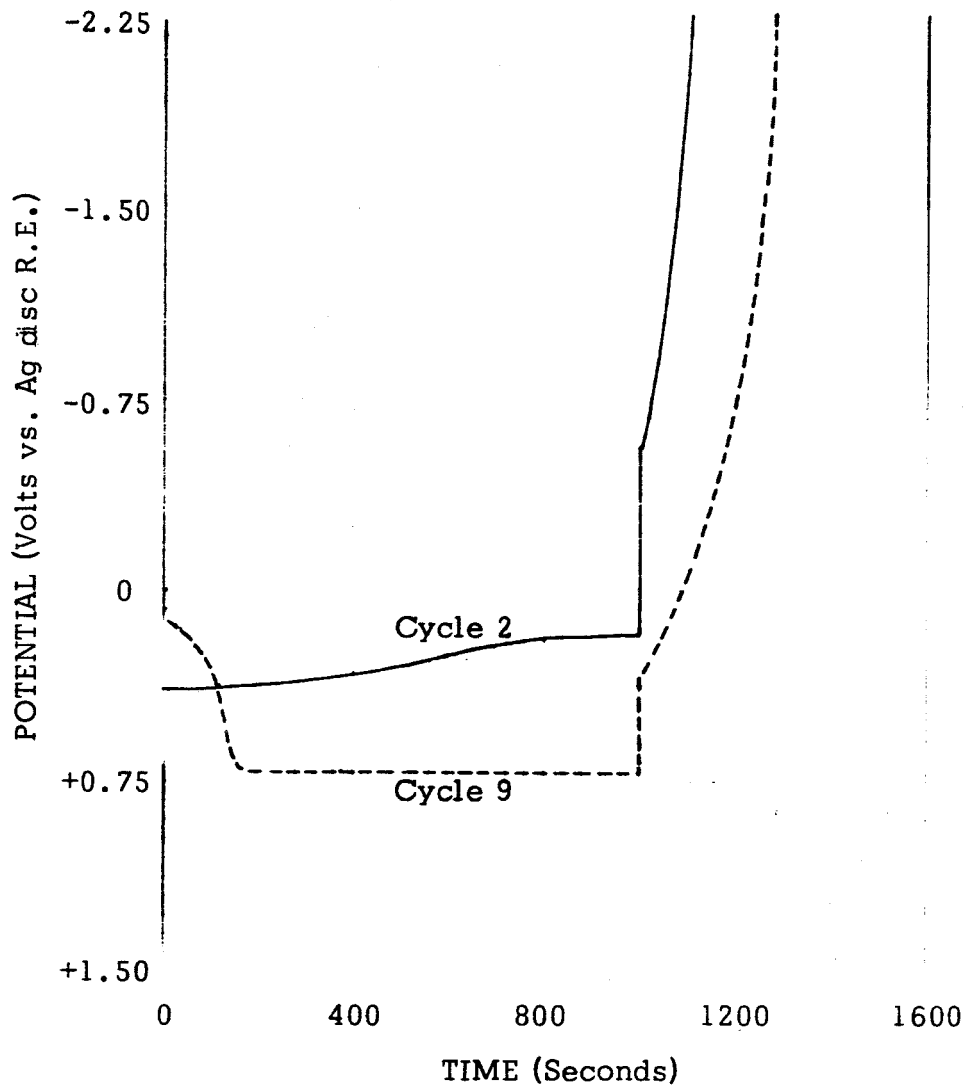
Figure 11: CYCLING OF COPPER ELECTRODE IN BUTYROLACTONE

Figure shows 2d and 9th cycle of a series of cycles performed on a porous copper electrode in butyrolactone, 0.5 M in LiCl. Cycling was performed by charging the 1 cm^2 electrode at 10 mA for 1000 seconds, followed by current reversal to a point of rapid polarization as indicated.
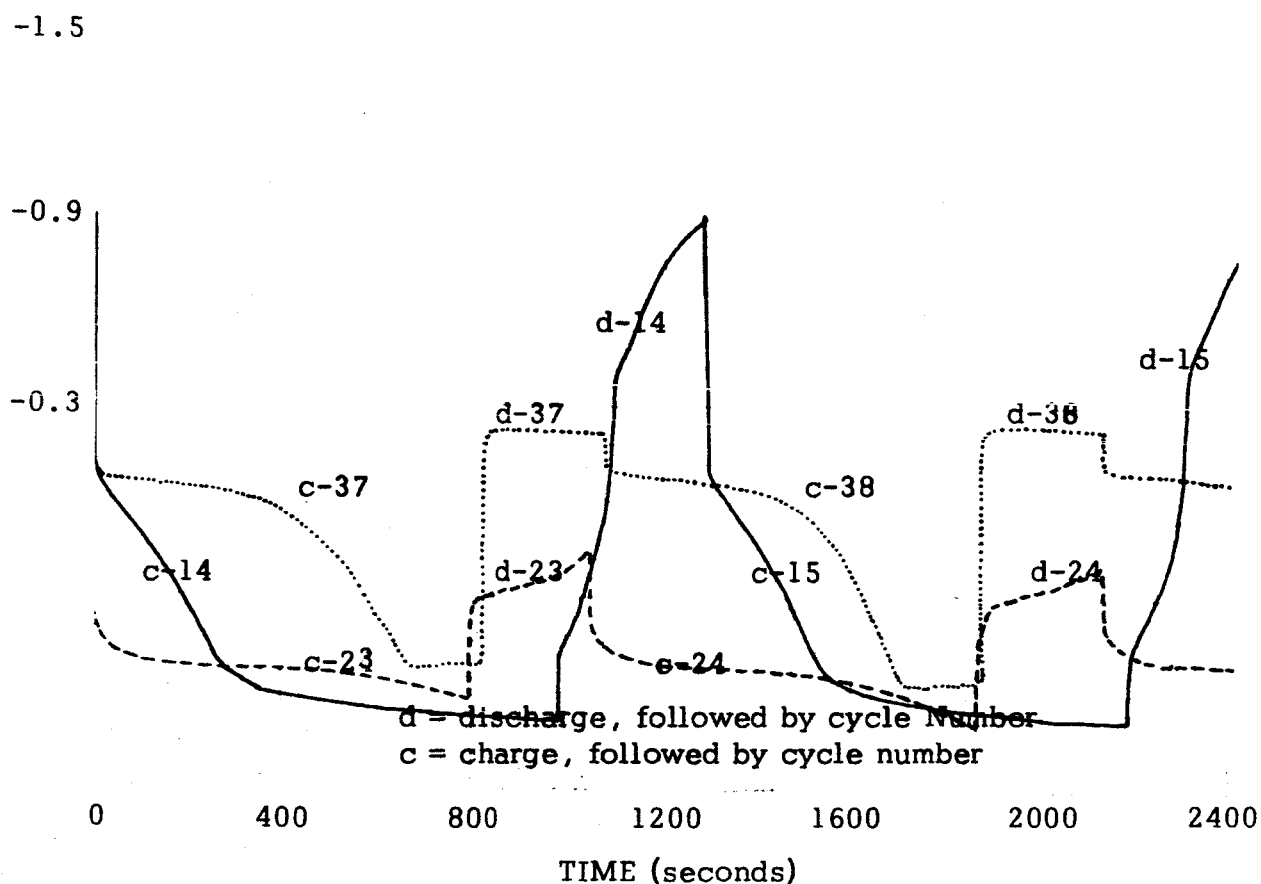
Figure 12:   CYCLING OF COPPER ELECTRODE IN DIMETHYLFORMAMIDE

Figure shows as examples of the trend observed, several cycles obtained
on a porous copper electrode in dimethylformamide, 0.5 M in LiCl.
Cycles 14 and 15 (solid line) were part of a group of cycles obtained by
anodization at 10 mA for 1000 sec. followed by cathodization to an arbitrary
cut-off voltage of -0.9 V. Cycles 23, 24, 3 7, and 38 were part of a
further group of cycles in which cycling was automatically done by charging
at 10 mA for 800 sec. followed by discharge at 10 mA for200 sec.

III. ANODES

III-A. Effect of Water on Lithium Deposition

We were particularly interested in using V.P.C. to determine the water content in total electrolytes -- solvent plus solute. The first problem concerned the ability to determine water in total electrolytes. In Figure 13 are shown three vapor phase chromatograms obtained with a propylene carbonate solution, initially 0.1 M in $LiBF_4$. Curve 'a' is that obtained before the deliberate addition of water; curves 'b' and 'c' are after the addition of water as indicated below. The determination of water from the chromatograms is discussed in the following section IV.

	Water added	Water found
Curve a	0.00%	0.025%
Curve b	0.10%	0.11%
Curve c	1.00%	0.96%

It might not be expected that water can be eluted satisfactorily from the total electrolyte because of decomposition reactions such as the following:

$$LiBF_4 + H_2O = LiOH + HF + BF_3$$
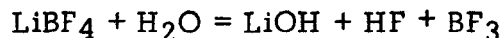
However, the same amount of water is found by both methods of operation, isothermal and temperature programmed runs. This is shown in Figure 14. The results were obtained in a propylene carbonate solution, initially 0.1 M in $LiBF_4$ which had been allowed to stand for several days under a flow of argon. The solid line is a trace of the results obtained by the isothermal run on a 0.4 Microliter sample. The area of the water peak is 0.22 in^2. The dashed line is for a programmed run obtained with a 4 microliter sample, ten times the volume used for the constant temperature run. The area of the water peak, shaded in Figure 14, is 2.37 in^2. In the constant temperature run it will be observed that no peaks are apparent between the water and the propylene carbonate. The first peak in Figure 14 is the air peak, the second is propylene oxide; both are significantly smaller than the water peak. The results indicate that major amounts of other materials than water and propylene carbonate are not present.

Figure 13: VAPOR PHASE CHROMATOGRAM OF WATER IN PROPYLENE CARBONATE
Performed with 0.8 microliter samples. Column temperature = 200° C.

Figure 14: VAPOR PHASE CHROMATOGRAMS IN PROPYLENE CARBONATE

Figures show the difference between isothermal runs and temperature programmed runs.

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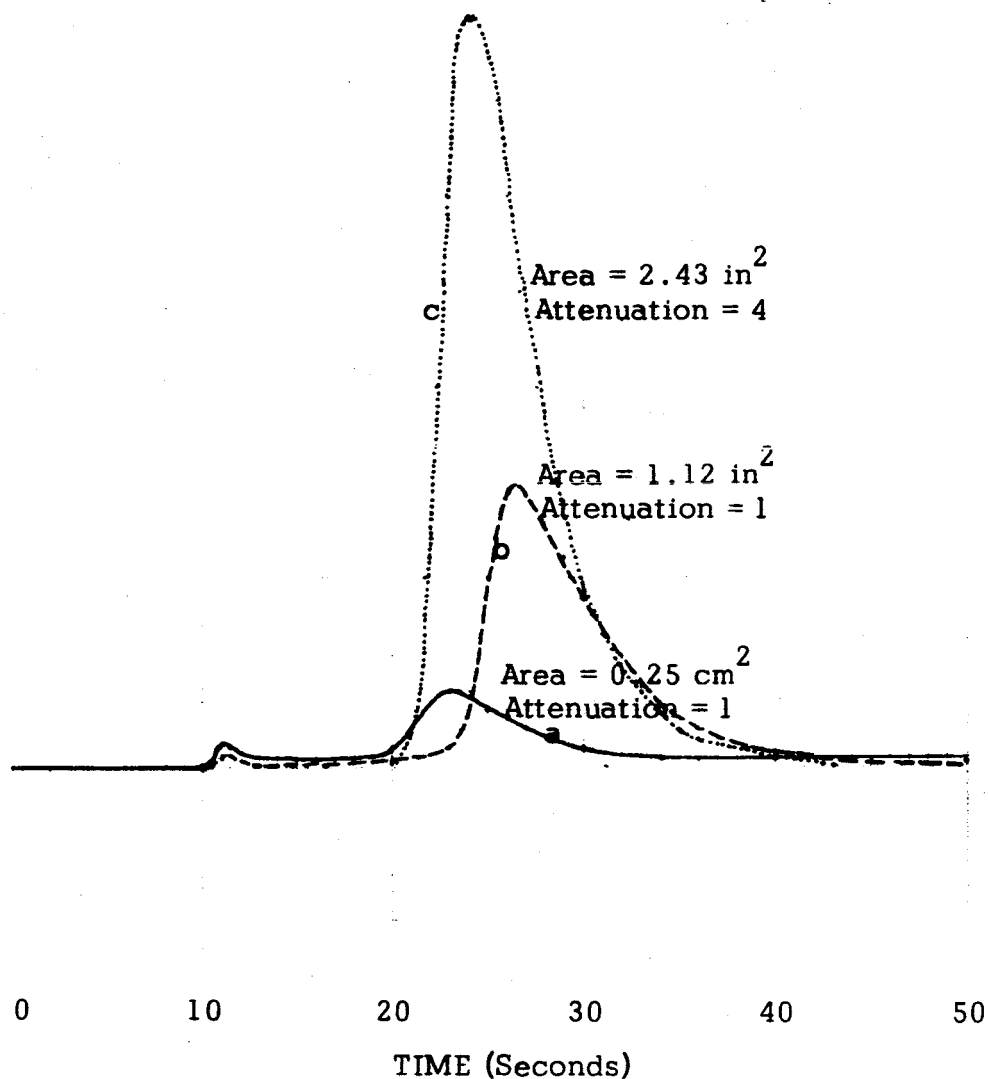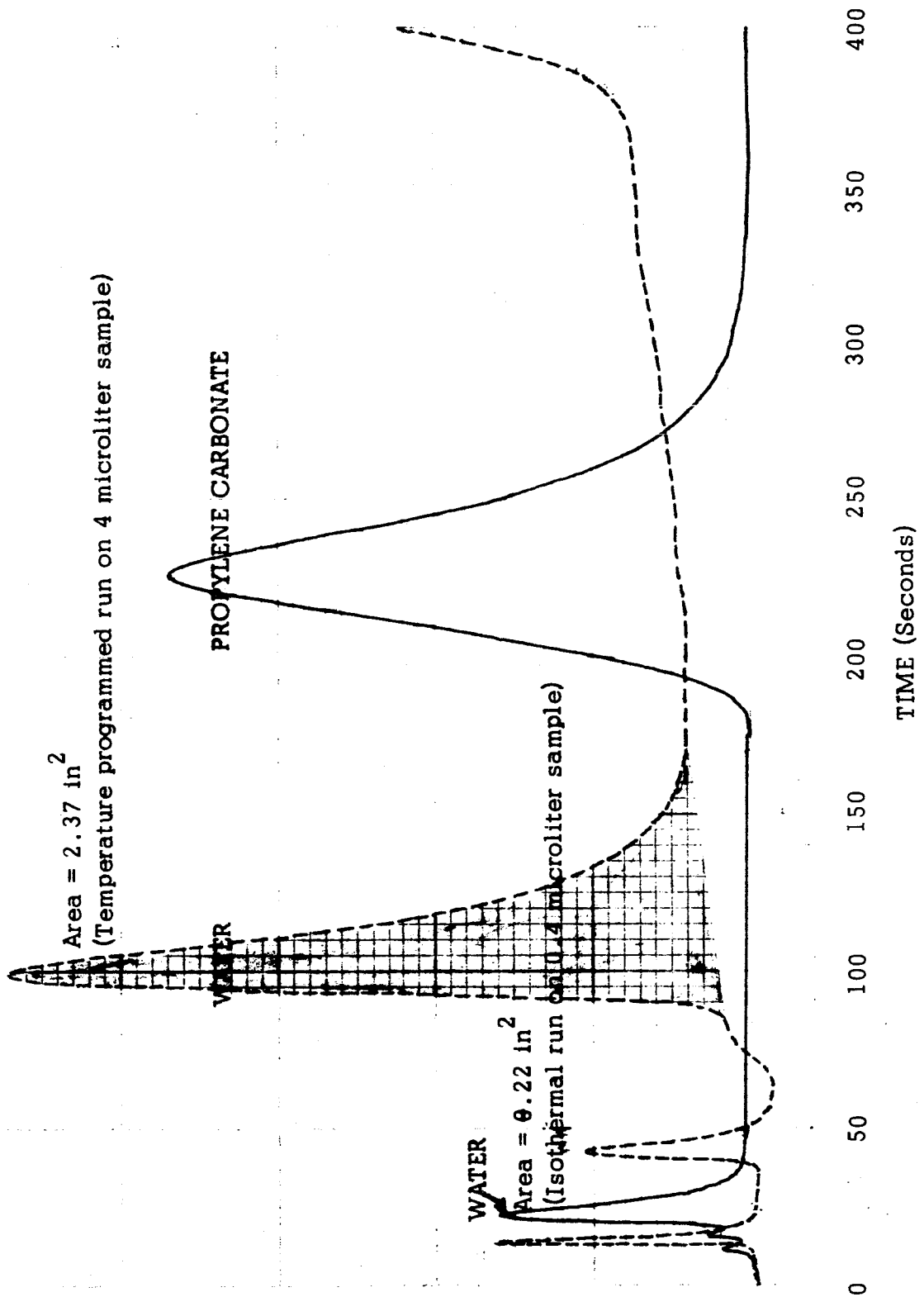Another question concerns the lower limits at which water may be detected. In Figure 15 are shown three runs obtained with temperature programming on 4 microliter samples. Curve 'A' is the run for a freshly prepared propylene carbonate solution, 0.1 M in $LiBF_4$. The shaded area, representing the water peak, corresponds to a concentration of about 0.01% by weight. Curve 'B' was obtained when the solution had stood overnight under a stream of argon. The measured area of the water peak corresponds to a water content of 0.30%. Curve 'C', presented for comparison, is obtained with a sample of propylene carbonate which contained 0.20% by weight of water. It will be observed that significant background is present, which makes difficult the determination of small amounts of water. We estimate that the limit of water content which may be determined under our procedures is about 0.003% by weight, or, in propylene carbonate, 0.002 M.

Although we are not yet confident that vapor phase chromatography necessarily gives an accurate measure of the total water content in the electrolytes -- solvent plus solute -- we do believe it provides at least a minimum estimate of the water content.

A series of electrochemical studies was undertaken in propylene carbonate solutions, 0.1 M in $LiBF_4$, concurrently with V.P.C. examination of the electrolytes. In Figures 16 and 17 are shown the most significant results.

The solid line in Figure 16 is the vapor phase chromatogram of the freshly prepared solution. The area of the water peak, 0.31 in^2, corresponds to a water content of about 0.03% by weight, or 0.02 M. The chronopotentiograms obtained in this solution on platinum electrodes at 7 and 0.7 mA cm^{-2} are shown in Figure 17 by the solid line curves.

This solution was then allowed to stand overnight, with argon continuously bubbled through the solution. The subsequent vapor phase chromatogram is shown by the dashed line in Figure 16. The area of the water peak, 1.66 in^2, corresponds to a water content of 0.17%, or 0.11 M. The concentration of water is thus about equal to that of $LiBF_4$. The chronopotentiograms obtained in this solution are shown in Figure 17. It will be noted that relatively little change is observed in spite of the five-fold increase in water.

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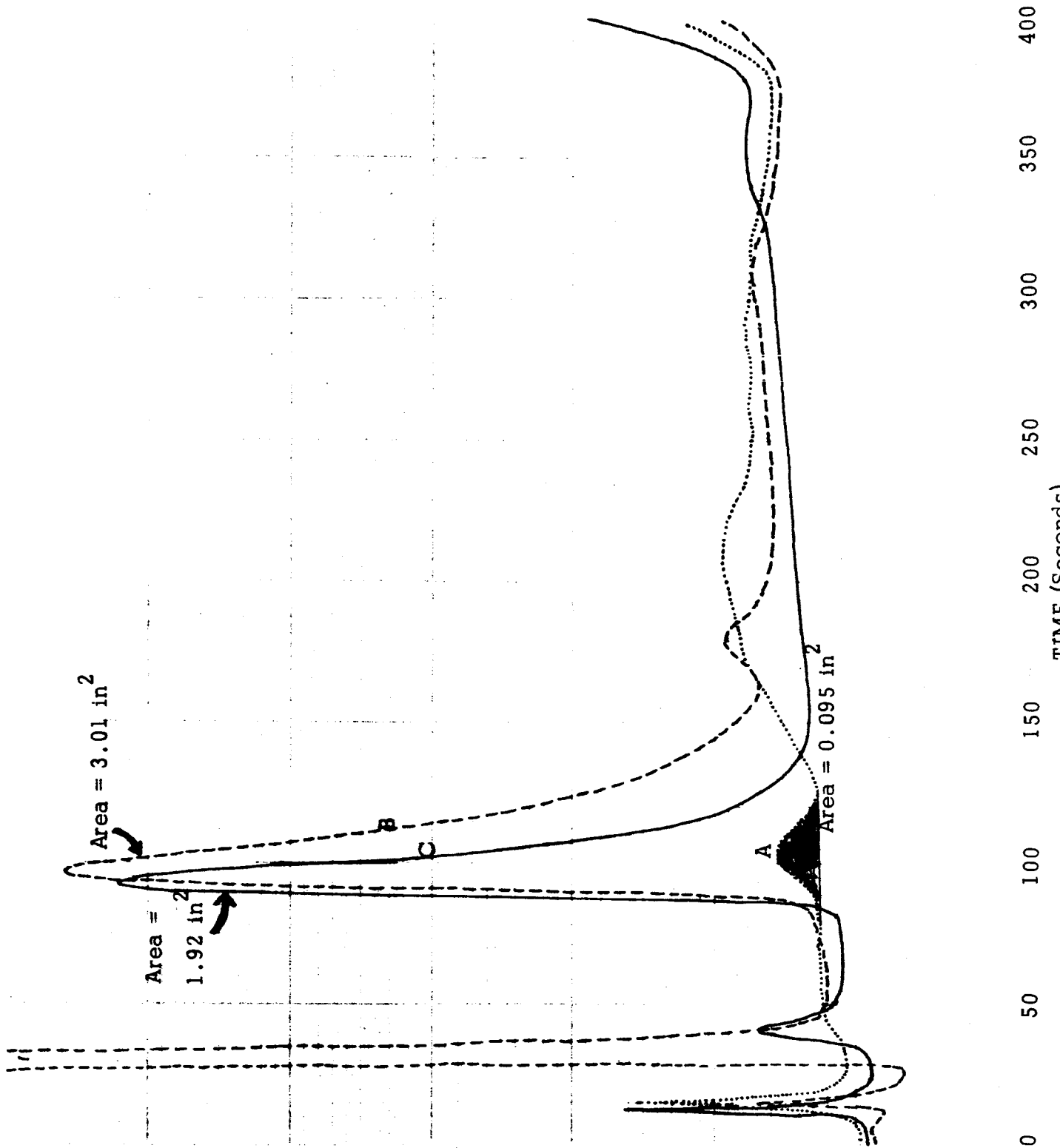
Figure 15: VAPOR PHASE CHROMATOGRAMS OF PROPYLENE CARBONATE

Performed with 4 microliter samples with temperature programming (see text)
all runs done at attenuation = 1.

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Area = 1.66 in^2
Attenuation = 1

Area = 0.31 in^2
Attenuation = 1

TIME (Seconds)
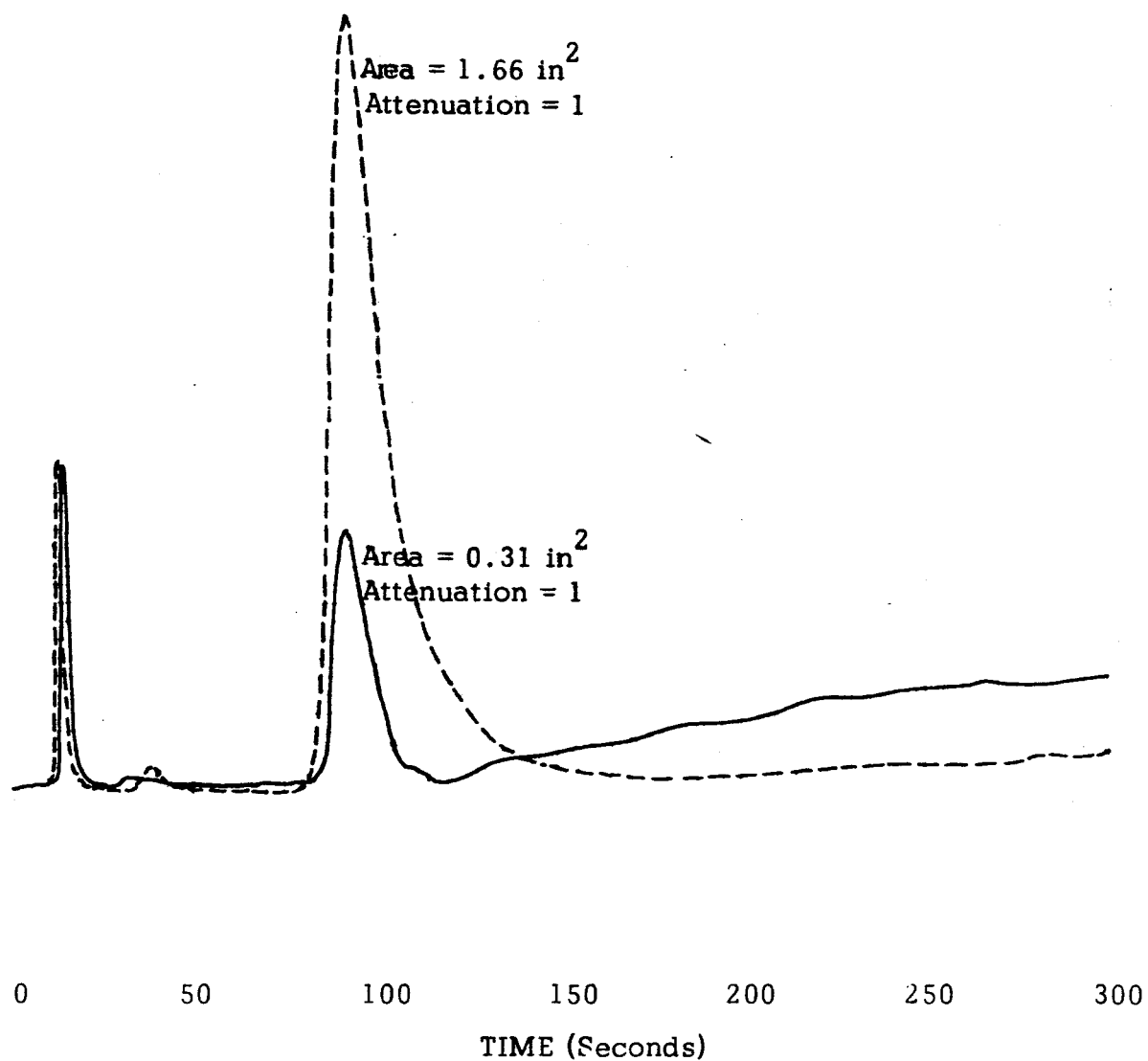
Figure 16: Vapor Phase Chromatograms of Propylene Carbonate

Performed with 4 microliter samples, with temperature programming (see text).
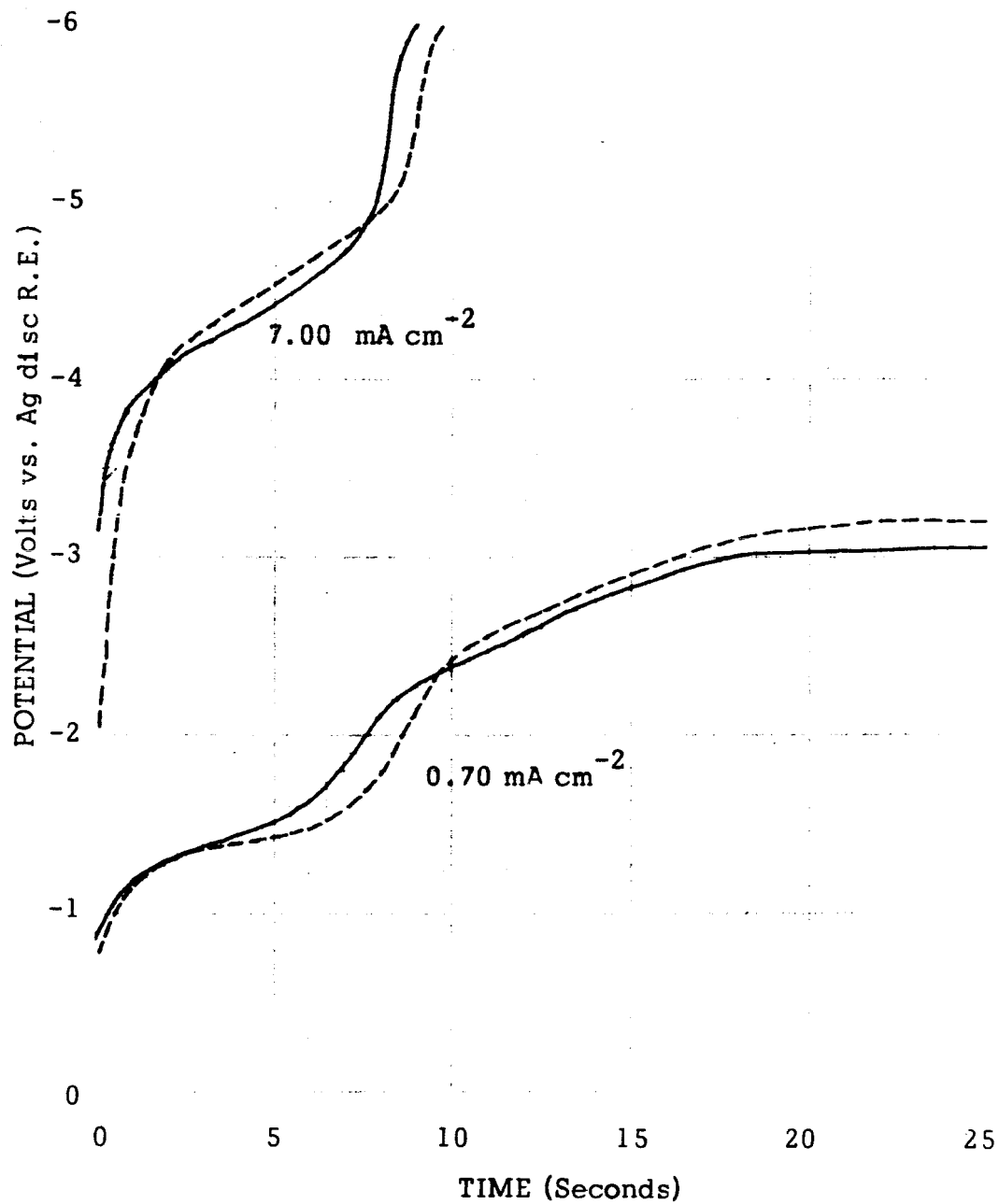
Figure 17: Cathodic Chronopotentiometry in Propylene Carbonate -- 0.1 M LiBF$_4$
Chronopotentiograms obtained on polished platinum electrodes at current
indicated. Solid lines are for the freshly prepared solution. Dashed lines
are for the solution which had stood overnight.

This latter solution was further examined with respect to lithium deposition on beryllium electrodes. The results are shown in the Table below:

TABLE 9
Deposition of Lithium in P. C. (0.11 M in water)

Deposition Conditions on Beryllium	Anodic Utilization
0.45 mA cm^{-2} for 25 sec.	80%
0.9 mA cm^{-2} for 25 sec.	83%
1.2 mA cm^{-2} for 250 sec.	72%, 68%
1.2 mA cm^{-2} for 250 sec. followed by 5 min. stirring	61%
1.35 mA cm^{-2} for 25 sec.	80%
1.8 mA cm^{-2} for 25 sec.	34%, 67%
2.7 mA cm^{-2} for 25 sec.	31%
3 mA cm^{-2} for 100 sec.	48%

We were, of course, quite concerned with the water pickup. Fifty ml. of a sample of distilled propylene carbonate was placed in a capped, 100-ml. cell. The water content was investigated with the results shown below:

Immediately after placing in cell	0.010%
After bubbling argon through for 3 hrs.	0.080%
After standing quiet for 15 hrs.	0.087%
After standing quiet for 60 hrs.	0.083%
After adding Molecular Sieve 4-A and stirring for 10 min.	0.058%
After adding Molecular Sieve 4-A and standing quiet 90 min.	0.030%
After adding Molecular Sieve 4-A and standing quiet 17 hrs.	0.019%

It appears the major source of contamination by water is from the argon. We are not yet certain whether this is the result of leaks in the deaeration system or a bad tank of argon.

An experiment to determine the effects of electrolysis on the composition of non-aqueous electrolytes was carried out. A 0.1 M solution of $LiClO_4$ in distilled P. C. was prepared and placed in a small volume H-cell (20 ml. of

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electrolyte per compartment). The cathode was a rectangular sheet of platinum foil, 6 cm^2 in total surface area. The anode was prepared from a folded strip of cleaned lithium ribbon. A silver wire reference electrode was also placed in each compartment. The electrolyte was deaerated with dried argon prior to placement in the cell. For the first test, electrolysis was performed for 15,000 sec. at 10 mA or 150 coulombs. A clean grey lithium deposit was obtained on the platinum which gassed slightly throughout the run. Samples for each compartment, before and after electrolysis, were examined with V.P.C. The solution, as prepared, contained 0.023% water and a trace of propylene oxide. After electrolysis the water in the cathode compartment was reduced to 0.009% and a small amount (ca. 0.001%) of a new component eluting 5 sec. after propylene oxide. The anode compartment composition was unchanged. The total reduction of water content was about 17.4 coulombs of the 150 coulombs passed.

The solution was further electrolyzed for 18 hrs. Electrolysis was performed at a current of 5 mA. The most significant result was the appearance of four new substances more volatile than water in both compartments. At a column temp. of 125°C, peaks were observed at 15, 18, 23, 27, 43, and 114 sec. The first is air and the last was water, which, in the cathode compartment was now reduced to 0.001%. The peak at 23 sec. has been tentatively assigned to propylene oxide, while the peak at 43 sec. could be isopropyl alcohol.

Due to the similar retention times of the four new peaks, resolution is poor even at low temperatures, which makes identification by substitution very uncertain.

III-B. Cycling of Lithium in Starved Electrolyte

The cell used in these experiments was again similar to that shown in Figure 8. The electrode plugs consisted of stainless steel rods milled at one end to form a cup to contain the electrode and grooved and fitted with O-ring seals. Except for the back surface of the cup the rest of the steel between the electrolyte and the seal was coated with Kel-F. Leakage did not appear to be serious. In the following experiments the counter electrode was bulk lithium metal pressed into the electrode cup. The stainless steel itself served as the

working electrode and its potential was monitored. The experiments were conducted in butyrolactone, 1 M in $LiBF_4$. Anodization was stopped as soon as excessive polarization signalled the discharge of the lithium metal formed during the preceding cathodization.

TABLE 10

Cycling of Lithium in Starved Electrolyte

Electrode Area = 0.85 cm^2	Cathodization	Anodization
Cell 1:		
Cycle 1	1 mA/1000 sec	1 mA/560 sec (56%)
Cycle 2	2 mA/500 sec	1 mA/585 sec (59%)
Cycle 3	4 mA/250 sec	1 mA/586 sec (59%)
Cycle 4	8 mA/125 sec	1 mA/532 sec (53%)
Cycle 5	2 mA/500 sec	1 mA/565 sec (56%)
Cycle 6	16 mA/63 sec	1 mA/482 sec (48%)
Cell 2:		
Cycle 1	2 mA/500 sec	1 mA/440 sec (44%)
Cycle 2	2 mA/500 sec	1 mA/610 sec (61%)
Cycle 3	2 mA/500 sec	1 mA/590 sec (59%)
Cycle 4	1 mA/1000 sec	1 mA/570 sec (57%)
Cycle 5	20 mA/50 sec	1 mA/300 sec (30%)
Cycle 6	13 mA/80 sec	1 mA/220 sec (22%)
Cell 3:		
Cycle 1	5 mA/100 sec	1 mA/170 sec (34%)
Cycle 2	5 mA/100 sec	1 mA/145 sec (29%)
Cycle 3	5 mA/100 sec	1 mA/133 sec (27%)
Cycle 4	5 mA/100 sec	1 mA/230 sec (46%)
Cycle 5	5 mA/400 sec	1 mA/971 sec (49%)

While these results are only tentative, and the experiments of primary interest in a preliminary evaluation of the cell construction, it is interesting to note that there is no gross deterioration of cycling efficiency until one goes to quite high currents (13-20 mA).

III-B-2.   Cycling of Lithium in Excess Electrolyte.

Preliminary studies on the cycling of the lithium electrode
were conducted in an H-cell in which the working electrode compartment contained
about 50 ml. of electrolyte, propylene carbonate 0.5 M in $LiClO_4$. The working
electrode consisted of the electrode support structure described on pages 91-92
of the Third Quarterly Report. Lithium foil was pressed into the cavity as des-
cribed in the following section III-C. The amount of lithium was about 125 coulombs
based on a one-electron change.

The electrode was cycled automatically. Both portion of the
cycle were for 1000 sec. at 10 mA. In Figure 18 are shown the results for Cycle 4.
The curves for cycles 1-16 were essentially identical, though the maximum occur-
ring on the charge curve as shown in Figure 18 was less for the other cycles. There-
after ensued a change in the cycling curves and beginning with cycle 22, the curves
had the appearance shown by the dashed line in Figure 18 for cycle 25. The anodic
efficiency varied randomly for the remaining cycles up to cycle 39 after which the
cycling was discontinued. The average recovery was 59%.

The results again indicate that no gross, catastrophic failure
occurs and are, therefore, most promising.

III-C.   Bulk Lithium Metal Electrodes

Work with bulk lithium metal electrodes is difficult because
of the rapid oxidative attack of the metal by the atmosphere. As described in the
Third Quarterly Report, pp. 48-52, preliminary studies on the discharge of bulk
lithium metal in propylene carbonate indicated that little activation polarization
is observed. That is, the anodic dissolution of lithium metal appears to proceed
with electrokinetic reversibility. This work was performed with the 1/16 in.
thick lithium ribbon. We sought to perform similar measurements with thin lithium
electrodes. The following procedure was evolved. Lithium ribbon, 1/16 in. thick
and 1/2 in. wide was pressed between two polished, stainless steel surfaces at
5000 lb. The two stainless steel surfaces with pressed lithium ribbon between

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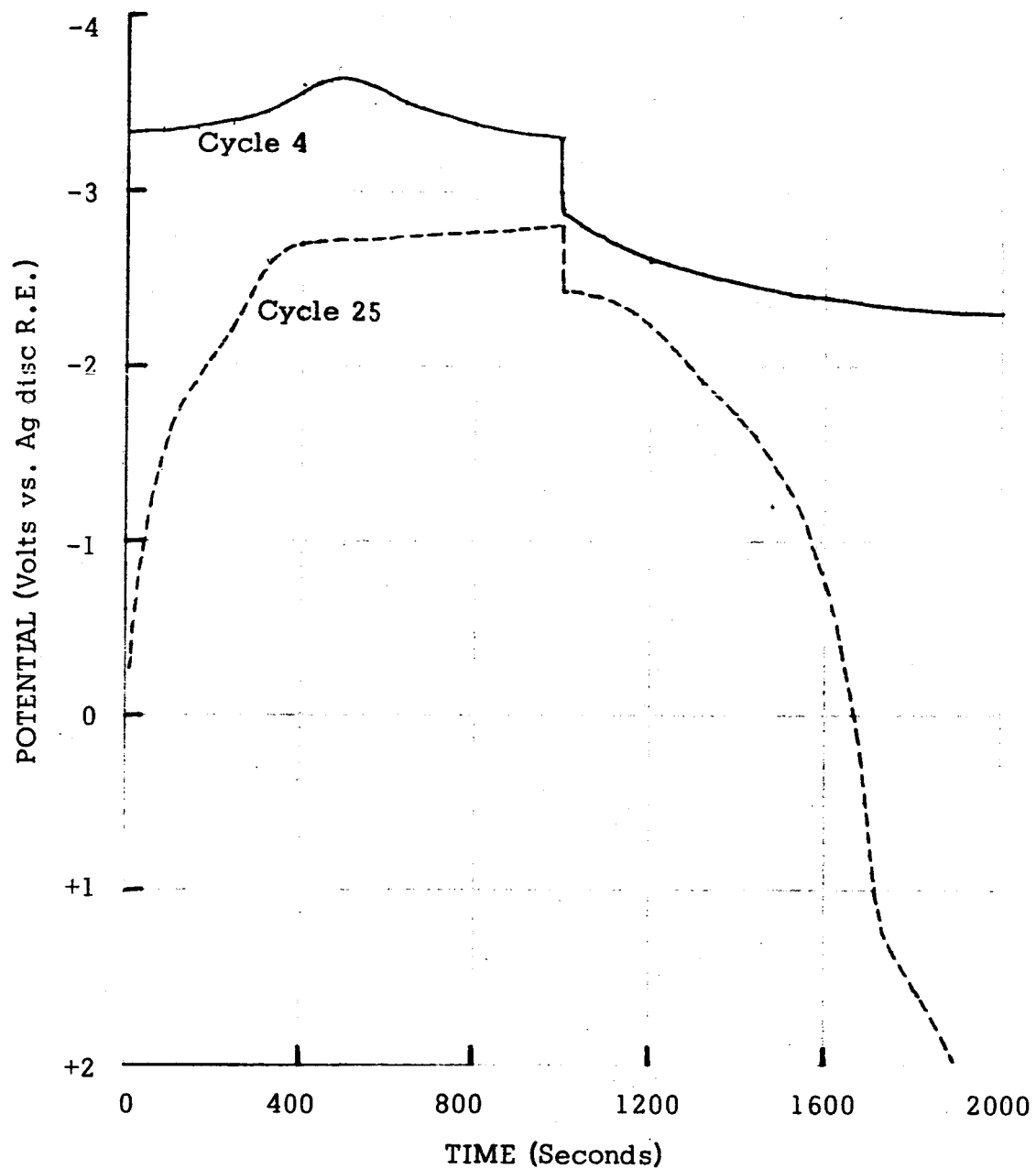
Figure 18: CYCLING OF LITHIUM IN PROPYLENE CARBONATE

Performed in propylene carbonate, 0.5 M in $LiAlCl_4$. See text for further discussion.

them are removed to the dry box without exposing the lithium to the atmosphere. There the stainless steel pieces are removed exposing the thin pressed lithium foil.

Three circular pieces of lithium are punched out of this foil. The die used is such that the piece of lithium will exactly fit into the electrode support structure described on pp. 91-92 of the Third Quarterly Report. The area is about 0.85 cm^2. Only the center piece is placed in the support structure. The other two pieces of lithium are dissolved in water and the base released is titrated to determine the total amount of lithium in the foil: and hence, knowing the area, the thickness may be calculated. The millimoles of lithium contained in the 0.85 cm^2 segments varied 1 to 1.3, which is a thickness of lithium of from 8 to 10 mils, or a capacity of 33 to 43 mA-hr cm^{-2}.

In the first experiment such segments were discharged anodically. A discharge at 11.2 mA cm^{-2} in propylene carbonate, 0.5 M in LiBF$_4$, gave 78% efficiency. A discharge at twice this current, 22 mA cm^{-2} gave 81% efficiency. We believe the lower efficiencies are due to the fact that significant amounts of the lithium were oxidized, in spite of the precautions taken, and thus not available for anodic oxidation.

In a second series of experiments a lithium electrode, prepared as described above, was studied in propylene carbonate, 0.1 M in LiBF$_4$. This is an electrolyte composition which has been extensively used in the past.

In Figure 19, cathodic chronopotentiograms are shown. These are compared with cathodic chronopotentiograms obtained on polished platinum electrodes in the same solution at similar current densities. These chronopotentiograms have not been corrected for iR drop. The calculated corrections are listed in the figure. The lithium metal open circuit potential in this solution was -3.2V versus the silver disc reference electrode.

Figure 19: CATHODIC CHRONOPOTENTIOMETRY ON LITHIUM AND PLATINUM
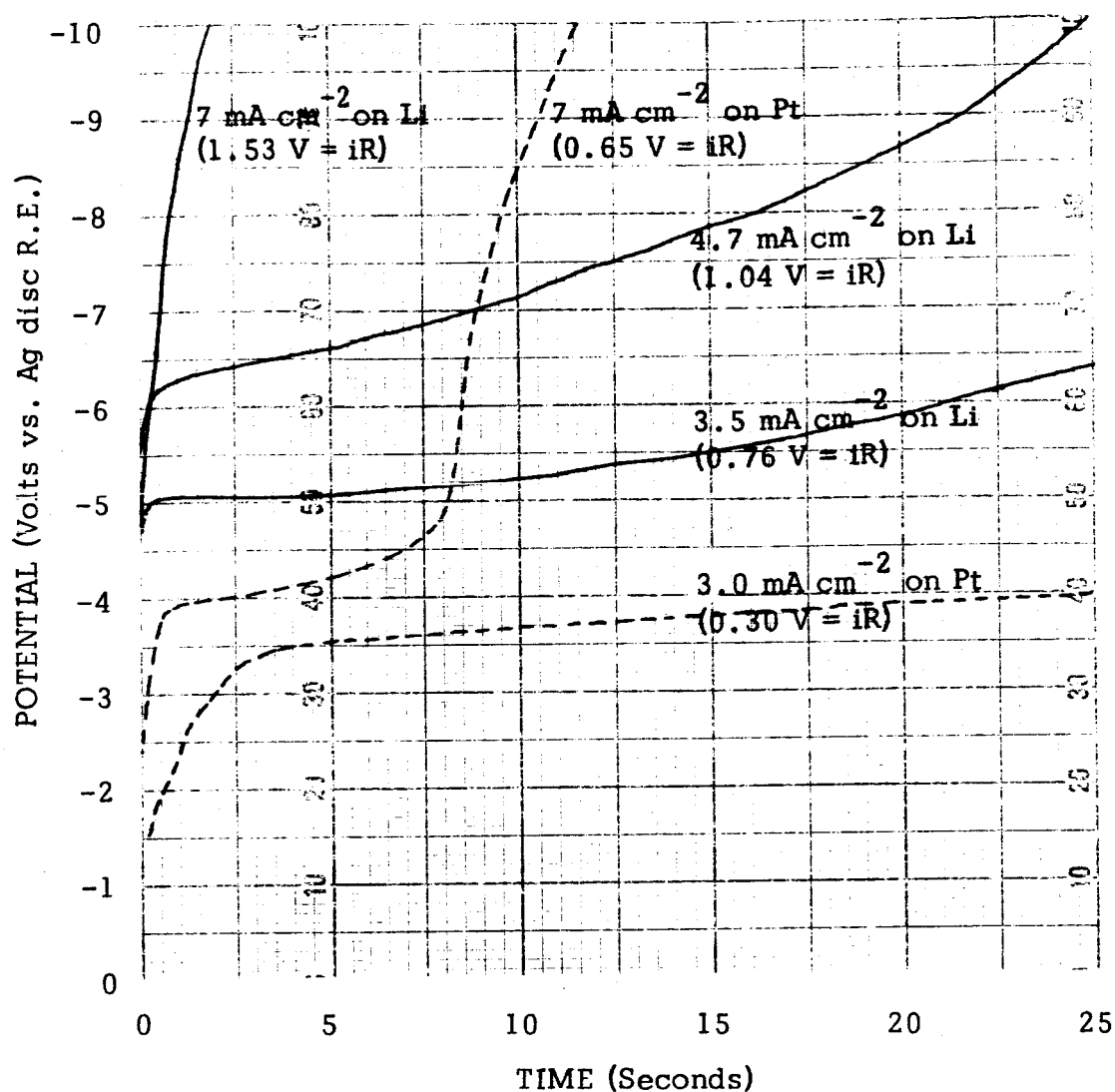Both series of measurements performed in propylene carbonate, 0.1 M in
LiBF$_4$. Curves are direct tracings of chronopotentiograms and have
not been corrected for iR drop. The calculated iR drop which should be
subtracted from the observed potential is given in parentheses.

Two major differences are observed. First, the potential at which reduction occurs on lithium is markedly different from the open circuit potential as shown below. The O.C.V. is $-3.1 \pm .1$ V.

	Current Density	E Observed	$-$ iR $=$	E Corrected
On Li:				
	4.7 mA cm^{-2}	-6.2V	$+1.0$ V	-5.2V
	3.5 mA cm^{-2}	-5.0V	$+0.8$ V	-4.8V
On Pt:				
	7.0 mA cm^{-2}	-3.9V	$+0.7$ V	-3.2V
	3.0 mA cm^{-2}	-3.5V	$+0.3$ V	-3.2V

Extended measurements of this type were not performed since the results obtained on lithium metal electrodes were quite variable; the reduction potential becoming more negative with increasing time of contact with the electrolyte.

The second major difference is the fact that no satisfactory transition time could be obtained.

The final series of experiments performed in this electrolyte with the lithium electrode consisted in investigating the anodization potential as a function of current. The following procedure was employed. Before each run the lithium was anodized for 50 sec. at 10 mA (0.85 cm^2 electrode) in stirred solution. Following this preliminary anodization, the electrode was allowed to stand in quiet solution for exactly one minute. The electrode was then anodized in quiet solution at the current indicated for exactly 25 sec. The anodic potentials remained quite constant during the entire 25 sec. The results are shown in Figure 20. The dashed line in Figure 18 is the current potential curve calculated if the measured potential is purely iR drop. The calculated resistance for the geometry employed in 255 ohms; the apparent resistance, however, is 333 ohms. This is significantly larger than any expected error in the calculation of iR drop and results, we believe, from the formation of a resistive film on lithium. This film may result through reaction of lithium with solvent or with impurities such as water in the solvent. As has been discussed in previous reports, we believe this film is probably lithium oxide. Its formation makes difficult the interpretation of any kind of measurements
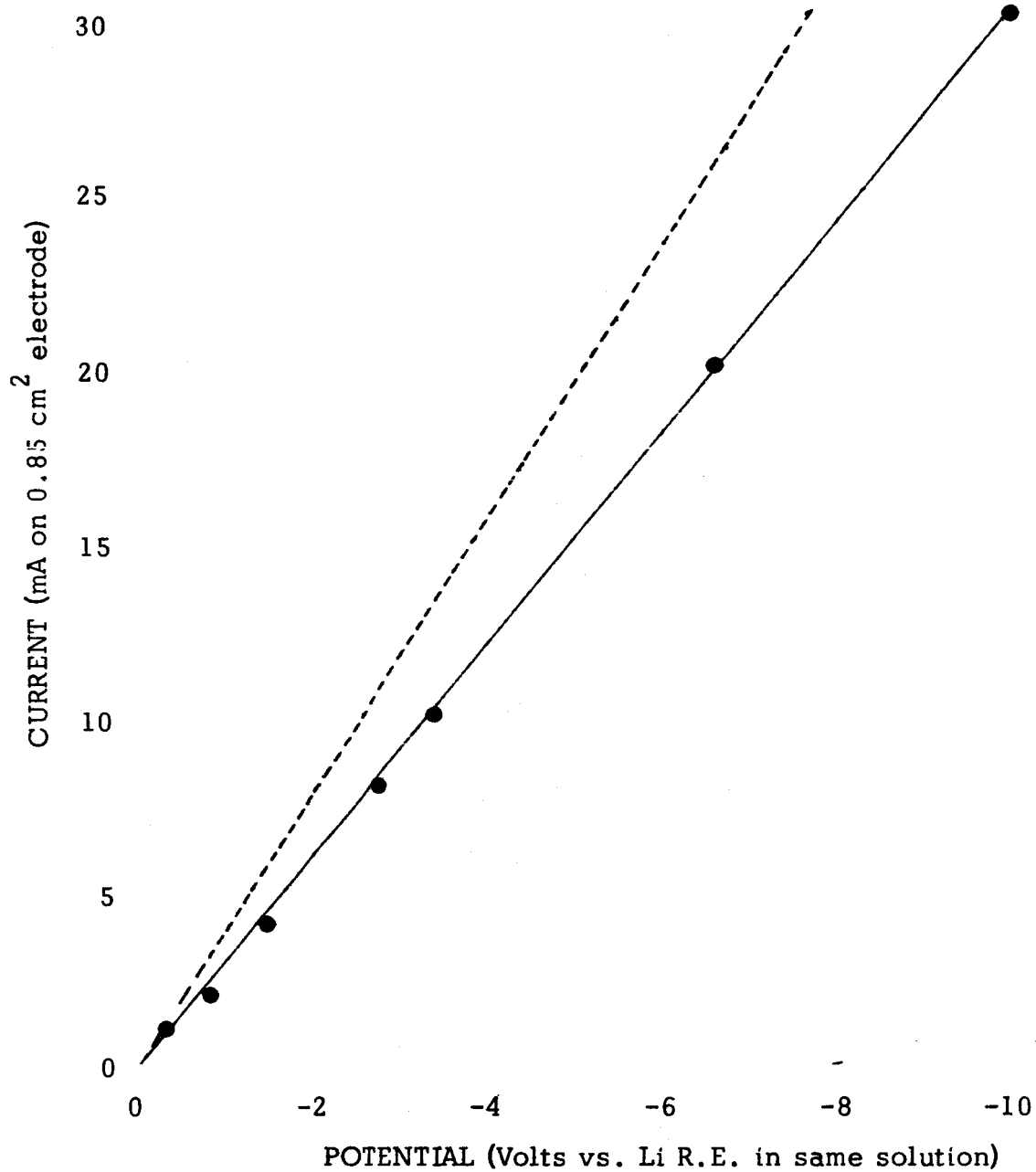
Figure 20: CURRENT-POTENTIAL CURVE FOR BULK LITHIUM ANODIZATION
See text.

performed with solid lithium electrodes.

III-D.   Lithium Deposition in Acetonitrile.

In the following section IV are discussed the results of chrono-potentiometric investigations in acetonitrile. In this section we report only the results of extended lithium depositions performed in this solvent.

In Figure 21 are shown some results obtained for cathodizations for a total of 3000 mC cm^{-2}. After deposition at the current indicated the current was reversed and anodic utilization determined in the usual fashion by dividing the number of coulombs recovered on anodic dissolution by the number of coulombs passed during the preceding deposition.

At lower total amount of cathodization the efficiencies were higher as indicated below for a series of runs performed in acetonitrile, 0.1 M in LiBF$_4$.

Current Density (mA cm^{-2})	Amount of Cathodization (mC cm^{-2})	Anodic Utilization
On Be:		
0.6	300	88%
3.0	300	87%, 86%
6.0	300	94%
12.0	300	75%
On Cu:		
1.0	500	49%
3.0	500	50%
5.0	500	71%, 47%
10.0	500	59%, 65%, 57%

Further study is required and at present one cannot say that acetonitrile is better or worse for a cyclable lithium electrode than are the other solvents, propylene carbonate, butyrolactone, and dimethylformamide.

50
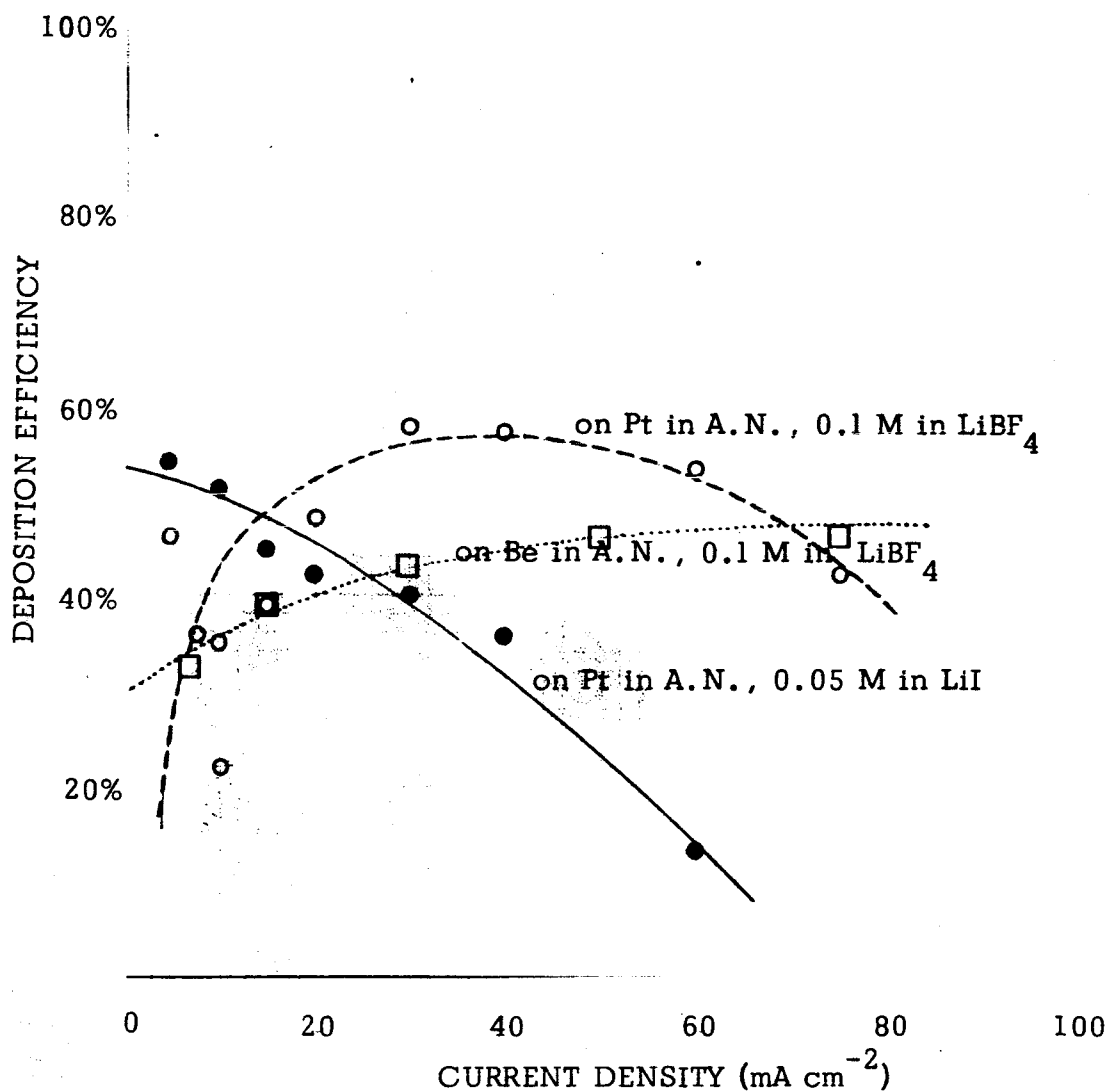
Figure 21: DEPOSITION EFFICIENCY OF LITHIUM IN ACETONITRILE

Results obtained in solution indicated, on substrate indicated, at
current density indicated for cathodic deposition. Deposition performed
in stirred solution for the time required to give 3000 mC cm^{-2} of deposition.
Subsequent anodic dissolution performed at 4 mA cm^{-2}. Efficiency calculated
by dividing the coulombs passed during anodic dissolution by the coulombs
passed during the preceding cathodization.

IV.   SOLVENTS

IV-A.   Solvent Purification

IV-A-1.   Propylene Carbonate

Most of our work has been done with propylene carbonate. These results will be discussed first. As discussed in the Third Quarterly Report, it had been found that the "as-received" propylene carbonate contains significant amounts of water and propylene oxide and a third major impurity, which was then unidentified. Isopropyl alcohol, propionaldehyde and propiolactone were absent in the starting material. It has since been found that propionic acid, propionic anhydride, and allyl alcohol are also absent. The proof of the absence of these constituents is given by the fact that, following the addition of these constituents to the propylene carbonate, subsequent vapor phase chromatographic examination discloses entirely new peaks. It has now been found that the major impurity, previously unidentified, is probably propylene glycol, since the deliberate addition of propylene glycol enhances the peak for this major impurity.

The determination of the water content in propylene carbonate by vapor phase is as follows. Two conditions of operation are followed:

a.   Isothermal runs

   Injector temperature: $220^{\circ}C$

   Detector temperature: $200^{\circ}C$

   Column temperature: constant at $200^{\circ}C$

   Water retention time: ca. 25 sec.

b.   Temperature programmed runs

   Injector temperature: $220^{\circ}C$

   Detector temperature: $200^{\circ}C$

   Column temperature: constant at $100^{\circ}C$ for first 100 sec. following sample injection, then increased at 48° per min. up to $200^{\circ}C$ at 175 sec. Held constant at $200^{\circ}C$ until sample has been entirely eluted.

Under both conditions of operation, the water content in weight percent is given by:

$$\text{\% water (by weight)} = \frac{(0.008)\,(\text{Chart speed, sec. in}^{-1})\,(\text{Area, in}^2)\,(\text{Attenuation})}{(\text{Sample size, microliters})}$$

This has been established by running a series of samples with varying known additions of water.

Vacuum distillation of two 3-kg quantities of propylene carbonate have been performed. The material was first passed through a column of molecular sieves (Linde 4A) into the pot. The column was operated at total reflux at about 5 mm Hg until constant temperature was obtained. The low boiling material distilled off was collected in a liquid nitrogen cold trap. Vacuum distillation was then continued at 5 mm Hg at a 9:1 reflux ratio. Successive fractions were collected and analyzed for the major component by vapor phase chromatography with the results shown in Table I below.

Although a total of seven, and possibly eight, peaks are observed in the V.P.C. analysis of propylene carbonate, only four peaks are present in more than trace amounts. Data on the retention times and identification of these four components are given below:

Table ll

Purification of Propylene Carbonate

Column Operation	Retention time (sec.) of Component			
	No. 1	No. 2	No. 3	No. 4
Constant temperature	13	17	83	216
Temperature programmed	31	96	329	---

Identification: Peak 1: Propylene Oxide

Peak 2: Water

Peak 3: Propylene Glycol

Peak 4: Propylene Carbonate

Results of Distillation

Conditions of Distillation				Amount of Component in weight percent			
Fraction No. and Vol.	Press.	Temp.	Reflux Ratio	No. 1	No. 2	No. 3	No. 4
As received				0.32	0.07	0.42	---
1 - 50 ml.	5 mm.	76.5	9:1	---	0.06	49.4	50.6
2 - 15 ml.	5 mm.	77-90	9:1	---	0.13	78.8	20.9
3 - 50 ml.	5 mm.	96	9:1	---	0.05	5.6	---

4 – 50	5 mm.	96	9:1	---	0.03	0.36	---
5 – 100	5 mm.	95	9:1	---	0.03	0.18	---
6 – 1000	5 mm.	94-95	9:1	---	0.04	0.06	---

Distillation 2:

1 – in cold trap	20 ml.			99%	0.03%	---	---
2 – 24	20 ml.	74-80	9:1	99%	0.04	78	---
3 – 38	20 ml.	80-96	9:1	---	0.06	li	---
4 – 60	20 ml.	96	9:1	---	0.03	0.12	---
5 – 1000	20 ml.	96	9:1	---	0.01	0.02	---
6 – 1000	20 ml.	96	9:1	---	0.002	0.006	---

Several facts are evident: (Propylene oxide is almost completely removed by distillation, passing into the cold trap during initial operations at total reflux, (2) With care, water can be reduced to 0.002%, which we believe is a satisfactorily low value to allow further solvent investigation, (3) Propylene glycol resists clean fractionation because of its high boiling point, and (4) All other impurities are removed in the early stages of distillation and do not present problems.

The first two fractions of the above first distillation, and the second fraction of the second distillation were combined and redistilled at 50 mm Hg in a small distilling apparatus, without a fractionating column. An initial 8 ml. fraction was obtained at 104°C and contained 91.3% propylene glycol, 8% water and about 0.5% water. In successive fractions, the temperature of distillation gradually increased to about 141°C for the final fraction, which was 58% propylene glycol, and the remainder propylene carbonate. Attempts will be made to characterize the first fraction in more detail to definitely establish whether the impurity is propylene glycol. The material, is like propylene glycol, very viscous.

IV-A-2. Butyrolactone

A total of six peaks are clearly defined for butyrolactone. As with propylene carbonate, only four peaks are present in more than trace amounts. The conditions of V.P.C. operation were the same as for

propylene carbonate. The data are shown below:

Table 12

Purification of Butyrolactone

Column Operation	Retention Time (sec.) of Component			
	No. 1	No. 2	No. 3	No. 4
Constant temperature	26	33	235	453
Temperature programmed	56	92	254	---

Identification: Peak 1: Unknown

Peak 2: Water

Peak 3: Unknown

Peak 4: Butyrolactone

Results of Distillation

Conditions of Distillation				Amount of Component in Weight Percent		
Fraction No. and Vol.	Press.	Temp.	Reflex Ratio	No. 1	No. 2	No. 3
As delivered				0.04	0.032	0.049
1 - in cold trap	10 ml			86	14	---
2 - 100	2.5-3	55°	9:1	0.01	0.025	0.08
3 - 71	7	76-80°	9:1	0.002	0.015	0.03
4 - 100	7-8	79-80	1:1	---	0.012	0.006
5 - 1000	7-8	76-80	1:1	---	0.005	---
Distillation 2:						
As received				0.038	0.11	0.004
1 - 113	8	77-80	9:1	0.021	0.021	0.019
2 - 90	8	77-80	9:1	0.004	0.009	0.015
3 - 1000	7	77-81	1:1	0.002	0.003	---
4 - 500	7	77-80	1:1	0.001	0.003	---

IV-A-3. Dimethylsulfoxide

A total of four peaks are observed in dimethylsulfoxide. The first is the air peak, which is small and will not be further considered. The

last peak is for dimethylsulfoxide, and for constant temperature runs at 200°C occurs at 75 sec. For temperature programmed runs, it occurs at about 230 sec. The middle two peaks are not resolved for constant temperature runs, having a retention time of about 24 sec. They are resolved under temperature programming, the first, an unknown component has a retention of 124 sec., the second, water, has a retention time of 160 sec.

Table 13

Purification of Dimethylsulfoxide

Fraction No. and Vol.	Pressure	Temperature	Reflux Ratio	Peaks 1 and 2 Amount of Component in Weight Percent
As received				0.21%
1 - 64	3-4	56-60	9:1	0.08%
2 - 150	3-4	62°	9:1	0.65%
3 - 600	3	60-62	1:1	0.15%

We believe dimethylsulfoxide is probably best purified simply by passing through a column of molecular sieves.

IV-A-4. Dimethylformamide

Dimethylformamide, as received, is quite pure. The only material present in significant amount is water. This material contained 0.016% by weight of water. About three liters were distilled at 8 mm Hg at 40-50°C. A liter of this material, which had stood over molecular sieves for two months, contained about 0.0036% water.

A molecular weight apparatus of the Cottrell type was obtained for measuring the boiling points of solvents at one atmosphere. The apparatus was modified by the addition of a mercury well to contain the thermometer and a drying tube for the reflux condenser. A sample of the dimethylformamide, which had stood over molecular sieves (water concentration=0.004% by weight), was used for the initial trails. The sample was boiled continuously for 10 days. After five hours, the boiling temperature with stem correction applied, was 152.7°C (Atmospheric pressure=758.4 mm Hg), and after 10 days, the

corrected boiling temperature was 152.8°C (Atmospheric pressure = 763.6 mm Hg). This material was then re-examined by vapor phase chromatography and the water content had increased from 0.004% to 0.064%. The concentration of the two minor impurities was about 0.002%. The significant increase in water content did not lower the boiling point within the degree of accuracy of the relatively simple apparatus employed.

IV-A-5. N-nitroso Dimethylamine

Preliminary investigation of the as-received material has been conducted. No attempt has yet been made to purify this solvent. It was necessary to conduct V.P.C. examination under different conditions than those described for propylene carbonate. Satisfactory resolution was obtained with isothermal runs performed at a column temperature of 150°C. Only three peaks were observed: The air peak at a retention time of 12 sec., the water peak at a retention time of 29 sec., and the solvent peak at a retention time of 107 sec. The amount of water in the as-reseived material was about 0.098% by weight.

IV-A-6. Acetonitrile

As described in the Third Quarterly Report, p. 6, acetonitrile has been distilled at atmospheric pressure at 81-82°C. It is not possible to determine the water content in acetonitrile by V.P.C. since the large solvent peak completely swamps the water peak. A variety of operating conditions were tried, but satisfactory resolution of the water peak for amounts of water less than 10% by weight could not be achieved.

IV-A-7. N-butyl Formate

Preliminary investigation of the as-received material has been conducted. No attempt has yet been made to purify this solvent. As was true with acetonitrile, no resolution of the water and solvent peaks can be achieved, and V.P.C. is not a satisfactory method for the determination of water content.

IV-B.   Cathodic Behavior in Propylene Carbonate Solutions

The electrochemical behavior observed during cathodization in various propylene carbonate solutions were described in the Third Quarterly

Report, pp. 11-36. Four additional solutions have been examined with the results described below.

IV-B-1. Propylene Carbonate, 0.1 M n-propyl Ammonium Hexafluophosphate

This solution was particularly interesting because it gave results characteristic of the presence of a soluble , reducible, impurity. In the past, we have noted that the presence of such impurities as water is somewhat paradoxical in that the expected reduction behavior is not observed. The results shown in Figure 22 indicate what should be expected and what is, in fact, observed if a soluble impurity is reduced without those extraneous complications water evidently produces. Constancy of $iT^{1/2}$ was observed at currents from 0.55 to 2.5 mA cm^{-2}. Successive, reproducible chronopotentiograms could be obtained on the same electrode.

IV-B-2. Propylene Carbonate, 0.1 M n-propyl Ammonium Tetrafluoborate

Chronopotentiograms were obtained at currents of from 0.075 to 5 mA cm^{-2}. At the lowest current, a small amount of background reduction was observed, but after 7 sec., the potential rose to -1.8V and slowly increased to -1.9V after 25 sec. At 5 mA cm^{-2}, the potential immediately rose to -3.1V and remained there for the 25 sec. of electrolysis. Vigorous gassing was observed.

IV-B-3. Propylene Carbonate, 0.1 M n-propyl Ammonium Iodide

Potentiostatic reduction in stirred solution gave satisfactory steady state currents with a limiting current plateau at between -0.7 and -11.2V or 0.25 mA cm^{-2}. However, satisfactory chronopotentiograms reflecting the presence of material giving this limiting current were not found. Anodic chronopotentiograms obtained on platinum were sufficiently well-defined to allow the establishment of transition time measurements. The value of $iT^{1/2}$ was 42 mA cm^{-2} $sec^{1/2}$, whereas a value of 20 would be expected for a one electron change in a 0.1 M propylene carbonate solution.

IV-B-4. Propylene Carbonate, 0.05 M $MgCl_2$

The results are shown in Figure 23. These results, we believe, reflect the growth of an insulating magnesium salt film.

POTENTIAL (Volts vs. Ag disc R.E.)

-5

-4

-3

-2

-1

0

Potentiostatic current vs. potential curve. Limiting current = 1.5

Cathodic chrono-potentiogram at 0.75 mA cm^{-2}. iT$^{1/2}$ = 3.0

TIME FOR CHRONOPOTENTIOMETRY (seconds)

0   5   10   15   20   25

0   0.5   1.0   1.5   2.0   2.5

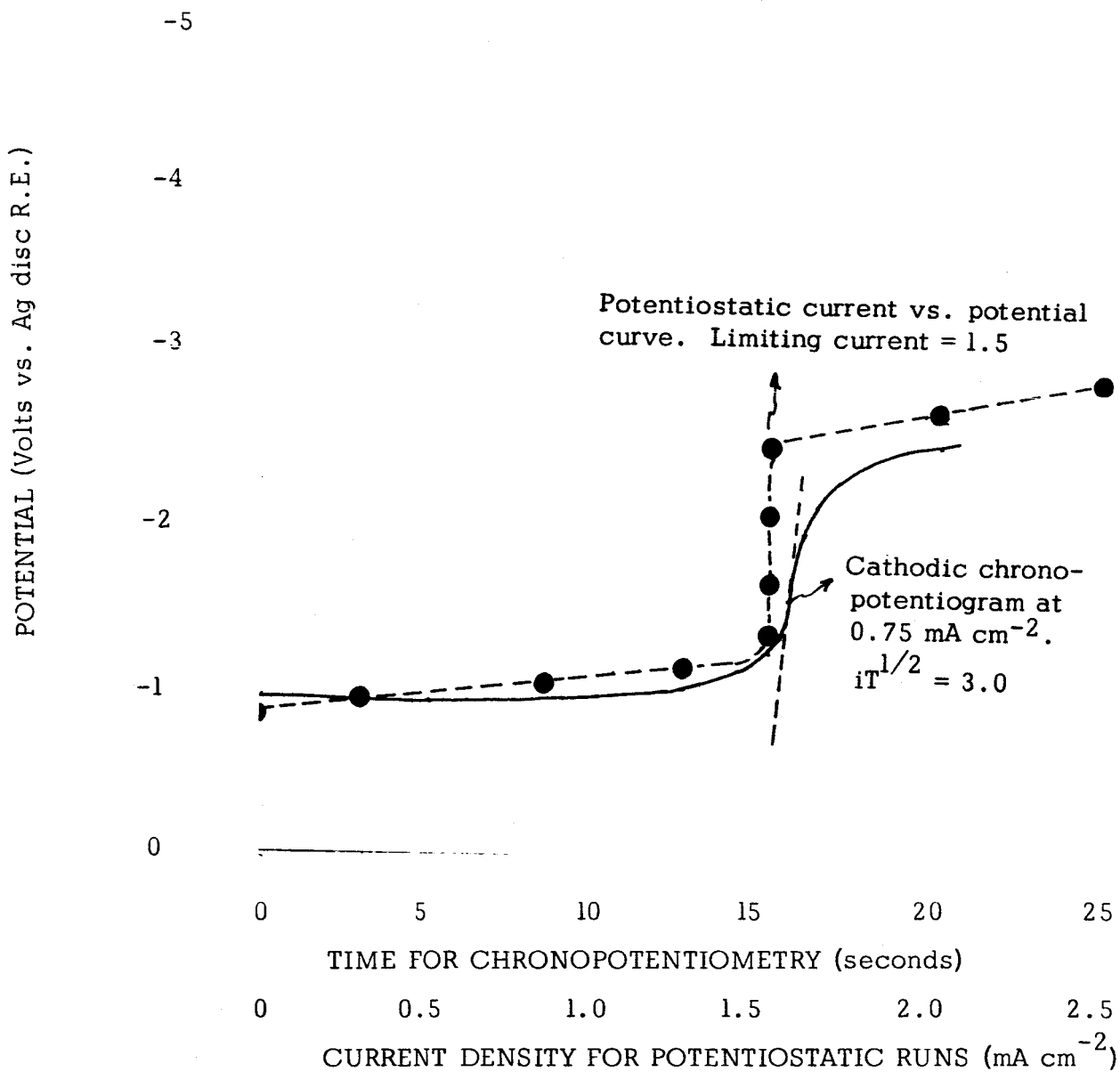CURRENT DENSITY FOR POTENTIOSTATIC RUNS (mA cm^{-2})

Figure 22:   REDUCTION IN PROPYLAMMONIUM SALT SOLUTIONS

Electrochemical measurements made on platinum disc electrodes in propylene carbonate, 0.1 M in tetrapropyl ammonium hexafluophosphate. Potentiostatic measurements made in stirred solution. Results indicate the presence of a soluble, reducible impurity. Increasing the concentration of salt to 0.15 M increased iT$^{1/2}$ to 4.1, indicating the impurity is present in the salt rather than the solvent.
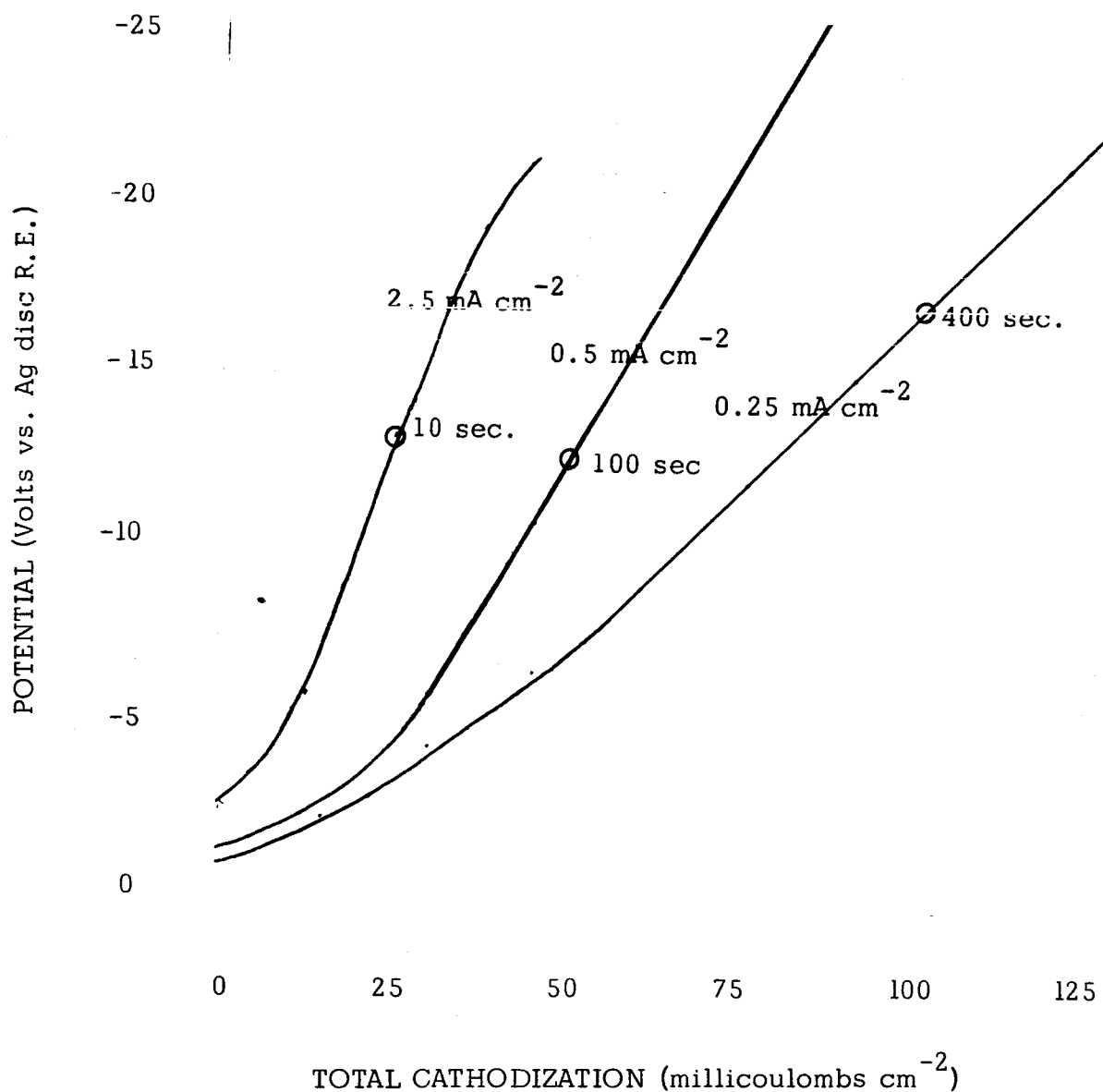
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Figure 23: REDUCTION IN MAGNESIUM SALT SOLUTIONS

Cathodization performed on platinum disc electrodes in quiet solution, propylene carbonate, 0.05 M in $MgCl_2$. The marked increased in potential with total cathodization indicates the build-up of insulating film on the elctrode.

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IV-C.   Cathodic Behavior in Acetonitrile Solutions

It is of interest to investigate a variety of solutes in each solvent in order to more fully characterize the electrochemical properties of the solvent. Five acetonitrile solutions have been examined. Typical chrono-potentiograms are shown in Figures 24 and 25. The dashed line and the solid circles indicate the transition time determination. The results are summarized below:

Table 14

Electrochemical Behavior in Acetonitrile

Solution	$iT^{1/2}$ (from fig.23-24) (mA cm^{-2} sec$^{1/2}$)	Specific Resistance (ohm-cm)	Equivalent Conductance ohm^{-1} cm^2 equiv^{-1}
0.1 M LiBF$_4$	64.4 (cathodic)	161	62
0.05 M LiBF$_4$	26.4 (cathodic)	250	80
0.05 M LiI	33 (cathodic)	204	98
	19 (anodic)	204	98
0.05 M KI	25.4 (cathodic)	174	115
	20 (anodic)	174	115
0.05 M AgClO$_4$	34.6 (cathodic)	156	128

Two problems were noted in obtaining chronopotentiograms in acetonitrile. The first was that it was impossible to obtain satisfactorily reproducible chronopotentiograms for transition times longer than about 10 seconds. Furthermore, the transition times were significantly larger than would correspond to the $iT^{1/2}$ values found for shorter transition times as shown in Figures 24-25. We believe this is due to the low viscosity of acetonitrile (0.345). Thus, one expects the density grandients built up to effect serious convection with a resultant enhancement of the transition time.
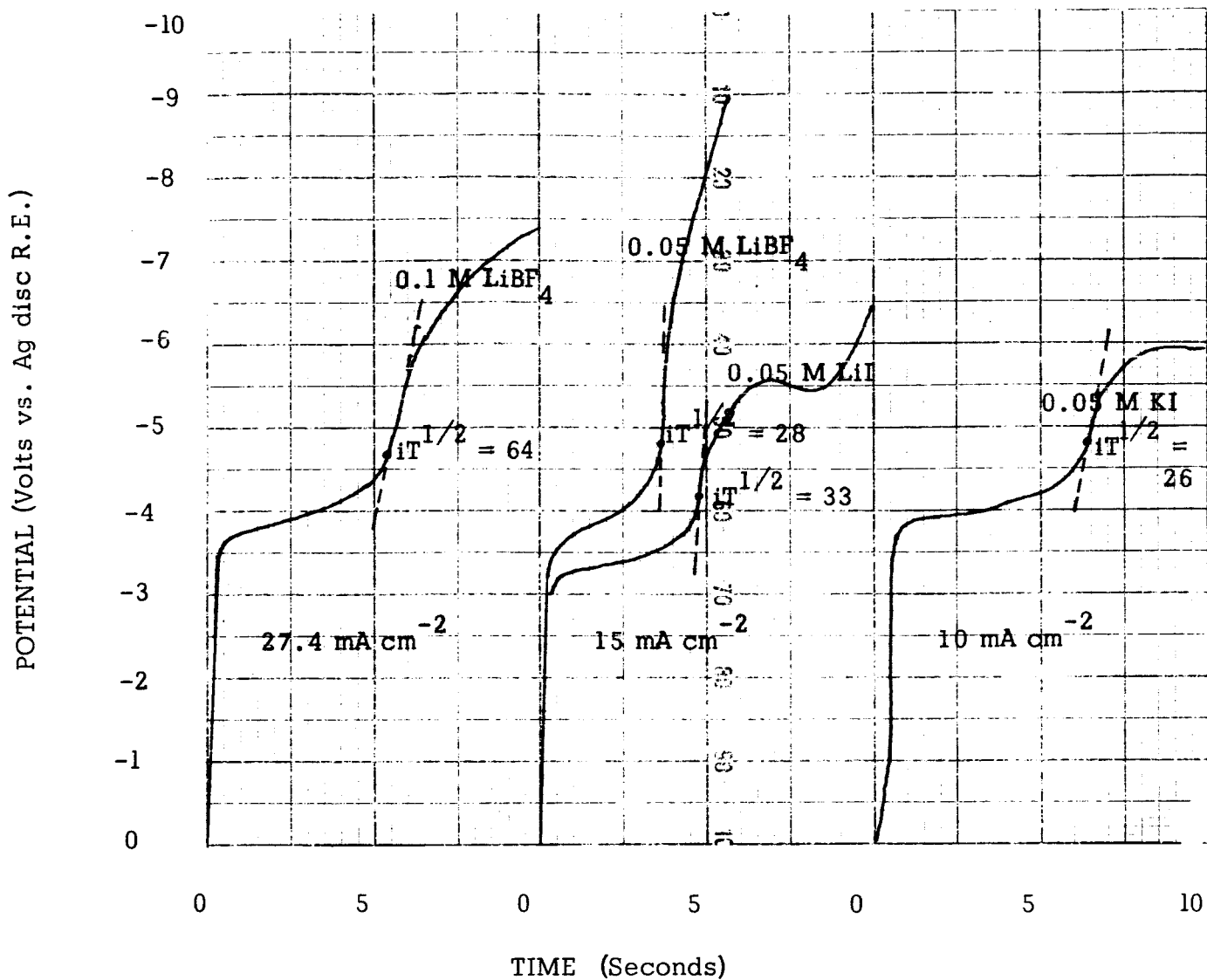
Figure 24: CATHODIC CHRONOPOTENTIOMETRY IN ACETONITRILE

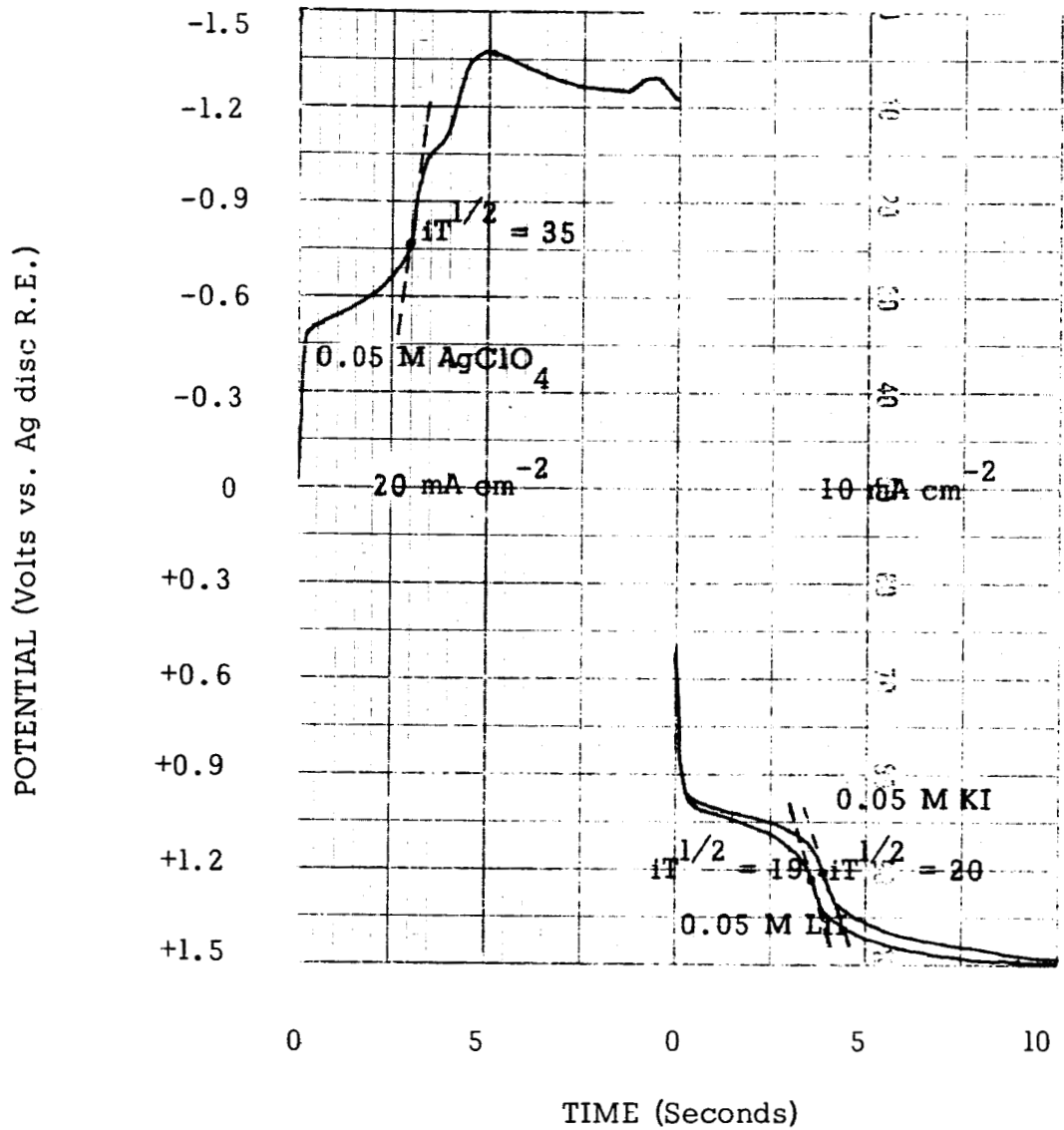Measurements performed on polished platinum disc electrodes under conditions indicated.

Figure 25: CHRONOPOTENTIOMETRY IN ACETONITRILE

Measurements performed on polished platinum disc electrodes under conditions indicated.

A second problem was that the chronopotentiograms for lithium and potassium were not reproducible on electrodes, which had been sitting in the solution for an extended period of time. In fact, electrodes which had sat in the solution for 10 minutes gave no transition times at all, but merely gave a drawn-out trace with the potential slowly increasing to more negative values. This probably reflects some absorption of solution impurities on the electrodes.

IV-D. Mass Transport Properties in Starved Electrolytes

In Figure 3 on page 25 is shown the type of cell in which we propose to investigate the behavior of electrodes in a starved electrolyte environment. One problem which will exist in the operation of such a system concerns the ability of ions to migrate from one electrode to the other. For meaningful measurements of electrode behavior to be made, it is necessary that the current used not be larger than the maximum rate at which such migration may occur. It was, therefore, of interest to get some idea about this maximum rate of ionic transport.

A cell identical to that shown in Figure 8 was used in these studies. One electrode consisted of a platinum foil; the other electrode consisted of silver foil pressed against a platinum gauze. The cell was filled with 0.8 ml, of 0.1 M $AgClO_4$ in propylene carbonate.

Cathodic chronopotentiograms were obtained on both electrodes. On platinum, the value for $iT^{1/2}$ was 17.5 mA $sec^{1/2}$ (ca. 0.85 cm^2 electrode); on silver, the value for $iT^{1/2}$ was slightly larger, 19.7 mA $sec^{1/2}$. We believe this was due to the fact that the silver surface has a larger area because of being pressed against the platinum gauze.

Next, the platinum electrode was cathodized potentiostatically. The current was recorded with time and steady state currents were achieved within 1.5 min. after the commencement of electrolysis. In Figure 26 are shown the results of the potentiostatic measurements and also a plot of $iT^{1/2}$ vs. E obtained from the chronopotentiograms on platinum. It will be observed that the limiting current ca. 2.5 mA is about 14% of the $iT^{1/2}$ (17.5).
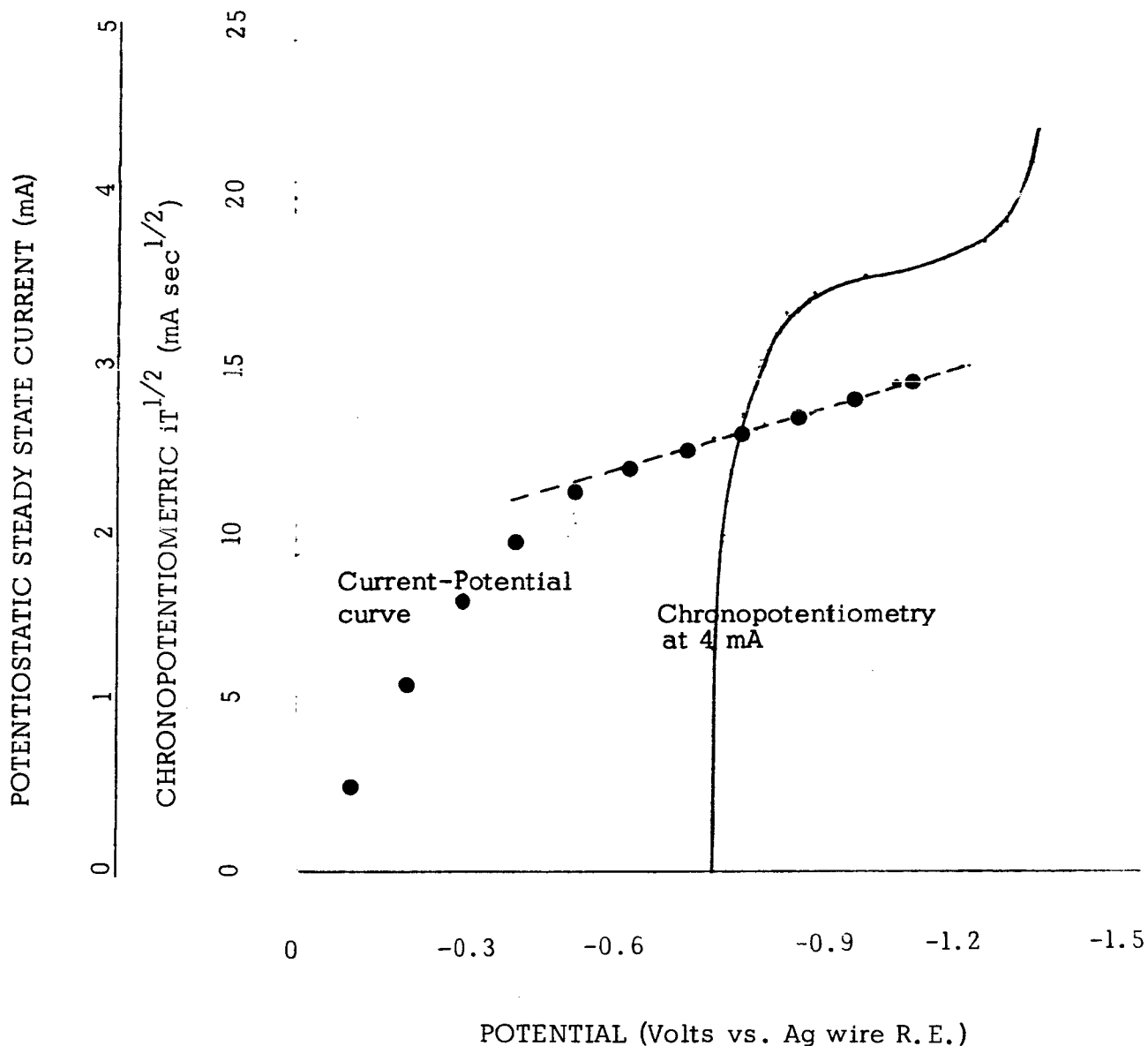
Figure 26: MASS TRANSPORT PROPERTIES IN STARVED ELECTROLYTE CELL

See text. Chronopotentiometry performed on 0.85 cm^2 platinum

electrode in starved electrolyte cell. From the chronopotentiogram

obtained at 4 mA cm^{-2} was calculated the $iT^{1/2}$ curve shown in the

figure. Current-potential curves also obtained on 0.85 cm^2 platinum

electrode in starved electrolyte cell by cathodizing the electrode

potentiostatically at the potential indicated and measuring the

resultant steady state current which was attained within 1 min. after

the commencemnt of electrolysis.

Two other cells were similarly assembled and subjected to electrolysis such that the silver electrode was anodically dissolved and silver cathodically deposited on the platinum electrode. The electrolysis were conducted at constant current, and the potential of the platinum electrode recorded. After a period of time, the potential shifted noticeably to more negative values -- just with a chronopotentiogram. From the time elapsed until this potential shift, we calculate the number of coulombs of deposition shown below. A 1-micron millipore separator was placed in front of the platinum electrode.

Amount of Silver on Ag Electrode	Amount of Silver Ions in Electrolyte	Deposition Current (on 0.85 cm^2 electrode	Coulombs of Deposition before Polarization
22 Coulombs	8 Coulombs	2 mA	20 Coulombs
22 Coulombs	8 Coulombs	.5 mA	19 Coulombs

The results indicate that satisfactory ionic transport through the millipore separator from one electrode to the other may occur without serious problems. The thickness of electrolyte is given by the volume, ca. 0.8 cm^3 divided by the electrode area, 0.85 cm^2, or about 0.94 cm. For a 0.1 M $AgClO_4$ solution in propylene carbonate, this would provide a resistance based on the specific resistance of 465 ohm-cm of 440 ohm. Before discharge, the resistance of the cell was measured and was 380 ohm. This is significantly less than that predicted and suggests, we believe, that as the electrodes were pressed together the distance between them was less than 0.94 cm, and some of the elctrolye had been squeezed out of the cell. It will be noted that the presence of the millipore separator did not increase the resistance.

V.   FUTURE WORK

Work will be concentrated in three areas:

1.   The cycling behavior of the lithium electrode. The cycling behavior will be studied with particular attention to the effects of electrode substrate, electrolyte composition and current density. It will be our objective to establish the nature of important differences so that appropriate recommendations can be made concerning the particular variables about which further study should be concentrated.

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2. Concurrent reactions during lithium deposition. Initial study will be given to the analysis of solutions in which prolonged cathodization has been conducted. Of immediate interest will be the effect of water. This will, as time allows, be followed by attempts to determine what other by-products are formed during cathodization for an indication of the deleterious nature of these by-products.

3. Anodic formation of Cathode Salts. Of major interest will be the attempt to find the conditions under which, during anodization of copper metal, insoluble salts are formed. The approach will be that, in most media when copper metal is anodized, soluble copper species are formed. An investigation of the processes which do occur will be undertaken. These results will be compared with those obtained when to the system are added materials such as LiF, which may be expected to result in the entrapment of copper through formation of CuF_2. The next step will be an attempt to find whether in a system where entrapment of copper species is indicated, this material can be cathodically discharged.

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