N66-35218

NASA CR-54969

RESEARCH AND DEVELOPMENT OF A HIGH CAPACITY, NONAQUEOUS SECONDARY BATTERY

Final Report

October 1964 - December 1965

by

R. G. Selim, K. R. Hill, and M. L. B. Rao

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract NAS 3-6017

P.R. MALLORY & CO. INC.
LABORATORY FOR PHYSICAL SCIENCE
NORTHWEST INDUSTRIAL PARK
BURLINGTON, MASSACHUSETTS

220

NASA CR-54969

FINAL REPORT
October 1964 - December 1965

RESEARCH AND DEVELOPMENT OF A HIGH CAPACITY, NONAQUEOUS SECONDARY BATTERY

by

R. G. Selim, K. R. Hill, and M. L. B. Rao

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

February 14, 1965

Contract No. NAS 3 - 6017

Technical Management
Space Power Systems Division
National Aeronautics and Space Administration
Lewis Research Center, Cleveland, Ohio
Mr. Robert B. King

P. R. Mallory & Co. Inc.
Laboratory for Physical Science
Northwest Industrial Park
Burlington, Massachusetts

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (Cont'd.)

LIST OF FIGURES

ABSTRACT

Some of the basic problems and fundamental limitations involved in the development of high energy density secondary cells are described. Special attention is given to the fundamental electrochemical problems peculiar to the lithium electrode. The basic theory of electrochemical measurement in poorly conducting solutions, in the total absence of supporting electrolyte, has been re-examined, with discussion based on concommitant experimental work. Cathodes, particularly CuF_2 and AgCl have been studied. The major problems concern the elementary electrochemical processes and the basic chemistry of the cathode salt - electrolyte systems; these problems are discussed and illustrated by experimental data. A detailed analysis of cell design criteria is presented, and the relevance of specific chemical and electrochemical processes to such criteria discussed.

RESEARCH AND DEVELOPMENT OF A HIGH CAPACITY, NONAQUEOUS SECONDARY BATTERY

by

R. G. Selim, K. R. Hill, and M. L. B. Rao

SUMMARY

The lithium electrode is discussed by first considering the cycling behavior in excess electrolyte in four solvents: propylene carbonate, butyrolactone, dimethylformamide, and dimethylsulfoxide. The cycling behavior is uniformly poor; at best, efficiencies of anodic discharge were only 80 - 90%, and the cycle life less than 40 cycles. The physical form of the deposit is bad, and the concurrent evolution of gas is undesirable in any closed cell. The cycling behavior was sensitive to a number of variables: the current density, the total amount of deposition, the substrate on which deposition was effected, the solvent, the solute, and the impurity level. Considering the number of variables involved, it was apparent that multiple-cycling screening experiments could not efficiently be performed, and single-cycle experiments were resorted to.

The single-cycle experiments were also difficult to interpret. It was clear that the reduction of lithium ions to metal was not a simple, reversible, one-electron reduction as is true, for example, of the reduction of silver ions in each of these solvents. It was also clear that the source of inefficiency did not lie merely in the presence of a co-reducible impurity. It was necessary to undertake a more basic study of the cathodic behavior in lithium salt solutions.

Before these more basic studies could be initiated, it was necessary to undertake a detailed review of the complexities involved in the study of electrochemical behavior in the lithium salt - organic electrolyte systems. Complications expected to exist, which are normally absent in typical aqueous electrochemical studies, include: the total absence of supporting electrolyte, and the effect of this on the mass transport and electrical double layer properties; the low conductivity of the solutions and the effect of the resultant iR drop included

in the potential measurements on allowing a resolution of the various potential terms, the extremely negative electrode potentials (i.e. more than 3 V negative to the point of zero charge on platinum) and the effect of this on double layer properties and in inducing other surface effects such as strong adsorption in the presence of the fairly large amounts of impurities (ca. 0.01 M).

In experiments conducted in five solvents: propylene carbonate, butyrolactone, dimethylformamide, dimethylsulfoxide, and acetonitrile, all of the complications recited in the preceding paragraph make it impossible to make any unequivocal measurement of the exchange current. The "apparent exchange current" is, in mA cm^{-2}, about equal to the concentration, in M l^{-1}. There is no evidence that the behavior of the lithium electrode is complicated by serious electrochemical "irreversibility".

The fundamental phenomena of interest are these:

At potentials positive to the open circuit potential of a lithium electrode in the same solution, there does occur on all solid metals examined (platinum, silver, copper, cobalt, nickel, aluminum, and beryllium) some cathodic reduction. This appears to be a surface limited rather than a mass transport limited process. We believe this to be the reduction of solvent or impurities with the formation of by-products which "deactivate" the surface towards further reduction. These by-products may be lithium salts or polymeric organic material.

The efficiency for anodic dissolution of lithium metal appears to be essentially 100%: Cycling "inefficiency" results from the inefficient deposition of lithium. Surprisingly, the efficiency is relatively constant, and <u>independent</u> of the current density, at currents below the limiting current. These efficiencies are about 80% (Note: we do not attach much importance to variations of ± 10%.) in all but acetonitrile, which was about 60%. We believe the explanation for this relatively constant, but current independent, efficiency reflects the cathodic reduction of solvent and/or impurities on the freshly deposited lithium surface.

Lithium metal is relatively inert toward propylene carbonate and butyrolactone -- we have not investigated the behavior of bulk lithium metal in the other three solvents, dimethylsulfoxide, dimethylformamide, and acetonitrile. We believe this apparent stability reflects the formation of passivating lithium salt films through direct reaction with electrolyte, and does not reflect the inherent rate of the lithium - electrolyte chemical reaction.

The similarity of the behavior of the lithium electrode in all of these solvents does not allow one to make a decision on the "best" system. A number of factors -- double layer effects, mass transport effects, surface effects, impurity effects, etc. -- influence the cycling behavior of the lithium electrode. A change in any of these may radically alter the performance of the lithium electrode. We see no evident reason why it should not be possible to find an electrolyte in which satisfactory cycling behavior is attained; this search will be expedited through more fundamental studies, which we have hoped to anticipate in this report.

Secondary cell cathodes are even more complex than the lithium anode. We have divided cathode behavior into three processes we believe necessary for efficient cycling: efficient anodic generation of metal ions; insolubilization of the electrogenerated metal ions within the domain of the electrode; and the dischargeability of the insolubilized material. The best total cycling behavior was obtained in propylene carbonate/0.5 M $LiAlCl_4$ solutions. The cycling efficiency, as calculated by the coulombs of electricity recovered on cathodization by the number of coulombs passed during the preceding anodic charge , was about 73% for over thirty cycles. This did not result from inefficient anodic generation of copper species, but through the solubility of copper (I) and copper (II) chloride in this media, which decreases the efficiency of cathodic discharge. Cycling efficiencies in 0.5 M LiCl solutions in butyrolactone and dimethylformamide were only 10 - 20%. This, again, is ascribed to the greater solubility of the copper chloride salts in these two media. As with the lithium electrode, cycling performance is a combination of so many factors, it did not seem reasonable to attempt to screen systems by the criterion of total cycling behavior; and the individual processes mentioned at the beginning of this paragraph were separately studied.

Five elements were of initial interest: iron, cobalt, nickel, copper and silver. Very early, we eliminated iron, cobalt, and nickel from consideration because of evidence that the "apparent exchange current"for anodic dissolution of these elements in all the solvents examined was so low that it did not seem likely that any of these three elements were suitable candidates for incorporation in secondary cell cathodes. In fact, when a cycle comprising "anodic dissolution" followed by "cathodic reduction" was performed with these metals, it was not certain that the anodization did not comprise oxidative decomposition of electrolyte or impurities, followed by cathodic reduction of these anodic by-products. Both silver and copper can be anodically oxidized in all five solvents of interest -- propylene carbonate, butyrolactone, dimethylformamide, dimethylsulfoxide, and acetonitrile -- with 100% efficiency. While silver goes into solution as silver (I), copper goes into solution, predominately as copper (I) rather than copper (II), except in dimethylformamide, where copper (II) is generated with 100% efficiency. Because of weight considerations, copper salts are superior to silver salts. Of the copper salts, the chlorides and fluorides are of primary interest.

The solubility of CuCl, $CuCl_2$, and CuF_2 was examined in propylene carbonate, butyrolactone, and dimethylformamide. It was apparent that specific effects, inducing solubilization, occurred. One such effect is the strong tendency for the formation of the chloride complexes, $CuCl_2^-$ and $CuCl_3^-$. Another effect inducing solubilization apparently was the displacement of copper ions from CuF_2 by lithium ions. The problem of solubility as a limitation to cell performance is most serious, and the thermodynamics attending solubilization have been investigated through measurements of the EMF series in the various solvents. The results suggest that it may be most difficult to find an electrolyte in which the copper salts are sufficiently insoluble to allow incorporation in cells with reasonable shelf-lives.

Finally, we have investigated the discharge behavior of several salts, particularly AgCl, CuF_2, and CuCl. There is little polarization for the discharge in excess electrolyte for the relatively low capacity (ca. 4 to 40 mA-hr cm^{-2}) electrodes used, and the discharge curves are quite flat. This indicates that the problems of concentration polarization and iR drop within the porous electrodes are not serious. The main problem was the inefficiency of discharge. Discharge efficiencies of 50% appeared to be the maximum attainable with CuCl and CuF_2 electrodes. It is assumed that this is caused by the following reactions, in which soluble products diffusing away from the electrode limit efficiency:

$$2\ CuCl + e^- = Cu^o + CuCl_2^-$$
$$CuF_2 + e^- = Cu^+ + 2\ F^- \quad (2\ LiF\ ?)$$

The discharge efficiency was a marked function of the electrolyte. This was particularly true for the discharge of AgCl, which could not be discharged at all in KPF_6 solutions, regardless of the solvent. This was ascribed to the precipitation of KCl which may either form passivating films on the undischarged AgCl or plug up the pores of the electrode. Discharge performance of AgCl, CuCl, and CuF_2 has been investigated in the range of 1 to 10 mA cm^{-2}. No polarization problems are encountered; we do not consider the discharge of these three materials to be limited by electrokinetic "irreversibility" inherent in the salts. Thus, it is reassuring to know that salts with reasonable capacities (4 - 40 mA-hr cm^{-2}) may be discharged at reasonable rates (1 - 10 mA cm^{-2}) in these relatively poorly conducting electrolytes.

A Principal problem in cathode cycling involves finding a suitable reservoir for the anions required to "insolubilize" the cations generated on anodic oxidation. It is unlikely that this reservoir can be a soluble material, since the weight of solvent necessary to keep this amount of material in solution would be many times the total electrode weight, and the energy density would be reduced to quite uninteresting levels. One must search for an insoluble salt reservoir, which may serve as a source of anions through reactions such as the following: $Cu + 2\ LiF = CuF_2 + 2\ Li^+ + 2\ e^-$. This process is discussed and, although we have not been successful in using it to effect the formation of CuF_2, the principle is valid as has been demonstrated by the successful anodic generation of insoluble AgCl from electrodes incorporating a mix of silver metal and LiCl in a non-chloride containing ($LiClO_4$) propylene carbonate solution, wherein LiCl is but slightly soluble.

Thus the problems connected with copper and silver salt cathodes are primarily "chemical" rather than "electrochemical" in nature. That is, the basic electrochemical processes -- efficient anodic generation and cathodic salt discharge without polarization -- do not limit electrode performance. The problem is chemical, and requires a search for systems in which the equilibria are such that these processes can occur with stoichiometric efficiency.

The problem in investigating isolated phenomena rather than total systems is, of course, the fact that the particular virtues or faults attending a specific phenomenon may not be those which prevail in an actual cell. Most of our experiments have been performed in excess electrolyte. It is possible that in a starved electrolyte configuration improvement may result. For example, the inefficient deposition of lithium may result from the co-reduction of small amounts of impurities which, in a starved electrolyte, may be quickly consumed allowing efficient operation thereafter. Similarly, the solubilization of copper salts may be satisfactorily decreased in the starved electrolyte to improve cathode performance. Therefore, it is necessary that prototype cells be examined with particular attention to the specific phenomena discussed in this report and their relevance to total cell operation.

For this purpose we recommend propylene carbonate as the solvent, since the lithium cycling efficiency is best in this solvent. We cannot yet recommend CuF_2 as a cathode since the electrolyte has not yet been found in which, via a salt transformation, the electrode can be cycled. We do recommend $CuCl_2$ as the cathode, and lithium as the anode. The energy density of the $Li/CuCl_2$ system is 503 watt-hr lb^{-1}. We recommend $LiAlCl_4$ as the solute, since LiCl is not sufficiently soluble in propylene carbonate, and there is no data on other possible lithium salts of chloride donating anions. The propylene carbonate/$LiAlCl_4$ is, of course, that in which reasonable cycling performance (73% for over 30 cycles) of porous copper electrodes has been attained. Our experiments indicate that the initial product of anodization is CuCl rather than $CuCl_2$, but there is no apparent reason why, in a starved electrolyte configuration, it should be impossible to further oxidize the CuCl to $CuCl_2$. Although a primary objective of prototype cell studies is to see how the efficiencies of cycling observed in excess electrolyte may be changed in starved electrolyte configurations, a second problem concerns the cell iR drop, and prototype cell studies should have, as a secondary objective, the determination of just how important this is, It is our opinion that, in order to keep the cell weight low, the thickness of electrolyte between the two electrodes must be so small that, in fact, the iR drop cannot be excessive. For example, for a cell comprising two electrodes, each with a capacity of 10 mA-hr cm^{-2} separated by an electrolyte thickness of 10 mils (0.0254 cm) with a specific resistance of 200 ohm-cm, the iR drop for discharge at the 10 hr rate (1 mA cm^{-2}) would only be 5 mV. We do not believe concentration polarization should be a problem at these currents, and the objective of prototype cell studies should be to find just what the problems are and whether they cannot be investigated and new systems screened through a more efficient procedure than those conventionally employed. We believe the $Li/LiAlCl_4$,$PC/CuCl_2$ system is satisfactory for such preliminary prototype cell studies with the objectives recited above.

I. INTRODUCTION

In this report it is our first objective to present the data accumulated during the contract period. It must be understood that the data is not meant to provide engineering guide lines, but to illustrate phenomena which have relevance to secondary cell operation.

A large share of this report is spent in a discussion of more theoretical concepts. In the course of our work it has been necessary to devote considerable time to a re-examination of a number of theoretical problems which have arisen in an attempt to properly interpret the data. It is our hope that the data and discussions will be of some help to individuals about to embark on a study of chemical and electrochemical behavior in nonaqueous systems. In many cases, the basic theory has not been developed to the point where its use is truly justified in explaining the data. Nevertheless, we have found it expedient to resort to the established theory as a formalism for representing and communicating facts. Calculations are frequently made, using established theory, primarily to focus attention on the general magnitude of various effects, and, hopefully, to spotlight areas in which theory is deficient.

This report is not arranged chronologically, but we have divided the discussion of the lithium electrode and of cathodes in a fashion we feel gives maximum emphasis to the major problems.

We would be misunderstood were it felt that the repeated emphasis on "problems" implies any doubt that the high energy density resident in certain systems cannot be extracted efficiently. To the contrary, we are encouraged by the fact that, of the many problems, none seem inherently insoluble. Any one of these problems may be decisive in determining the performance of a specific system, but none of the problems have not been encountered before in the history of electrochemistry and been solved.

Our emphasis on "problems" results from our conviction that, considering the almost infinite number of systems conceivable, and the large number of variables to which performance of a system is sensitive, it would be almost impossible to undertake the kind of screening program which would really be effective in exposing the "best" systems. It seems more sensible to consider specific problems which are assumed to have relevance to cell operation, and then to investigate new systems with respect to the degree to which these specific problems there exist. In short, for which properties should a system be screened? We hope to have provided some answers to this question.

Given the existence of certain "problems", it is not necessarily obvious how these problems should be studied. That is, given certain objectives of screening, it must then be decided how these objectives can be realized. In our work, we have critically examined these "screening techniques".

We have not attempted to present all of the data obtained, but to present the results of our analysis of the data, and to use the data as illustrations of the conclusions reached in this analysis.

The abbreviations and symbols used in this report are summarized in Appendix I.

II. THE LITHIUM ANODE

II-A. Extended Cycling Experiments

II-A-1. Introduction

The purpose of these long term cycling experiments was to see what significant variations in cycling efficiency and cycle life exist in different electrolytes and under different cycling conditions for the cathodic deposition of lithium on charge and the anodic dissolution of lithium on discharge.

II-A-2. Experimental

In most of these experiments cycling was performed in 50-100 ml. of solution. Argon was passed through the solution prior to cycling to remove the oxygen. Thereafter, argon was passed over the surface of the solution. No stirring was used; the cycling experiments were performed in quiet solution.

The working electrode consisted of a one centimeter square piece of copper foil. The total surface area was 2 cm^2 and the initial deposits seemed to be fairly uniformly distributed over the entire surface. Hence, we use this area for calculating the current density.

The counter electrode was a piece of lithium ribbon (1/16 in thick) in the same compartment as the working electrode. The total area of the lithium ribbon was about 10 cm^2.

The reference electrode was simply a piece of silver wire in the same solution as the working and counter electrodes. As subsequently described in this report, the potential of the silver wire is sufficiently reproducible and well-poised to allow its use as a reference electrode for experiments of the type reported in this section.

Constant current was applied by an electronic constant current power supply, Electronics Measurements Models C614 and C620.

The potential of the reference electrode versus the grounded working electrode was measured with a high impedance electrometer, E-H Research Laboratories Model 230. The output of this instrument was fed to a strip chart recorder, Moseley Model No. 680, and the cycling continuously monitored.

The procedure for automatic cycling is conveniently discussed with reference to the experimental data shown in figure 1 on page 4. Consider the upper figure where results for the initial three cycles are shown. Deposition was initially conducted for a fixed period of time -- in this case 1000 sec. A timer was used which, after the pre-set time of deposition would reverse the current and anodic dissolution of the previously deposited lithium began. The strip chart recorder was fitted with a microswitch so that, at a pre-set potential, the current was again reversed and cathodic deposition resumed. For the results shown in figure 1, the microswitch was set so the current would be reversed at -1.5 V versus the silver wire reference electrode. Thus, to summarize, cathodic deposition (charging) was done for pre-set and constant periods of time on all cycles; anodic dissolution (discharge) was done to a pre-set potential, which was the same on all cycles.

II-A-3. Results and Discussion

Four solvents were used:

Propylene carbonate (PC)
γ - Butyrolactone (BL)
Dimethylformamide (DMF)
Dimethylsulfoxide (DMSO)

Another solvent, acetonitrile (AN), in which studies were performed as described in later sections of this report, was not used for these extended cycling experiments.

The following electrolytes were examined exactly as described above. Cathodic deposition was conducted at 5 mA cm^{-2} for 1000 for each cycle. Anodic dissolution was also conducted at 5 mA cm^{-2} to a cut-off voltage of -1.5 V vs. the silver wire reference electrode. Anodic utilization is calculated by dividing the coulombs passed during anodization to the cut-off potential by the coulombs passed during the previous cathodic deposition.

PC - $LiClO_4$ (Note: LiCl is not sufficiently soluble in PC to serve as a satisfactory electrolyte.)

PC - $LiBF_4$

PC - $LiAlCl_4$
PC - LI
BL - $LiClO_4$ (Note: the behavior of $LiClO_4$ and $LiBF_4$ solutions are, in general, so similar that the BL/$LiBF_4$ solution was not examined.)
BL - $LiAlCl_4$
BL - $LiAlCl_4$, LiCl
DMF - $LiClO_4$
DMF - LiCl
DMSO - $LiClO_4$

In figure 1 are shown the results for the initial and final cycles obtained in one of the better systems. The charge-discharge curves were quite well-defined in the sense that, on the anodic discharge of lithium the potential remained quite constant with time, and subsequent polarization marking the end of anodic discharge was quite sharp. Thus the completion of anodic discharge is quite unambiguously defined, and does not depend on the common but arbitrary pre-assignment of a "cut-off" voltage.

Further discussion of the curves shown in figure 1 is useful. The difference in potential between the cathodic deposition and the anodic dissolution during the initial cycles reflects the iR drop included in the measured potential between the working and reference electrodes. This will be discussed in more detail in section II-C-3a of this report. Towards the end of cycling, significantly greater polarization is observed on discharge, though the anodic discharge curve is still sufficiently well-defined to allow an unambiguous determination of the completion of anodization and, hence, the calculation of anodic utilization.

In figures 2 and 3 are shown the cycling results obtained in the ten basic electrolytes listed above. Again, anodic utilization is calculated by dividing the time required for anodic discharge by the time of the previous cathodic charging, since the current for both anodization and cathodization were equal.

In the three solutions for which the results shown in figure 2 were obtained, the lithium deposits were not good. By the last cycle, there was a heavy, fluffy deposit on the electrode which extended as much as one centimeter away from the electrode. In most runs there was also visible gassing.

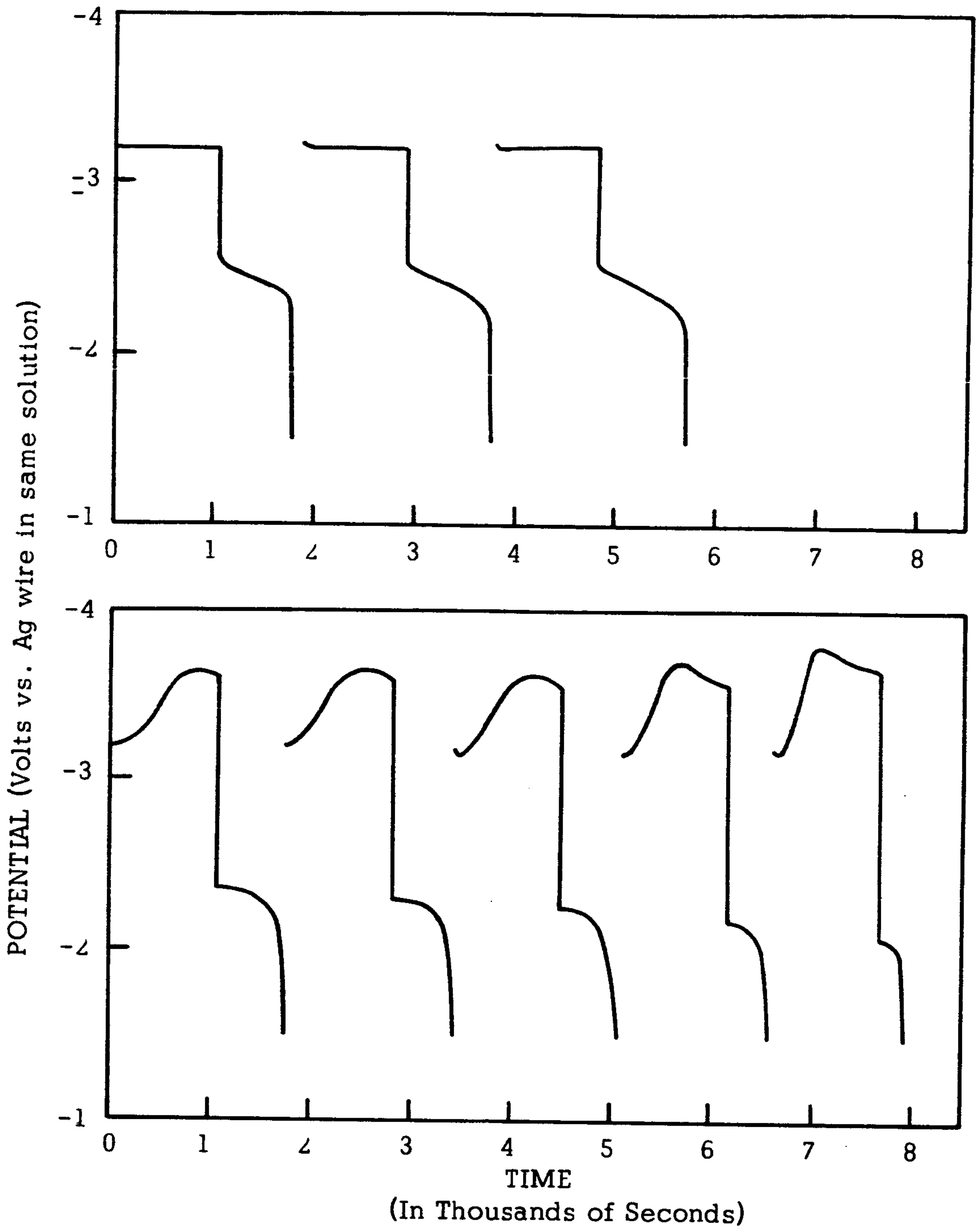


Figure 1: LITHIUM CYCLING IN PC/0.5 M $LiAlCl_4$

On copper electrode at 5 mA cm^{-2}
Upper figure: Cycles 1 - 3
Lower figure: Cycles 35 - 39

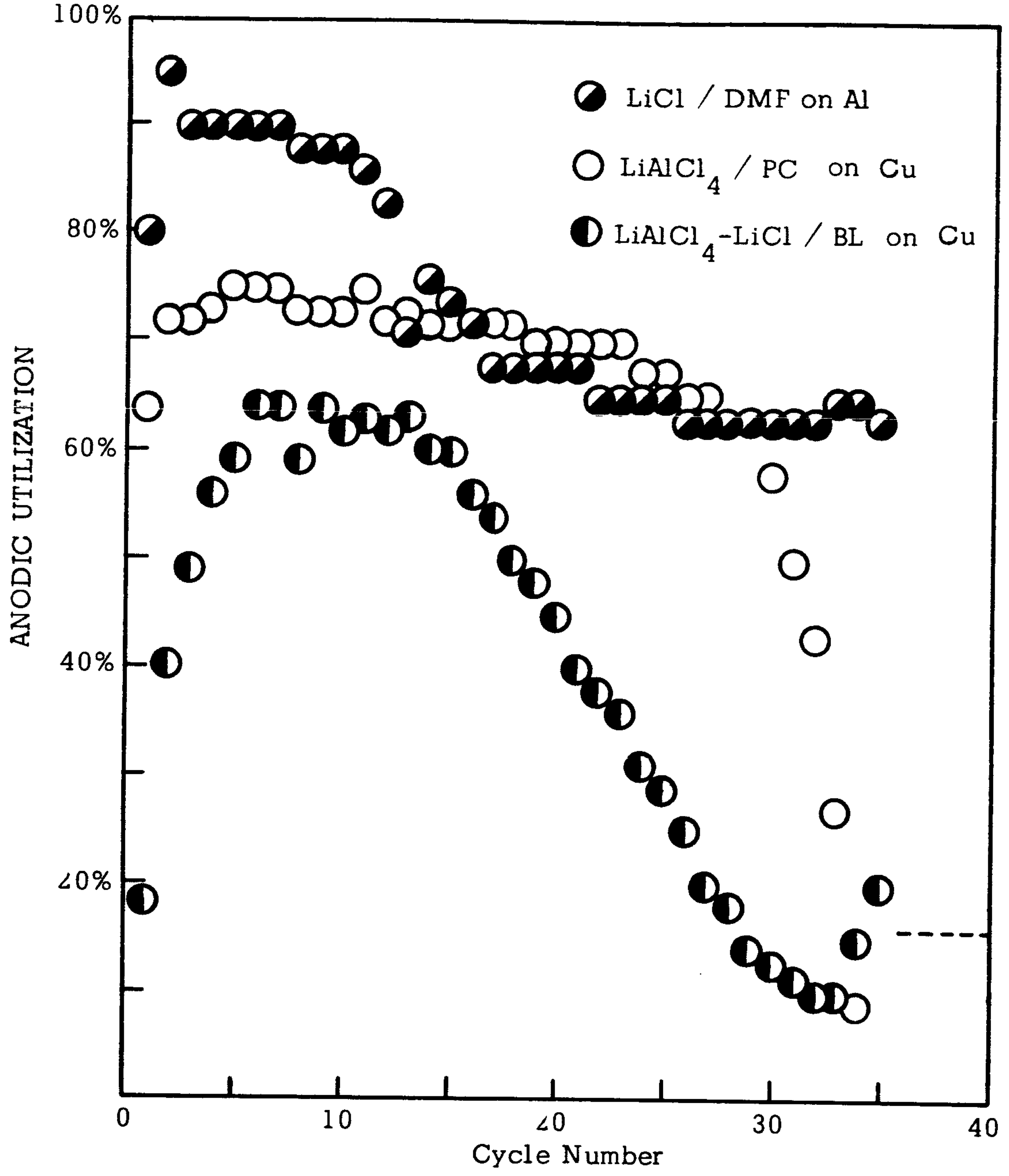


Figure 2: LITHIUM CYCLING

Anodic utilization on substrate indicated for cycling at 5 mA cm^{-2} in electrolyte indicated. Each solution was 0.5 M in each solute indicated

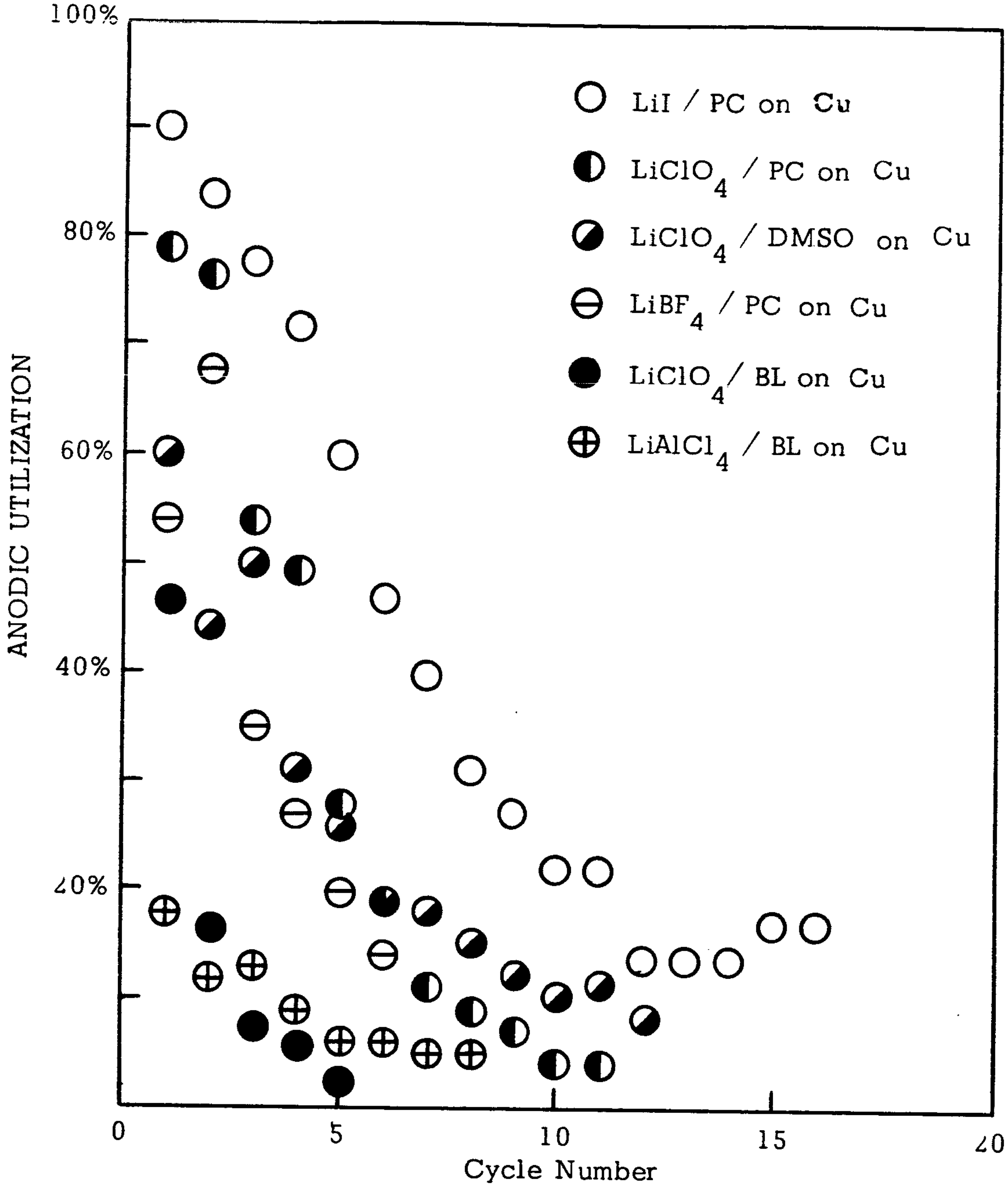


Figure 3: LITHIUM CYCLING

Anod. utilization on substrate indicated for cycling at 5 mA cm^{-2} in electrolyte indicated. Each solution was 0.5 M in each solute indicated

The conditions under which cycling was performed were modified. Attention was focussed on the PC/$LiAlCl_4$ electrolyte. Although the DMF/LiCl electrolyte gave better cycling performance, as shown in figure 2, the copper salts, CuCl, $CuCl_2$, and CuF_2 were all found to be soluble in this electrolyte to more than 0.05 M; therefore, the DMF/LiCl electrolyte seemed a less likely candidate for incorporation in a cell, and data on lithium cycling in this electrolyte would be of less interest.

A study of the data obtained in this work has shown that an estimation of the relative merits of different systems is conveniently expressed in terms of three quantities: The maximum anodic utilization realized, the number of cycles for which anodic utilization was greater than 60%, and the number of cycles before "failure". The definition of "failure" is rather arbitrary. Examination of the data in figures 2 and 3 will show that there is a decrease in anodic utilization with cycle number and that, finally, there is a leveling off in the amount of anodic utilization to values of about 10% or less. The cycle number at which this leveling off appears is defined to be the point of "failure".

In table 1, p. 8, these data are given for the results represented in figures 2 and 3.

In table 2, p. 9, these data are given for runs obtained in the PC/$LiAlCl_4$ solution under various conditions of cycling.

In table 3, p. 11, these data are given for runs obtained in propylene carbonate, using $LiAlCl_4$ but varying the electrolyte composition.

Finally, in table 4, p. 12, the effect of varying the electrode substrate is shown for the PC/$LiAlCl_4$ electrolyte.

TABLE 1

CYCLING PERFORMANCE, VARIATION IN ELECTROLYTE

Substrate: copper metal

Solute Concentration: 0.5 M

Current: 10 mA (ca. 5 mA cm^{-2})

Time of Cathodization: 1000 sec (ca. 5000 mC cm^{-2})

Electrolyte:	Maximum Anodic Utilization	Cycles with over 60% anodic utilization	Cycles until failure*
PC/$LiClO_4$	78%	2	6-F
PC/$LiBF_4$	54%	0	6-F
PC/$LiAlCl_4$	75%	29	34-F
PC/Li I	90%	5	16-F
BL/$LiClO_4$	47%	0	5-F
BL/$LiAlCl_4$	18%	0	8-F
BL/$LiAlCl_4$ + LiCl	64%	9	31-F
DMF/$LiClO_4$	5 %	0	3
DMF/LiCl(1)	95%	35	35
DMSO/$LiClO_4$(2)	60%	1	12-F

* When the letter, F, does not follow the cycle number, this indicates the cycling was arbitrarily discontinued.

(1) performed on aluminum instead of copper

(2) performed at 2 mA (1 mA cm^{-2}) instead 10 mA, since negligible utilization was obtained on the first cycles at the higher current.

TABLE 2

CYCLING PERFORMANCE, VARIATION IN CYCLING CONDITIONS

Substrate: copper metal (2 cm^2)
Electrolyte: PC/$LiAlCl_4$ in concentration indicated

Concentration (Ml^{-1})	Other Variations	Current (mA)	Capacity for cathodization (mC)	Maximum Utilization	Cycles above 60%	Cycles until failure*
0.5	--	10	10,000	75%	29	34-F
0.5	(1)	10	"	71%	10	18-F
"	"	"	"	74%	14	21-F
"	"	"	"	78%	10	12
"	on porous copper	"	"	86%	36	36
"	(2)	"	"	77%	10	10
"	in stirred	"	"	48%	0	9-F
"	(3)	"	"	< 5%	0	2
"	(1)	2	"	83%	28	30
"	--	10	5,000	90%	74	90
"	--	10	1,000	72%	105	513-F
"	--	2	5,000	86%	27	86-F
"	--	2	1,000	85%	48	(4)
"	--	25	10,000	66%	3	14-F
1.0	--	10	10,000	85%	34	49
0.1	--	"	"	56%	0	8-F
(5)	--	2	"	66%	2	9-F
(6)	--	"	"	67%	3	10-F
(7)	--	"	"	67%	2	5-F

TABLE 2 (Continued)

* When the letter, F, does not follow the cycle number, this indicates the cycling was arbitrarily discontinued

(1) In a small H-cell. The working and counter electrodes were in separate compartments, each containing about 4 ml. of electrolyte

(2) On porous copper in the small H-cell described in (1), above.

(3) With the electrode wrapped in fiber glass filter paper.

(4) Utilization remained at 9% for cycles 80-436, when cycling was discontinued.

(5) In PC/0.5 M $LiClO_4$

(6) In PC/0.5 M $LiBF_4$

(7) In BL/0.5 M $LiClO_4$

TABLE 3

CYCLING PERFORMANCE, VARIATION IN SOLUTE COMPOSITION

Substrate: copper metal, 2 cm^2
Current: 10 mA (ca. 5000 mC cm^{-2})
Time of cathodization: 1000 sec. (ca. 5000 mC cm^{-2})
Solvent: Propylene carbonate

Solute	Maximum Utilization	Cycles above 60%	Cycles until failure
0.5 M $LiAlCl_4$	75%	29	34
0.5 M $LiAlCl_4$, 0.125 M $AlCl_3$	70%	33	41
0.5 M $LiAlCl_4$, 0.5 M $AlCl_3$	40%	0	5
0.5 M $LiAlCl_4$, 1.0 M $AlCl_3$	23%	0	7
0.5 M $LiAlCl_4$, saturated with LiCl	54%	0	18
0.5 M $LiAlCl_4$, saturated with $CuCl_2$	29%	0	5
0.5 M $LiAlCl_4$, 0.2% by volume in H_2O	67%	4	9
0.5 M $LiAlCl_4$, 0.2% by volume in propylene glycol	72%	19	25
0.5 M $LiAlCl_4$, 0.1 M in n-propylammonium tetrafluoborate	31%	0	2
0.5 M $LiAlCl_4$, 0.1 M in morpholinium hexafluophosphate	14%	0	2
0.5 M $LiAlCl_4$, prepared by direct addition of LiCl and $AlCl_3$ to propylene carbonate followed by overnight pre-electrolysis at -2.0v vs. silver wire (Li OCV in the solution is ca. -2.7 V)	63%	7	20
o.5 M $LiClO_4$, 0.1 M $AlCl_3$	63%	3	12
0.5 M $LiClO_4$, 0.1 M $AgClO_4$	30%	0	16
0.5 M LiI, 0.1 M KI	90%	2	16
"$LiAlCl_4$" solution prepared by bubbling chlorine gas through 0.5 M $AlCl_3$ solution for 4 hours. A 10 cm^2 lithium ribbon was placed in the solution for 16 hrs. Argon was then bubbled through the solution for 16 hrs. Argon was then bubbled through the solution for 30 min. before cycling	14%	0	4

TABLE 4

CYCLING PERFORMANCE, VARIATION IN ELECTRODE SUBSTRATE

Electrolyte: PC/0.5 M $LiAlCl_4$

Electrodes all 2 cm^2 in total area (both sides)
Amount of Cathodization: 10,000 mC (ca. 5,000 mC cm^{-2})
Electrolyte: Propylene carbonate/0.5 M $LiAlCl_4$

Substrate	Current (mA)	Maximum Utilization	Cycles above 60%	Cycles until failure*
Cu (flat)	10	75%	29	34-F
"	2	83%	28	30-F
Cu (porous)	10	86%	36	36
Ag (flat)	10	95%	42	45
Ag (active) **	10	63%	1	22-F
Pt (flat)	10	***98%	43	43
"	2	***93%	41	41
Be (flat)	10	63%	1	11-F
"	2	43%	0	30-F

* When the letter, F, does not follow the cycle number, this indicates the cycling was arbitrarily discontinued

** Active silver electrode prepared by oxidizing silver metal in 1 M HCl at 5 mA cm^{-2} for 100 sec. The film of AgCl was reduced at the same current in the same solution, giving a film of finely divided silver on the electrode.

*** The anodic discharge curves on platinum were very poor, and the high efficiencies reflect the use of an arbitrary -1 V cut off (vs. the silver wire).

It must be emphasized that these experiments were not performed under conditions even approximating those extant in an actual cell. The only other work of which we are aware, concerning the cycling of the lithium electrode, is that of the group at Lockheed Missiles and Space Company.(1) They report results obtained by placing a nickel electrode insulated with glass fiber separator, between two lithium electrodes and the cell placed in a polypropylene case. Cathodic deposition was performed at constant current for a given time. Anodic discharge was continued until the cell potential became less than 2 V. These cycling conditions closely approximate our own. They further report that the maximum efficiencies are equal to those obtained using smooth plate electrodes in a 100 ml. volume of electrolyte.

The electrolyte was propylene carbonate, 0.63 M in $LiAlCl_4$. The results shown below, represent the data shown in Figures 9 and 10 of Reference 1.

Current Density (mA cm^{-2})	Time (min.)	Capacity on Cathodization (mC cm^{-2})	Maximum Efficiency	Cycles above 60%	No. of cycles reported
0.6	3	108	70%	19	29
0.6	10	360	65%	4	15
0.6	45	1500	65%	2	10
1.0	3	180	66%	12	33

II-A-4. Conclusions

The relatively low efficiency and cycle life, the gassing produced during cathodization, and the poor physical form of the lithium electrodeposit do not suggest that the lithium electrode at present is a likely candidate for incorporation in secondary cells.

(1) J. E. Chilton, Jr., et. al. Lockheed Missiles and Space Company, Final Report, Air Force Contract No. AF 33(615)-1195, Task No. 817304-10, Project No. 8173, Technical Report AFAPL-TR-64-147, February 1965.

As seen from the data contained in Tables 1-4, the variations in cycling performance are not as marked when the conditions of cycling are varied as when the electrolyte composition and electrode substrate are varied. The existence of such marked variations is promising, since this suggests that the lithium electrode may not be inherently unsatisfactory, given the proper environment in which to operate.

Until an environment is found in which, in excess electrolyte, the lithium electrode can be cycled satisfactorily, it seems unnecessarily wasteful of time and money to attempt improvements through the usual procedures of battery development.

The search for a proper environment is best made, first through a more detailed examination of single cycle performance in a relatively limited number of electrolytes. When proper interpretation of single cycle performance can be made, a more exhaustive screening program may be instituted.

II-B. Single Cycle Experiments

II-B-1. Introduction

Extended cycling experiments are needlessly time consuming and are not, at this time, particularly useful except in a most general way, since they do not suggest what modifications might be made to improve performance.

Single cycle experiments were performed in order to develop a clearer picture of lithium electrode behavior and to suggest reasons why the extended cycling experiments showed such variations. It was assumed that the best environment for lithium cycling would be that in which little polarization occurred on cathodic charge or subsequent anodic discharge and in which 100% anodic utilization was realized. It was assumed that such an environment would be one in which the cumulative deleterious effects of prolonged cycling would be minimized.

II-B-2. Experimental

In these experiments a conventional H-cell was used as shown in Figure 4. The working electrode compartment (200 ml. of solution) was separated by a glass frit from the counter electrode compartment (25 ml. of solution). The counter electrode compartment had a stopcock at the bottom so the counter electrode solution could be easily replaced if it was feared that reaction products might diffuse into the working electrode compartment.

Agitation was provided by a magnetic stirrer of conventional design with a Teflon coated stirring bar.

The top of the working electrode compartment was closed by a Teflon piece in which were drilled holes for the working electrode and the deaeration apparatus. Argon either passed through the solution through the fritted glass tube, or across the surface of the liquid. The argon was passed through a tube containing P_2O_5 before reaching the cell.

The counter electrode was a coil of platinum wire.

The working electrode is shown in Figure 5. Actually it comprises six separate working electrodes surrounding the center reference electrode. As will be discussed in the succeeding section I-C-3a such an electrode design is particularly convenient for experiments of the type described in the remainder of this report. The working electrode consists of six metal discs, each 0.2 cm^2 in area, imbedded in epoxy and surrounding the center silver disc. The epoxy did not appear to be attacked by any of the five solvents used except dimethylformamide.

The electrical circuitry is shown schematically in Figure 6, and is conventional in design. Mercury relay switches were used to avoid contact jitter. The constant current supply and the potentiostat are never both on at the same time. When the constant current supply is on, the potential of the working electrode (grounded) versus the reference electrode is measured by the electrometer. The essential operational features of the potentiostat, enclosed

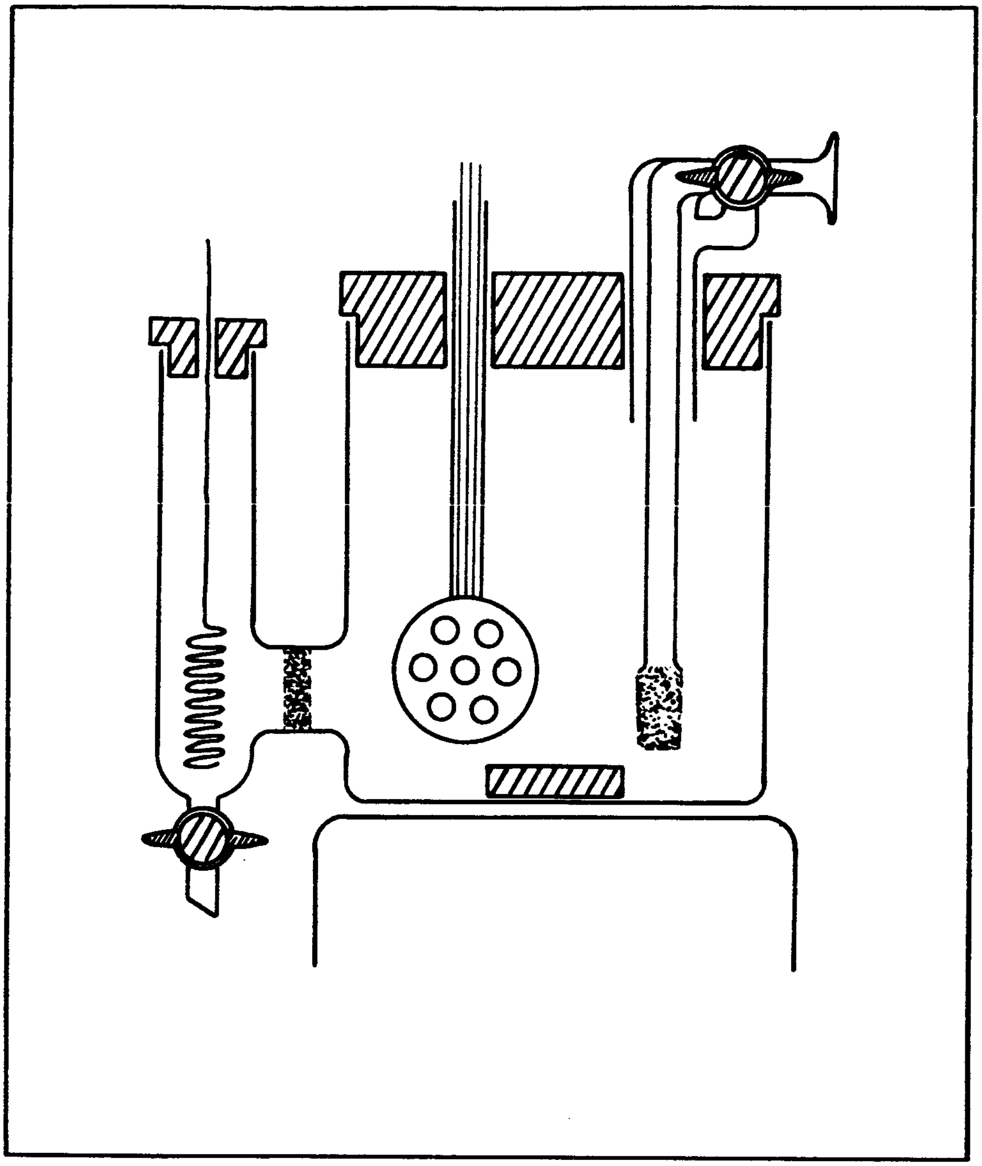


Figure 4: ELECTROLYSIS CELL.

H-cell, showing counter electrode compartment at left , in which, through Teflon stopper, is inserted platinum coil counter electrode. Large working electrode compartment is at the right, in which, through milled Teflon stopper, are inserted working electrode (see figure 5 on next page) and dearation bubbler, with provision for passing gas over surface of solution.

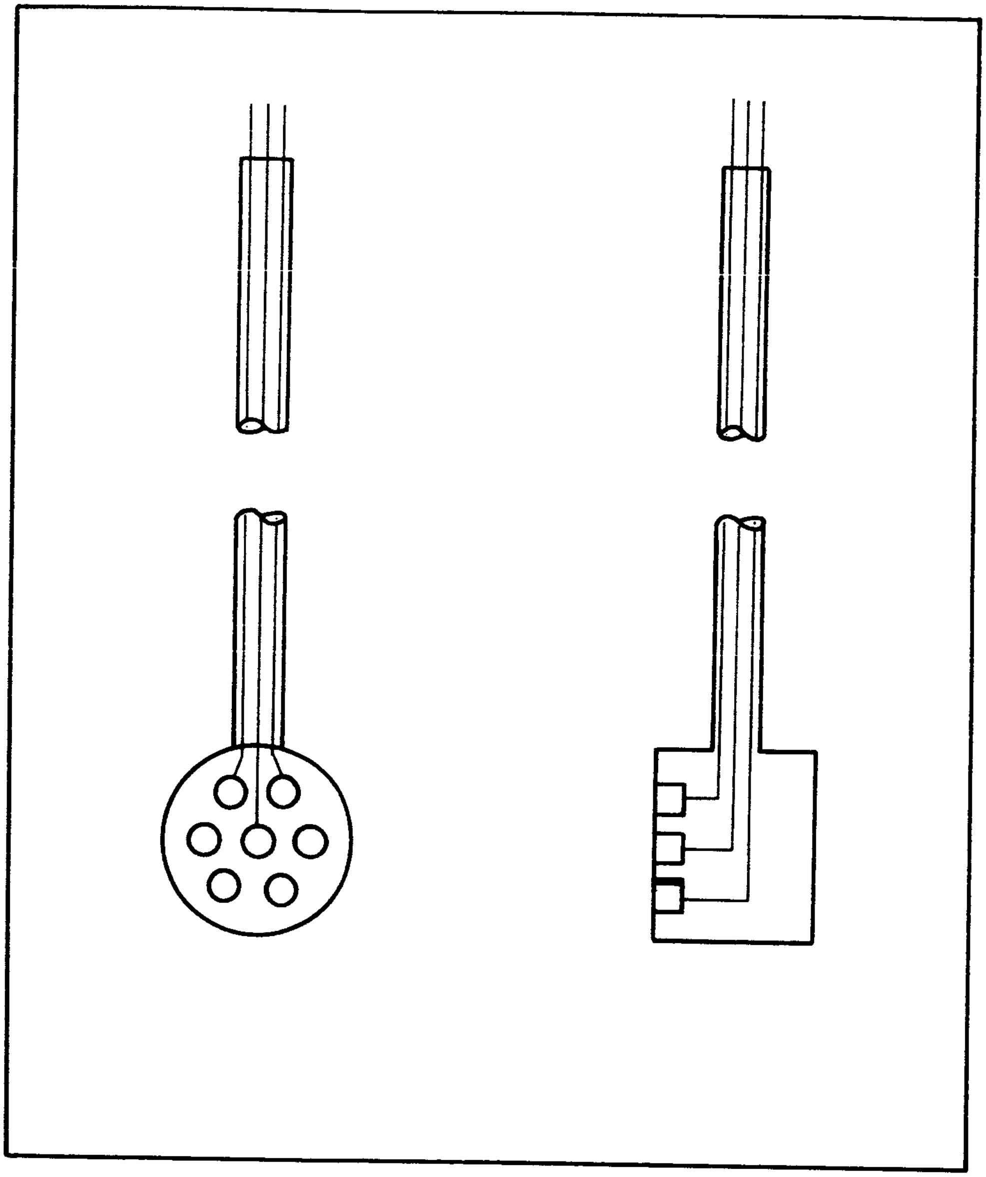


Figure 5: WORKING ELECTRODE

Six working electrode discs, each 0.2 cm^2 in area, imbedded in epoxy resin, placed concentrically about the center disc reference electrode. Individual leads to each electrode.

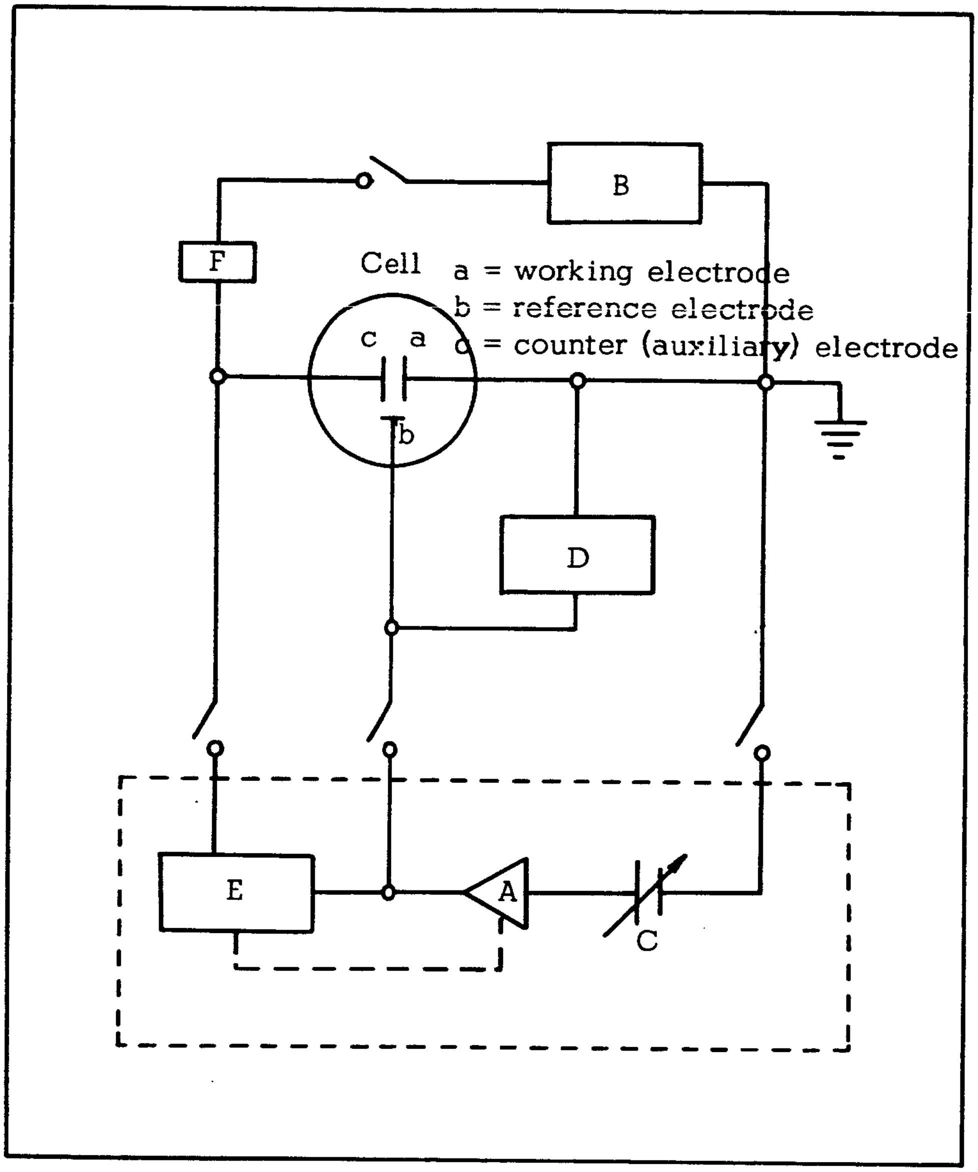


Figure 6: ELECTRICAL CIRCUITRY FOR ELECTROCHEMICAL EXPERIMENTS

A - amplifier within potentiostat
B - electronic constant current supply
C - variable voltage supply (either external or within potentiostat)
D - electrometer
E - power supply within potentiostat
F - current reversal switch

in dashed lines, are thus: When the potentiostat is on, the internal electrometer compares the difference in potential between the reference and working electrodes (measured by the external electrometer, D) and the potential across the variable voltage, C. The internal electrometer commands the internal power supply, E_t to deliver, through the cell, current such that the potentials of B and C stay the same. The potentiostat is not constructed so that rapid switching from the off to the on position can be made. Three external mercury relays simultaneously perform the switching function, shown schematically in figure 6.

The constant current supplies were Electronics Measurements instruments, Models C 614 and C 630. The electrometer was an E-H instrument, Model No. 230. A Wenking potentiostat was used. All switching was done with mercury relays, C.P.Clare and Co. Model HGS 1014. The potential measured by the external electrometer was recorded either by a Varian Model G-14 strip chart recorder, or oscillographically with a Tektronix No. 555 instrument.

The solvents were purified by vacuum distillation as discussed in section IV. The salts, $LiAlCl_4$ and $LiBF_4$, were synthesized as described in Appendix II. No other purification of salts was attempted. The argon (Linde Co.) was reported to be 99.996% pure, and no further purification was attempted.

II-B-3. Results and Discussion

II-B-3-a. Basic Experiments

The basic experiments consisted in cathodizing the electrode in stirred solution at constant current. The electrode is cathodized for a given period of time after which the current is reversed. Anodization is continued until marked polarization indicates the removal of anodically oxidizeable material. This constitutes a single charge-discharge cycle. The appearance of the potential-time curve is essentially that shown in figure 1, p. 4, for the first cycle.

Propylene carbonate has been the solvent of primary interest in our work to date. In table 5 are shown typical results obtained as a function

TABLE 5

SINGLE CYCLE PERFORMANCE IN PROPYLENE CARBONATE

Substrate: Polished platinum disc (0.2 cm^2)
Electrolyte: PC/$LiClO_4$
Amount of Cathodization: 1000 mC cm^{-2}

Concentration of $LiClO_4$	Current Density (mA cm^{-2})		Potential (V vs. Li^o)		Anodic Utilization	
0.05 M	0.75		-0.18 --0.5*		29%	
	1.50		-0.19		53%	
	2.50		-0.15 --0.2		63%	
	3.00		-0.23		35%	
	5.00		-2.23		4%	
0.10 M	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
	0.50		to - 0.75*		15%	
	1.00		to - 0.46*		36%	
		2.00		--		37%
	2.50		-0.12		74%	
		3.00		-0.16		76%
		4.00		-0.13		75%
	5.00	5.00	-0.20	-0.17	76%	78%
		6.50		-0.25		74%
		7.25		-0.25		53%
	8.00		-0.25		66%	
	10.00		-0.30		55%	
	12.50		-1.02		8%	
0.20 M	3.00		-0.06 - -0.22*		68%	
	6.00		-0.11		78%	
	8.00		-0.10		79%	
	12.00		-0.12		83%	
	14.00		-0.17		77%	
	16.00		-0.20		81%	
	18.00		-0.32 --0.53*		78%	
	20.00		-0.30		64%	
	22.00		-1.25		9%	
0.30 M	5.00		-0.09 - -0.14*		80%	
	7.50		-0.10		81%	
	10.00		-0.09		81%	
	12.50		-0.09		82%	
	15.00		-0.11		81%	
	17.50		-0.15		78%	
	20.00		-0.12 - -0.18*		75%	
	22.50		-0.11 -0.22*		74%	
	25.00		-0.21		71%	
	27.50		-1.39		26%	

* steady state potentials not observed

of current density and solute concentration. The potentials are given versus a lithium electrode in the same solution and have been corrected for iR drop as indicated in section II-C-3. The lithium reference electrode was obtained by electrodepositing lithium on the silver disc R.E. for an extended period of time.

It will be observed that at the low and high current ends of the range of current densities employed, the utiliza tions were markedly lower than at intermediate values, where the anodic utilization was relatively constant over a range of current densities. The maximum current density at which a sharp decrease in utilization is obtained and a marked increase in polarization (i.e. more negative potentials) is taken to be the limiting current for lithium ion reduction in stirred solution. The approximate values are given below:

Concentration of $LiClO_4$	Approximate limiting current (mA cm^{-2})
0.05 M	4.0 ± 1
0.10 M	11.3 ± 1.3
0.20 M	21 ± 1
0.30 M	26.3 ± 1.3

In table 6 are shown results obtained in three other solvents: butyrolactone (BL), dimethylsulfoxide (DMSO), and acetonitrile (AN). These single cycle experiments were not performed in DMF because, during the time required for a complete series of runs, the epoxy electrode support was visibly, though slowly, attacked by the solvent. The potentials were not measured in the runs reported in table 6.

The same general behavior is observed as in the results shown in table 5. It will be noted that approximate limiting currents are observed in some cases, but are not as well defined by a sharp decrease in recovery as was true for the examples shown in table 5.

II-B-3-b. Auxiliary Experiments.

These experiments were intended to give some information concerning the important questions: Why is the anodic utilization low? And, is low anodic utilization deleterious?

TABLE 6

SINGLE CYCLE PERFORMANCE IN BL, DMSO, AND AN

Current Density (mA cm^{-2})	Anodic Utilization	Current Density (mA cm^{-2})	Anodic Utilization
BL/0.1 M $LiBF_4$ (1000 mC cm^{-2})		BL/0.5 M $LiClO_4$ (500 mC cm^{-2})	
1.0	45%	10	84%
2.0	62%	20	85%
3.0	69%	30	83%
4.0	67%	40	64%
7.5	66%	50	45%
10.0	51%	70	34%
12.5	50%		
17.5	33%		
20.0	5%		
BL/0.1 M $LiBF_4$* (1000 mC cm^{-2})		DMSO/0.1 M $LiClO_4$ (3000 mC cm^{-2})	
2.5	0	2.5	40%
4.0	42%	5.0	84%, 86%
5.0	46%	10.0	71%
7.5	41%	15.0	56%
10.0	36%	20.0	2%
12.5	0	30.0	2%

* using a sample of $LiBF_4$ obtained commercially

AN/.1 M $LiBF_4$ (3000 mC cm^{-2})		DMSO/0.05 M LiI (3000 mC cm^{-2})	
5.0	46%	3	85%
7.5	34%	5	85%
10	22%, 35%	7.5	81%
20	48%	9.0	2%
30	58%		
40	57%		
60	53%		
75	42%		
AN/0.05 M LiI (3000 mC cm^{-2})			
5	54%		
10	51%		
15	43%		
20	42%		
30	40%		
40	36%		
60	13%		

It is convenient to introduce three terms, the use of which will facilitate further discussion, and an understanding of which will bring into clearer focus the problems attending lithium cycling. These terms are:

Proto-reduction: all cathodic processes occurring at potentials positive to that of the lithium electrode. If lithium metal is deposited at unit activity, no lithium metal deposition should occur at potentials positive to the open circuit potential of a lithium electrode in the same solution. The charging of the double layer is also considered a proto-reduction.

Meso-reduction: cathodic reduction occurring concurrently with lithium deposition.

Teleo-reduction: Cathodic reduction occurring at potentials significantly negative to that of the lithium electrode.

The data shown in tables 5 and 6 give evidence of all three types of reduction, if the anodic utilization is an accurate reflection of deposition efficiency.

(1) Teleo-reduction

We first consider briefly the concept of the "limiting current", i_L. The limiting current is the maximum rate at which an electroactive species can reach the electrode. It is convenient to use the Nernst diffusion layer concept. This assumes that there exists next to the electrode an immobile layer of solution with a thickness, d_D, and across which the concentration gradient is linear.

Across this diffusion layer electroactive species are compelled to move toward the electrode by diffusion because of the creation of a concentration gradient during electrolysis, $\partial C/\partial x$ (C = concentration, x = distance); and, in the absence of supporting electrolyte, by migration, because of the creation of a potential gradient, $\partial \phi/\partial x$.

We consider a 1:1 univalent salt, present at a bulk concentration, C^O, one ion of which is electroactive. Fick's first law for linear mass transport gives, for the flux of the electroactive ion:

$$f_1 = D_1(\partial C_1/\partial x) + \frac{C^O\lambda_1}{F}(\partial \phi/\partial x) \qquad (1)$$

and for the counter ion, which is not electroactive in this example.

$$f_2 = D_2 (\partial C_2/\partial x) - \frac{C^o \lambda_2}{F} (\partial \emptyset/\partial x) \qquad (2)$$

In equation (1) and (2), f = flux, D = the diffusion coefficient, λ = the ionic equivalent conductance, F = the faraday, x = the distance away from the electrode surface. For the steady state situation, the current is constant and given by $i = f_1 F$, the product of the flux of the electroactive ion and the faraday. To preserve electroneutrality at all points away from the diffuse double layer, $C_1 = C_2$, therefore, $\partial C_1/\partial x = \partial C_2/\partial x$. Furthermore, the net flux of the counter ion must be zero in the diffusion layer, otherwise there would be a net change in concentration of the counter ion in the diffusion layer. This change in concentration of the electroactive ion is, of course, avoided by their ability to pass across the electrode - solution interface. From the fact that $\partial C_1/\partial x = \partial C_2/\partial x$ and $f_2 = 0$, we may combine equations (1) and (2) to give:

$$f_1 = (D_1 + \frac{\lambda_1 D_2}{\lambda_2})(\partial C_1/\partial x) \qquad (3)$$

The relationship is simplified when one assumes that the relationship between equivalent conductance and the diffusion coefficient is given by:

$$D = RT\lambda/zF^2 \qquad (4)$$

which is exact only at infinite dilution. Then, since $i = f_1 F$, and, substituting into equation (3) the values for the equivalent conductances from equation (4) one obtains:

$$i = 2 F D_1 (\partial C_1/\partial x) \qquad (5)$$

This is the current in the absence of supporting electrolyte. In the presence of sufficient supporting electrolyte, the potential gradient, $\partial \emptyset/\partial x$, is negligible and equation (1) becomes:

$$i = F D_1 (\partial C_1/\partial x) \qquad (6)$$

The Nernst diffusion layer concept assumes that the concentration gradient is linear across the diffusion layer, and we then write equation 5:

$$i = 2 F D_1 (\Delta C_1/\Delta x) = 2 F D_1 (C^o - C)/d_D \qquad (7)$$

where C^o = the bulk concentration, C = the concentration at the electrode surface, and d_D = the thickness of the diffusion layer.

For systems in which the thickness of the diffusion layer, d_D, is constant, the maximum current which can flow, the limiting current, is, from equation (7) that value which obtains when C = 0; that is, when the concentration of electroactive species at the electrode surface is zero. Thus:

$$i_L = 2 F D_1 C^o/d_D \qquad (8)$$

From equation (6), assuming a linear concentration gradient, the limiting current is $i_L = F D_1 C^o/d_D$ in the presence of excess supporting electrolyte. If the same diffusion coefficient obtains in both cases, and the diffusion layer thickness is unchanged, the limiting current in the total absence of supporting electrolyte will be exactly twice that observed in the presence of excess supporting electrolyte.

While the Nernst concept of a linear concentration gradient is not correct, it has historically proved useful to assume that there exists an "effective diffusion layer" thickness which is a constant for systems with constant geometry, mode and rate of agitation, and viscosity. In our experiments in stirred solution, the magnetic stirrer is set at a value close to the maximum rate of stirring which can be obtained before the stirring bar is dislodged. It has been observed that the variation in limiting currents measured experimentally on well-behaved systems are not significant between this setting and a setting half the maximum setting. Therefore, we consider our experiments to be performed under conditions in which an "effective diffusion layer" is operative.

A more detailed discussion of limiting currents in agitated solution is given by Delahay(2) and Vetter(3). The importance of this concept to our work will be apparent throughout the remainder of this report.

If there were no proto-reduction or meso-reduction; that is, no reduction at potentials positive to the lithium electrode, and no reduction concurrent with lithium deposition, then the efficiency of deposition should be 100% at values below the limiting current for the lithium ion. While the results shown in table 5 suggest that a limiting current, approximately proportional to the lithium ion concentration exists, this must be checked, since catalytic and kinetic

(2) P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers, Inc. New York, 1954, pp. 217-249.

(3) K. J. Vetter, Elektrochemische Kinetik, Springer-Verlag, Berlin, 1961, pp. 165-170.

effects may exist, which give spurious limiting currents, insofar as the limiting currents reflect a process limited by the mass transport of the lithium ion.

The cathodic reduction of silver was studied under conditions identical to those which prevailed in all our work in stirred solution. The solution was PC/0.02 M $AgClO_4$. The deposition was performed potentiostatically and the resultant steady state currents, which were established within seconds after applying the potential, were measured and showed the oscillations about a mean value typically observed for such measurements in stirred solution. The average current is reported in table 7 below. The potentials were corrected for iR drop. The equivalent conductance of the solution was 25.8 $ohm^{-1}\ cm^2\ M^{-1}$.

Table 7

POTENTIOSTATIC CATHODIZATION IN PC/$AgClO_4$

Corrected potential (V vs. Ag disc R.E.)	Current Density ($mA\ cm^{-2}$)
-0.014	0.50
-0.014	1.05
-0.015	1.60
-0.029	2.10
-0.070	2.50
-0.098	2.95
-0.104	3.35
-0.220 to -0.970	3.60 = the limiting current

To calculate the expected limiting current for lithium ion reduction we combine equation (4), p. 24, with equation (8), p. 25, and recall that $\lambda = t_+ \Lambda$, where t_+ is the transference number for the cation. One obtains:

$$i_L = 2\,R\,T\,t_+ \Lambda\, C^o/F\, d_D \qquad (9)$$

On the assumption that the transference numbers are the same for Ag^+ and Li^+, and that the diffusion layer thickness, d_D, is the same in all cases. The ratio of the limiting current for lithium reduction to that for silver reduction is:

$$i_L(Li^+)/i_L(Ag^+) = \Lambda_{(LiClO_4)} C^o{(LiClO_4)} \;/\; \Lambda{(AgClO_4)} C^o{(AgClO_4)}$$

From the data given preceding table 7, $C^o_{(AgClO_4)} = 0.02$, and $\Lambda_{(AgClO_4)} = 25.8$ $ohm^{-1}\ cm^2\ M^{-1}$, and from the data given below, combined with the measured limiting current for silver reduction, 3.60 $mA\ cm^{-2}$, we calculate the following

Concentration of $LiClO_4$ ($M\ l^{-1}$)	Measured equivalent conductance ($ohm^{-1}\ cm^2\ M^{-1}$)	Calculated limiting current ($mA\ cm^{-2}$)
0.05	20.7	7.2
0.10	18.6	13.0
0.20	15.4	21.5
0.30	13.0	27.5

The agreement with the values shown on page 21 is quite satisfactory, and provides strong evidence that the decreased efficiency of lithium at the higher currents does reflect mass transport limitation.

To further define the conditions which exist during our measurements in stirred solution, we calculate the effective diffusion layer thickness from equation (9), p. 26:

$$d_D = \frac{(2)(0.00002\ M\ cm^{-3})(8.3\ J\ M^{-1}\ deg^{-1})(300\ deg)(0.5)(25.8\ ohm^{-1}\ cm^2\ M^{-1})}{(0.0036\ A\ cm^{-2})(96{,}500\ C\ M^{-1})}$$

$$= 3.7 \times 10^{-3}\ cm$$

This is a reasonable value and may be compared with the value obtained in the less viscous aqueous solutions where, for a 0.00195 M $AgClO_4$ solution, we found the limiting current at the same rate of stirring to be 1.12 mA cm^{-2}. Using the literature value of 61.9 $ohm^{-1}\ cm^2\ M^{-1}$, the limiting equivalent conductance of the silver ion, we calculate:

$$d_D = 1.74 \times 10^{-3}\ cm$$

Again, we emphasize that the above calculations of diffusion layer thicknesses are presented to facilitate comparison of our work with that of other workers since d_D is, in effect, the summation of a variety of experimental conditions.

We shall, in the remainder of this report, use the following numbers for estimating the expected limiting current:

i_L in stirred P C (in mA cm^{-2}) = 180 x Concentration ($M\ l^{-1}$)

i_L in quiet PC (in mA cm^{-2}) = 40 x Concentration ($M\ l^{-1}$)

The latter value is obtained from our repeated observation that limiting currents in quiet solution are about one-fourth their value in stirred solution. The number, 180 is obtained by dividing the measured limiting current, 3.6 mA cm^{-2} by the concentration of $AgClO_4$, 0.02 $M\ l^{-1}$ -- the results for which are shown in table 7.

The general conclusion may be made that teleo-reduction occurs at currents above the limiting current for lithium reduction, and the onset of teleo-reduction at currents above the limiting current results in decreased efficiency for lithium deposition. This teleo-reduction presumably is of solvent or of the counter anion.

(2) Proto-reduction. This includes all processes which occur and consume electricity when the electrode potential is <u>positive</u> to the open circuit potential of a lithium metal electrode in the same solution.

It is convenient to consider two types of proto-reduction: surface limited processes and mass transport limited processes. Both processes will lower the efficiency of lithium deposition.

For a mass transport limited proto-reduction there should exist a limiting current, $i_{L-Pr.}$. There should be <u>no</u> lithium deposition at $i < i_{L-Pr.}$. At $i > i_{L-Pr.}$ the efficiency for lithium deposition should be:

$$\%\ \text{efficiency} = i - i_{L-Pr.} / i$$

This is not consistent with the data shown in tables 5 and 6. For example, we take the data given for run No. 1 in the 0.1 M $LiClO_4$ solution shown in table 5. Only 15% anodic utilization was obtained at 0.5 mA cm^{-2}. Using the above equation one then calculates for $i_{L-Pr.}$ a value of 0.425 mA cm^{-2}. Then, at 10 mA cm^{-2} one calculates an expected efficiency, using this value for $i_{L-Pr.}$, of 96%. However, the measured efficiency was only 55%.

The simple statement that <u>the efficiency of lithium deposition is relatively constant over a fairly wide range of current densities</u>, is equivalent to the statement that the cause of lithium inefficiency does not lie in the mass transport limited reduction of species more easily reduced than lithium.

More significant is the fact that no limiting current for proto-reduction can be obtained in most solutions. That is, one cannot measure a value for $i_{L-Pr.}$ independently. For example, if the potential of an electrode.

such as platinum, silver, copper or nickel is held at potentials slightly positive to the lithium electrode (e.g. +0.1 V), the resultant current rapidly decays to small values, typically of the order of 0.05 mA cm^{-2} after about two minutes. Furthermore, this small current does not display the oscillations about an average value characteristic of mass transport limited currents; and the current is the same in both stirred and quiet solution. (See Vetter's monograph for a further discussion(4)).

If there were significant mass transport limited proto-reduction, the material responsible for this reduction should be thermodynamically able to oxidize lithium metal. The rate at which electrodeposited lithium reacts with an electrolyte (PC or BL) is typically of the order of 0.1 mA cm^{-2}. A typical experiment is the following: In a PC/0.266 M $LiBF_4$ solution, cathodization was performed at 5 mA^{-2} cm for 50 sec. in stirred solution. After waiting the indicated period of time the deposit was anodized at 1 mA and the anodic utilization calculated:

Waiting time before anodization	Anodic Utilization (mC cm^{-2})
1 min.	185
3 min.	161
5 min.	150
17 min.	117

These points fall on a curve which extrapolates to 200 mC cm^{-2} at t = 0 (i.e. 80%) and the curve has a slope of 0.22 mC sec^{-1} (0.22 mA cm^{-2}) at t = 0. However, 80% efficiency would correspond to a limiting current for protoreduction of 1 mA cm^{-2}. Nevertheless, reduction at 0.8 mA cm^{-2} for 25 sec. gave 74% anodic utilization.

Proto-reduction may also be surface limited. Examples would be:

1. Alloy formation: If lithium can alloy with the electrode substrate, the activity of the metal will be less than unity and reduction will occur at potentials positive to the lithium electrode potential.

---

(4) Vetter, *op. cit.*, p. 306

2. Double layer charging.
3. Reduction of adsorbed material (e.g. oxygen)
4. Reduction of oxide films
5. Coverage of active sites by reduction products.

While all of these may occur, the total amount of electricity consumed during the process can hardly be a significant fraction of the total current passed in the examples shown in Tables 5 and 6. This will be discussed in more detail in Section II-C of this report.

It must be concluded that proto-reduction, either mass transport limited or surface limited cannot alone account for the low anodic efficiencies. One must then consider the following possibilities:

1. The deposit may not be sufficiently adherent to the electrode substrate to allow full anodic utilization.
2. Anodic efficiency may be low, and not reflect the efficiency of the preceding cathodic deposition.
3. Significant meso-reduction may occur. (Note: We purposely use the term meso-reduction rather than co-reduction. Co-reduction would occur in the presence of a material which alone is capable of reduction at potentials more positive than the lithium potential. Meso-reduction specifically refers to concurrent reduction of some other material than the lithium ion which does <u>not</u> occur unless lithium is <u>also</u> being cathodically deposited.)

These factors are considered in the following three sections:

(3) Physical form of Electrodeposited Lithium.

There is a significant difference in the appearance of lithium deposits formed from solutions of $LiAlCl_4$ and those formed from solutions of the other lithium salts. The $LiAlCl_4$ solution deposits are darker colored and tend to form whiskers and dendrites. This has been noted by Chilton, et al.(5), who state, "This loss of lithium metal from the electrode during cathodic formation

(5) Chilton, et. al., <u>op. cit.</u>, p. 20.

is one of the contributing factors to the low anodic utilization of electroformed lithium which has been observed for this ($LiAlCl_4$) electrolyte system."

In other solutions the deposit is lighter colored, sometimes almost white, and very adherent. As discussed in Section (3) experiments indicate that significant amounts of such deposits are not mechanically lost from the electrode.

(4) Anodic Efficiency

There are several possible procedures for determing the cathodic efficiency for lithium deposition:

1. Evolution of hydrogen
2. Change in electrode weight
3. Formation of base
4. Anodic recovery

None of these methods is unambiguous. The first method presents a number of experimental problems. The results may not be straighforward if there is produced concurrently with lithium, materials which react with water to evolve hydrogen or if there exist materials which consume the hydrogen formed by the reaction of lithium with water.

Electrode weight changes are not satisfactory since other materials may be occluded in the lithium deposits.

The formation of base through the reaction of lithium with water. As previously reported by us(6) there is evidence for the formation of basic lithium salts such as Li_2O, LiOH, and Li_2CO_3. Thus, we have found in a typical series of experiments(7) that when 15,000 mC cm^{-2} of cathodization are performed in PC/1.0 M $LiClO_4$ at currents of from 2.5 to 100 mA cm^{-2} the amount of base recovered when the electrode was immersed in water was equivalent to the amount of current passed during the previous cathodization to within a few percent. This was true even when the anodic utilization was as low as 15%. This has also been noted by Chilton and co-workers(8), who report efficiencies

---

(6) R. G. Selim, and K.R.Hill, P.R.Mallory Co. Inc., Final Report NASA contract No. NAS3-2780, August 1965, p. 93.

(7) R. G. Selim, Proceedings 18th Annual Power Sources Conference, May 1964, p. 88.

(8) Chilton, et. al., op. cit., p. 17

based on the formation of base through reaction with water of 95-100% for PC solutions of $LiClO_4$, LiBr, and $LiAlCl_4$, while anodic utilizations in these solutions were, respectively, 84%, 80%, and 50%.

Finally, cathodic efficiency may be determined by anodic oxidation if the anodic oxidation is efficient. In spite of the fact that a number of groups have been concerned with the development of cells incorporating lithium anodes, there appears to have been little careful work concerning the inherent anodic discharge efficiency of bulk lithium metal. Keller and co-workers(9) report essentially 100% utilization efficiency for lithium anodic dissolution at currents of 10 mA cm^{-2}.

The following experiments were performed by us using bulk lithium metal. Lithium ribbon, 1/16" thick, obtained from Foote Mineral Co. was used in these experiments. An electrode support structure shown in Figure 7 was fabricated. The steel rod was imbedded in the epoxy to provide mechanical strength when the electrode was pressed. The thin cavity was made by molding a zinc disc in the epoxy, and, after the epoxy had hardened, the zinc was removed by dissolution in dilute acid, exposing the platinum base. Again the silver disc served as the reference electrode and the electrode was calibrated as described in Section II-C so corrections for iR drop could be made.

Lithium metal, cut from the ribbon, was pressed into the cavity. It was necessary that the electrode surface next to the platinum substrate be scraped clean, otherwise stable open circuit potentials could not be obtained. When these conditions were met, the potential of the bulk lithium electrode in PC/1 M $LiBF_4$ was -3.1 V use the silver disc R.E. This is the same potential obtained vs. the silver disc R.E. when lithium is electrodeposited on platinum or other metal substrates.

It was also necessary that the electrode surface in contact with the solution be scraped clean, otherwise, during the passage of current, polarization was extensive, as will be later described.

(9) J. Farrar, R. Keller, and M. M. Nicholson, Rocketdyne, Final Report, USAEL Contract DA-36-039-AMC-03201(E), June 1965, p. 19.

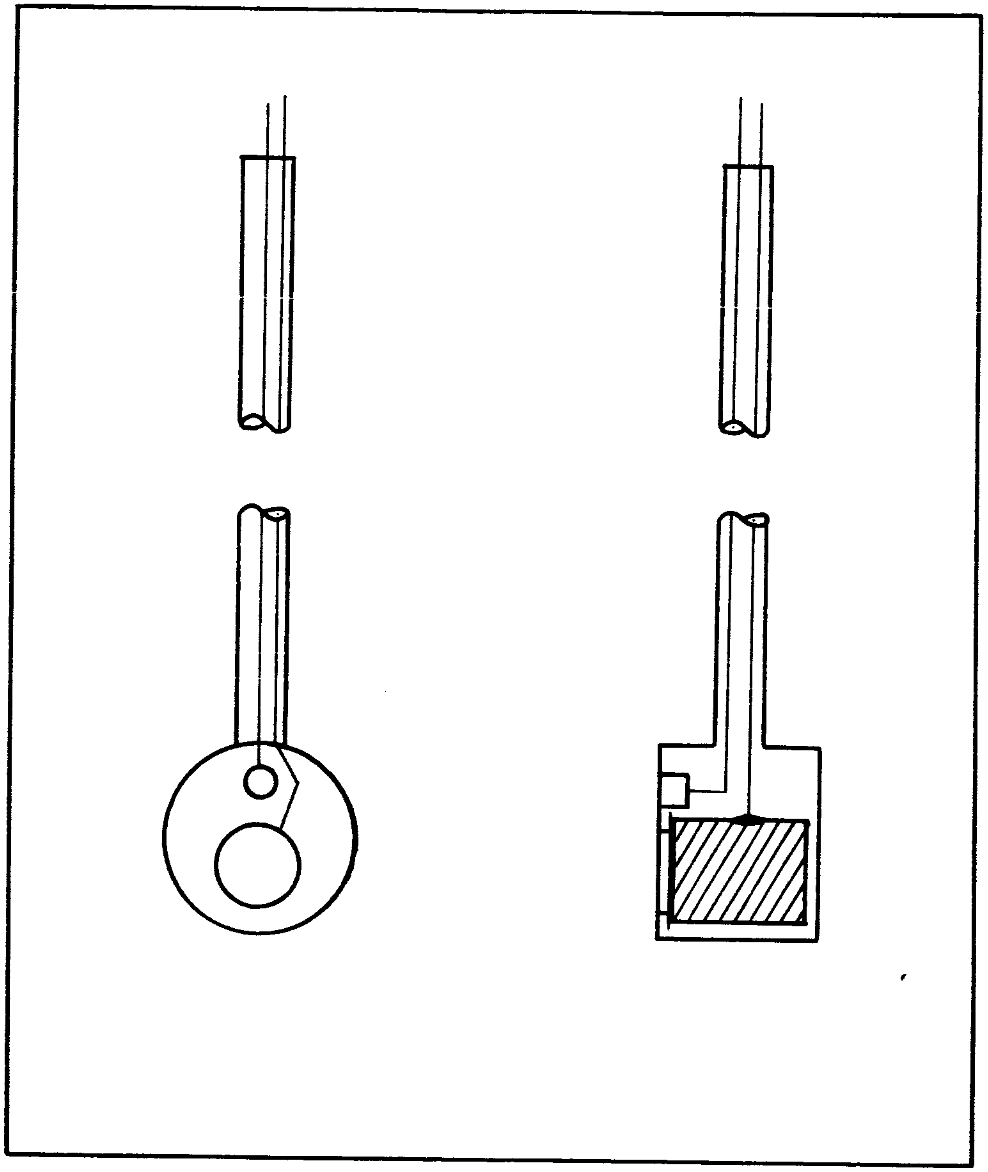


Figure 7: RECESSED ELECTRODE

Constant current pulses were applied for 30 sec. in quiet solution. After each pulse the O.C.V. immediately returned to the initial O.C.V. of -3.1 V vs. the silver disc R.E.. After one minute of quiet stand the next greater current pulse was applied. The results are shown in Figure 8. The results indicate that the observed polarization is largely iR drop.

The amount of lithium contained in the electrode described above is inconveniently large. The following procedure was adopted. Lithium ribbon (1/16" thick) was pressed between two polished, stainless steel blocks at about 5000 lb. The stainless steel blocks were separated, exposing a thin sheet of lithium metal. The lithium electrode was punched out of the center of the sheet by a die, giving an electrode pellet which just filled the cavity in the electrode support. The surface was cleaned by brief contact with methanol and immediately immersed in the solution.

To determine the amount of lithium contained in the electrode, indentical punchings were made on each side of the place where the lithium had been punched out. These were treated in identical fashion with methanol and immersed in water. The liberated base was titrated with standard acid and it was assumed the amount of liberated base was equivalent to the amount of metallic lithium, since the amount of oxidation to form LiOH was small in comparison with the total amount of material. The amount of lithium contained in the 0.85 cm^2 area cavity was between 1-1.3 millimoles, about 10,000 to 15,000 mC cm^{-2}. From the bulk density of lithium one calculates electrode thickness of 8 to 10 mils.

A series of runs were performed in which the lithium was first anodized at 11.7 mA cm^{-2} for 50 sec. in stirred solution. It was presumed this might serve the function of electrolytic cleaning. The stirrer was turned off and the electrode was allowed to stand quiet for 1 min. Finally, the electrode was anodized at the indicated current for 25 sec. The potentials were quite constant during the anodization. The potential was measured against that of an electrodeposited lithium electrode in the same solution, PC/0.1 M $LiBF_4$. The correction for iR drop was made as described in Section II-C of this report. The results are shown in table 8.

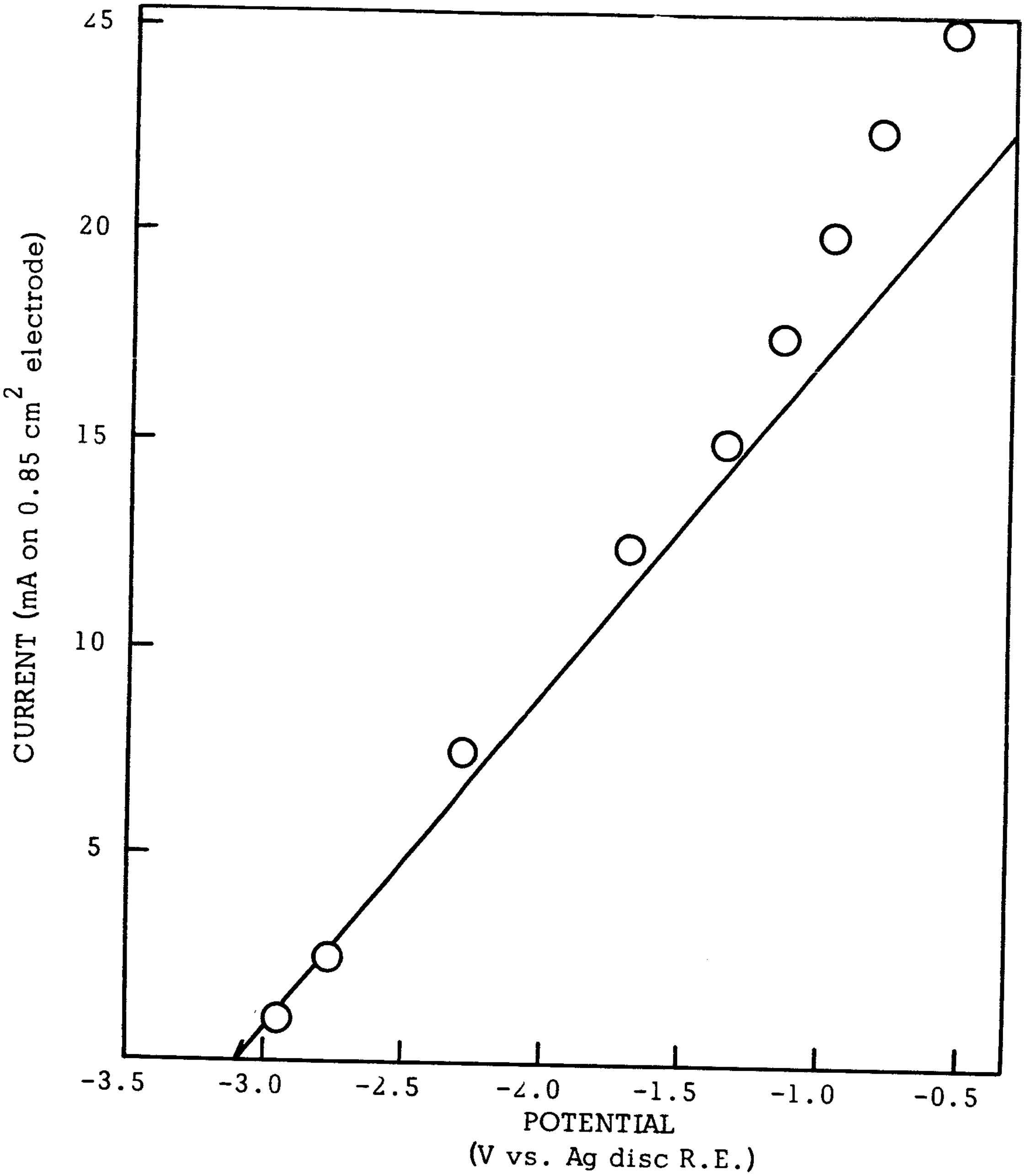


Figure 8: ANODIC VOLTAMMETRY ON LITHIUM METAL

On bulk lithium metal pressed into recessed electrode (Fig. 7) in PC/1.0 M $LiBF_4$. Potential measured against silver disc R.E., against which the open circuit potential of the bulk lithium was -3.1 V. The solid line is the calculated iR drop. The fact that the observed points fall along this line indicates that the polarization is largely only iR drop.

TABLE 8

POLARIZATION OF BULK LITHIUM

Current Density (mA cm^{-2})	Measured Potential (V vs. Li^{o} R.E.)	iR Correction	Corrected Potential (V vs. Li^{o} R.E.)
1.17	+0.45	-0.25	+0.25
2.35	+0.80	-0.51	+0.29
4.71	+1.45	-1.02	+0.43
9.40	+2.80	-2.04	+0.76
11.2	+3.40	-2.50	+0.90
23.5	+6.60	-5.10	+1.50
35.3	+9.90	-7.65	+2.25

The points fall on a linear plot with a slope of 47.5 ohm. The actual iR correction was made by multiplying the current density by 217 ohm. As will be later discussed, we do not believe the iR correction is in error by more than about 5% (11 ohms). We believe the polarization observed is probably iR drop through a resistive lithium salt film formed on the electrode through chemical reaction with the electrolyte.

Lithium electrodes prepared in the same fashion as above were anodically discharged to determine the anodic recovery. The anodic discharges were flat, and the polarization observed when all of the lithium had been removed was sufficiently sharp to give unambiguous measures of the anodic efficiency. The results are shown in Table 9 below.

TABLE 9

DISCHARGE EFFICIENCY OF BULK LITHIUM

Solution	Current Density (mA cm^{-2})	Efficiency	Observed Potential (V vs.Ag^{o} R.E.)	iR Correction	Corrected Potential
PC/0.5 M LiBF	23.5	81%	-1.15	1.96	-3.11
"	11.8	78%	-1.98	0.98	-2.96
BL/1 M $LiBF_4$	35.3	92%	-1.25	1.80	-3.05
"	17.7	98%	-1.80	0.90	-2.70
"	1.8	83%	-2.90	0.09	-2.99

The open circuit potential of the lithium electrode in the same solution vs. the silver disc R.E. is -3.1 ± 0.1 V. We estimate an error in the iR correction of ± 5% (as discussed in Section II-C), thus it can be seen that, with one exception, the run in butyrolactone at 17.7 mA cm^{-2}, there is negligible polarization on discharge.

It is of interest to compare the results in Table 8 for amounts of bulk lithium in the range of 10,000 to 15,000 mC cm^{-2} with those obtained for comparable amounts of electrodeposited lithium. The following experiments were performed in PC/1.0 M LiBF$_4$. All measurements were performed in stirred solution. Deposition was performed on polished platinum disc electrodes of the design shown in Figure 5.

TABLE 10

DISCHARGE EFFICIENCY OF ELECTRODEPOSITED LITHIUM

Deposition Current (mA cm^{-2})	Amount of Cathodization (mC cm^{-2})	Anodization Current (mA cm^{-2})	Anodic Utilization	E obs.	iR	E corr.
25	1,500	50	84%	-1.10	-2.12	= -3.12
25	1,500	75	83%	0.00	-3.18	= -3.18
25	1,500	100	67%	+1.12	-4.24	= -3.12
25	1,500	125	58%	--		--
25	3,000	10	87%	-2.50	-0.42	= -2.92
25	3,000	50	80%	-1.10	-2.12	= -3.22
25	3,000	75	65%	+0.20	-3.18	= -2.98
10	3,000	100	51%	+1.35	-4.24	= -2.89
25	3,000	100	75%	+0.90	-4.24	= -3.34
25	6,000	10	78%	-2.88	-0.42	= -3.30
25	6,000	100	46%	+0.80	-4.24	= -3.44
25	30,000	20	47%	-2.00	-0.84	= -3.30
50	30,000	100	34%	-2.00	-4.24	= -3.85
25	30,000	100	36%	-0.60	-4.24	= -4.84

Although these data are not complete enough to establish definite trends, certain tentative conclusions may be drawn. First, the deposits for the larger two amounts of deposition are heavy and dendritic, and extend a significant distance away from the electrode. It is likely that the correction for iR drop, which is based on an effective distance between the working and reference electrodes, is too large in these cases, hence the potentials are significantly more negative than is reasonable. For the 1,500 and 3,000 mC cm^{-2} of deposition, the average corrected potential is -3.15 V vs. the silver disc R.E. Considering a variation of 5% in the iR correction, this is in excellent agreement with the measured potential of a lithium electrode in the same solution vs. the silver disc R.E.

The apparent decrease in anodic utilization at 100 mA cm^{-2} is consistent with either of two hypotheses: (1) loss of electrical contact on discharge through preferential anodic dissolution of the base of the lithium dendrites, or (2) passivation through formation of insoluble lithium salts on discharge. (100 mA cm^{-2} is close to the limiting current expected in stirred 1 M PC solutions.) The hypothesis that lithium is mechanically removed from the electrode resulting in low efficiencies is not consistent with the data shown in Table 10, for then utilizations would probably be less at the lower currents, since a longer time is required for discharge and the proportionate amount of lithium lost through physical removal would be greater and the anodic utilization would be less.

From the results reported in this section on the anodic dissolution of bulk and electrodeposited lithium, and on the polarization characteristics of bulk lithium we conclude that there is no evidence that, at moderate anodic currents (i.e. of the order of 10 mA cm^{-2}), significant polarization or passivation of lithium metal occurs hence, there is no reason why anodic efficiency should not inherently be 100%. It must be concluded that anodic utilization may be low because:

(1) Loss of electrical contact on anodization through preferential anodic attack of the base of the lithium dendrites.

(2) Concurrent reaction of lithium with electrolyte through continual exposure of fresh lithium during anodization. This assumes that a chemically passivating film normally inhibits rapid reaction with electrolyte.

(3) Inefficient cathodic deposition.

(5) Cycling of Lithium in Cell Type Environments.

While the behavior of the lithium electrode in excess electrolyte is not entirely satisfactory, it was desirable to learn to what extent similar behavior is encountered in environments which approach those extant in actual cells. For this work cells were constructed as shown schematically in Figure 9.

These cells comprised a Teflon tube, milled inside to form an internal shoulder which served to separate the two electrodes. The working electrode simply comprised a stainless steel rod, milled to fit closely in the Teflon tube. A cavity was drilled in the rod. The back of the cavity was the current collector and the rest of the exposed surface was coated with Kel-F. The counter electrode was a Teflon rod, milled to fit inside the Teflon tube. A piece of platinum gauze served as the current collector. Both electrode tubes were provided with O-rings for a tight fit. In the shoulder was drilled a small hole in which a tapered silver wire was inserted. Before assembly, a piece of lithium ribbon was pressed against the platinum counter electrode current collector. The two electrode tubes were then pushed into the Teflon tube, but not tightly against the shoulder. Electrolyte was put into the cell through the small hole in the shoulder with a syringe. The two electrode plugs were pushed tightly together against the shoulder. Excess electrolyte was removed through the hole in the shoulder. The silver wire electrode was pushed into the hole and electrolysis begun.

From the volume of the two cavities, calculated from the area (0.82 cm^2) and the depth (0.18 cm), and the volume within the shoulder, calculated from the internal diameter (1.65 cm) and the width of the shoulder (0.22 cm), one calculates a total electrolyte volume of 0.77 cm^3. For 1 M electrolyte, this is 0.77 milliequivalents of electrolyte or 74,000 mC.

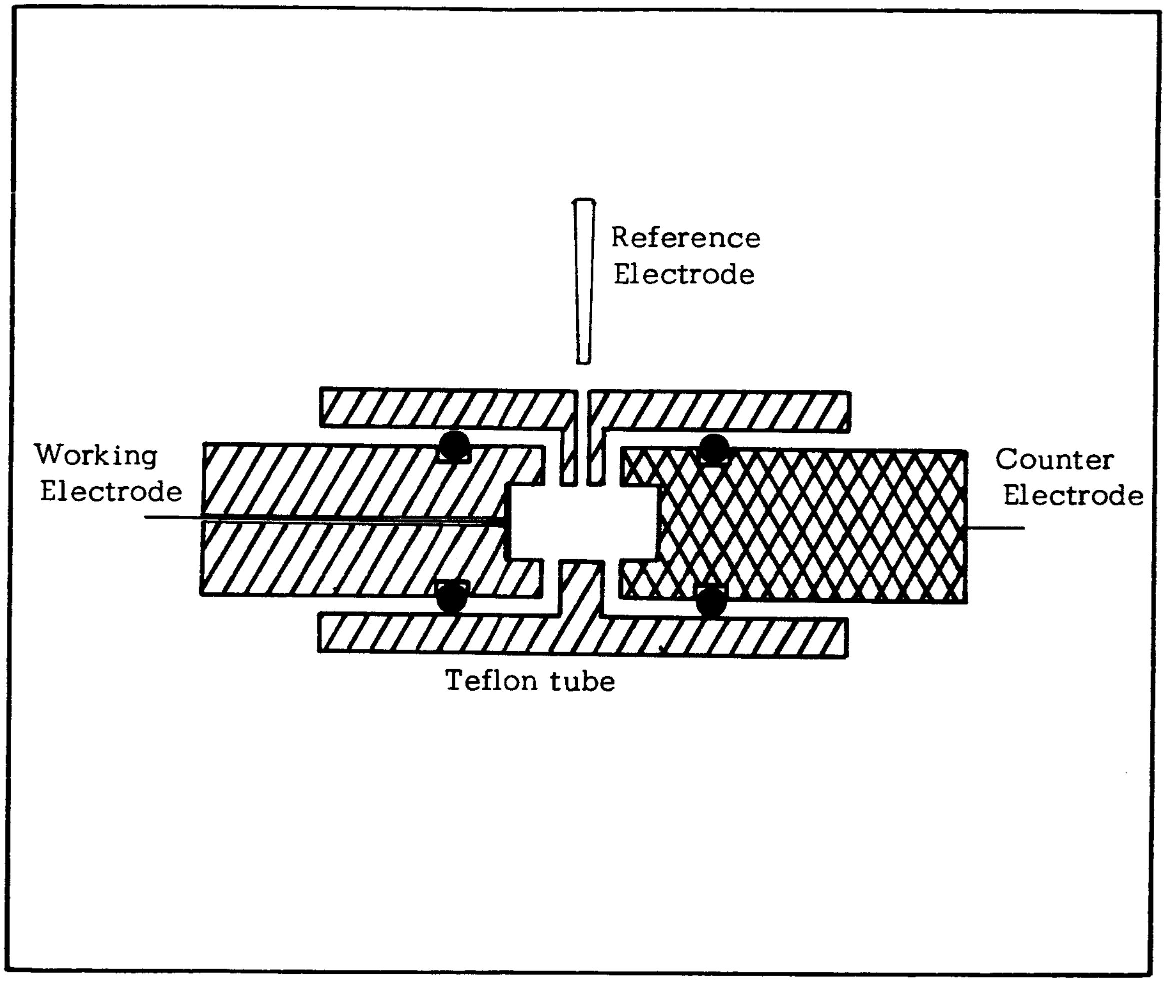


Figure 9: CELL FOR STARVED ELECTROLYTE STUDIES

See text, p. 39, for complete description.

The potential of the working electrode, on which lithium was deposited and re-oxidized anodically, was monitored versus the silver wire R.E. The data are shown in table 11. Except where indicated the discharge curves were flat. Polarization occurred in a number of cases. The potential would drift positive by as much as 1-2 V. Even so, there was a much more abrupt potential jump at the end of the discharge, allowing an unambiguous calculation of anodic utilization. All discharges were conducted at 1.22 mA cm^{-2}.

So many variables are involved that it is difficult to evaluate the data. In general, there seems to be no marked difference between the observations in minimal electrolyte and those in excess electrolyte.

In Cell 1 there appears to be a decrease in efficiency in going from a deposition current of 4.9 to 9.8 mA cm^{-2}. In Table 5, one notes a decrease in efficiency in stirred solution, BL/0.5 M $LiClO_4$, in going from 30 to 40 mA cm^{-2}. Considering that the concentration in cell 1 is 1 M, and that the limiting currents in quiet solution are about one/fifth that in stirred solution it is reasonable to expect a decrease in efficiency in cell 1 in the current range 12-16 mA cm^{-2}. The data for cell 1 probably reflect this.

In Cell 2 we observe both a decrease in efficiency in going to the higher currents and also a slight improvement during the first few cycles as seen in Figures 2 and 3.

In Cell 3 the initial three cycles were quite low. It is interesting to note that the initial cycles for cells 1, 2 and 3 show decreasing utilization with increasing deposition current. This is the reverse of what one would expect were there significant proto-reduction. We have no explanation for the improvement noted for cycles 4 and 5 following pre-electrolysis at +0.2 V.

In Cell 4 cycles 1 and 2 agree with previous conclusions that for small amounts of deposition, there is not a significant difference in anodic utilization over a fairly wide current range (here, 1.2 to 12 mA cm^{-2} with 65-68% efficiency). Cycles 2 and 3 and cycles 4 and 5 show the significant improvement in utilization efficiency during the first few cycles. Cycles 4-7

TABLE 1 1

CYCLING OF LITHIUM IN MINIMAL ELECTROLYTE

Cycle No.	Charging Current (mA cm^{-2})	Amount of Charge (mC cm^{-2})	Anodic Utilization	Comments
In BL/1 M LiBF$_4$	(Stainless steel working electrode)			
Cell No. 1				
1	1.2	1,200	56%	
2	2.4	"	59%	
3	4.9	"	59%	
4	9.8	"	43%	Polarized on discharge
5	2.4	"	57%	Re-check of cycle 2
6	19.5	"	48%	No polarization
7	2.4	"	39%	Re-check of cycles 2 and 5
Cell No. 2	(Stainless steel working electrode)			
1	2.4	1,200	44%	
2	"	"	61%	
3	"	"	59%	
4	1.2	"	57%	
5	24.0	"	30%	
6	15.3	"	21%	
7	2.4	"	39%	Recheck of cycle 1
Cell No. 3	(Stainless steel working electrode)			
1	6.1	610	34%	
2	"	"	29%	
3	"	"	27%	
	Anodize working electrode at +0.2V vs. Ag wire R.E., i decays to 0.05 mA cm^{-2}			
4	"	"	46%	
5	"	2,400	48%	
In PC/1 M LiBF$_4$				
Cell No. 4	(Aluminum working electrode)			
1	1.2	120	65%	
2	12.0	1,200	68%	
3	12.0	1,200	80%	
4	12.0	12,000	51%	
5	12.0	12,000	62%	Polarized on discharge
6	12.0	30,500	38%	"
7	12.0	30,500	27%	"
Cell No. 5	(Aluminum working electrode, glass fiber separator between shoulder and working electrode)			
1	12.0	30,500	51%	Polarized on discharge
2	12.0	"	42%	"
3	12.0	61,000	5%	"
Cell No. 6	Same as cell No. 5)			
1	12.0	61,000	36%	"
2	12.0	"	24%	"

show the diminished utilization with fairly large amounts of deposition.

Cells 4 and 5 again show the lowered efficiency with increasing amount of deposition. However, it must be noted that the amount of solute corresponds to only 74,000 mC, and the lower utilizations might reflect the effects of significant ionic depletion in the electrolyte.

In general, it is seen that there are not marked differences between the cycling behavior observed in the minimal electrolyte and those obtained in excess electrolyte, and this gives one some confidence that data obtained in excess electrolyte serve as useful indices of the performance expected in cell type environments.

The final series of experiments was designed to see what effects are observed when lithium is deposited in a cell type environment, with particular attention to the role of the separator. For these experiments the electrode support shown in Figure 7 was used.

The smooth platinum substrate was sandblasted after each run to clean the surface. As will be discussed in Section II-C, a tenacious dark deposit remains on the electrode after lithium deposition. This deposit cannot be removed by organic solvents or by any mineral acids other than aqua regia. It was undesirable to use the latter because of some attack on the epoxy. Some runs were also performed on a substrate prepared by electrodepositing copper on the roughened platinum at 12 mA for 500 sec. from an aqueous cupric sulfate solution.

Two types of separator materials were used: Millipore (Millipore Filter Corp. Catalog No. NCWPO2500), or Glass fiber filter (Reeve Angel Grade 934AH).

The electrode was prepared as follows: The separator disc was placed over the electrode cavity. The separator was held in place by covering the entire surface of the electrode support with masking tape; a circle was cut out of the masking tape. This circle was the same area as that of the electrode

($0.85\ cm^2$), and was placed to fit over the electrode. The masking tape was firmly pressed over the rest of the epoxy; this held the separator firmly in place; the only part of the separator exposed was that directly over the electrode substrate.

The electrode was filled by placing it in a solution identical to that used for the succeeding electrolysis runs. The cell was enclosed and evacuated by water aspiration. It was necessary to do this by increasing the water pressure slowly, over a period of 15-20 min., to the maximum vacuum allowed. If this were not done, the separator would rupture. When the vacuum was released a small bubble formed beneath the separator, filling about 5% of the volume between the substrate and the separator.

Electrolyses were performed in PC/0.5 M $LiClO_4$. For comparison, runs were also performed on electrodes without imposition of the separator. The electrodes were cathodized under the conditions indicated. The potential was continuously measured versus the silver disc R.E. The open circuit potential of an electrodeposited lithium electrode in the same solution was -3.2 ± 0.1 V vs. the silver disc R.E. Without the separator, the potential during cathodization remained constant at the value indicated. With the separator in place the behavior was quite different. Immediately on cathodization the potential initially rose to that indicated below. Thereafter the potential slowly became more negative by 1 to 1.5 V. The bubble beneath the separator expanded uniformly throughout cathodization. Finally, as the bubble filled the volume between the electrode and separator the potential rose sharply by several volts and thereafter oscillated jaggedly over a range of about 1 V. The time at which the bubble filled the space and the potential abruptly changed is here termed the "time of completion". The results are shown in Table 12 below.

TABLE 12

EFFECT OF SEPARATORS ON LITHIUM DEPOSITION

Run	Substrate	Filter	Current Density (mA cm^{-2})	Initial Potential (V vs. Ag^{o})	Time of Completion or Time of Deposition (sec)	Anodic Utilization
1	Pt(polished)	none	12	--	1000	69%, 70%
2	Pt(rough)	"	12	-4.20	1000	56%, 52%
3	Pt "	millipore	6	-3.8	1440	
4	"	"	"	"	1700	
5	"	glass fiber	"	"	1050	
6	Cu(1)	none	12	-4.60	50	23%
7	"	"	6	-4.00	100	22%
8	"	"	2.4	-3.75	250	26%
9	"	"	1.2	-3.60	500	14%
10	Cu(2)	"	12	-4.70	50	37%
11	"	"	6	-3.95	100	53%
12	"	"	1.2	-3.62	500	36%
13	Cu	millipore	6	-3.9	560	
14	"	"	"	"	730	
15	"	"	1.2	-3.5	2800	
16	"	"	"	"	2100	
17	"	glass fiber	"	"	2070	

(1) in quiet solution

(2) in stirred solution

It is of interest to compare estimates of the amount of gas evolved with the amount of current passed. The electrodes had an area of about 0.85 cm^2 and the depth of the cavity was about 0.15 cm. This gives a volume of about 0.04 cm^3. Assuming the gas to be at atmospheric pressure one may divide by 22.3 cm^3 mM^{-1}, giving 0.0018 mM of gas.

The amount of total current passed is given by the current density times the area (0.85 cm^2) times the "time of completion". This, divided by the Faraday gives the results shown below:

Run	Milliequivalents
3	.075
4	.088
5	.054
13	.029
14	.038
15	.029
16	.022
17	.021

Assuming gas formation to effectively consume two electrons per molecule this would indicate a consumption of from 4% of the current in run 4 to 18% of the current in run 17. Since the measured lithium utilization is considerably less than the difference between 100% and the above values one must conclude that:

(1) the assumptions underlying the calculations are seriously in error,

(2) a significant amount of gas is escaping through the separator,

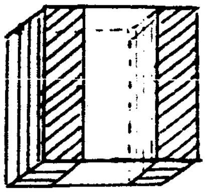
(3) the gas is quite soluble or reacts with the electrolyte,

(4) the anodic utilization on the rough platinum and copper substrates is an inaccurate measure of the lithium deposition efficiency.

II-B-4. Conclusions and Cell Design Criteria

In order to properly evaluate the data presented in this section is is useful to give some consideration to cell design criteria, to see just how good or bad the results are.

We consider a simple cell, comprising two electrodes, one cm^2 in area separated by a layer of electrolyte, shown below.



The energy density of such a cell is given by the equation:

$$E.D. = \frac{(V-iR)Q}{W_q + W_c} \tag{11}$$

where V is the open circuit potential, Q is the capacity, and W_q and W_c the weight of electrodes and of electrolyte respectively. We neglect the weight of other supporting structures and the packaging. It is, of course, desirable to minimize the amount of electrolyte, both to decrease the excess weight of the cell and also to decrease the iR drop. Since it is not realistic to consider cells in which no electrolyte is present, it is of interest to see what the maximum energy density can be for various "thicknesses" of electrolyte. It is also realistic to consider what effects result as a function of the rate of discharge. In this case we consider the rate to be the time required to completely consume electroactive material. We may express equation 11 thus:

$$E.D.\ (\text{Watt-hr } g^{-1}) = \frac{(V - Qk_2L/t)Q}{Q/k_1 + k_3 L} \tag{12}$$

where V = open circuit potential (Volts); Q = capacity (A-hr cm^{-2}); L = thickness of separator (cm); t = rate (hrs) k_1 = capacity/ weight conversion factor (A-hr g^{-1}); k_2 = electrolyte resistivity (ohm-cm); and k_3= electrolyte density (g cm^{-3}).

For a given thickness of electrolyte and a given rate, there will be a capacity at which the enery density will be maximum. This is found by differentiating equation 12 with respect to Q, and setting the differential equal to zero. One obtains:

$$Q\ (\text{for maximum E.D.}) = \frac{-\dfrac{k_2k_3L^2}{t} + \sqrt{\dfrac{k_2{}^2k_3{}^2L^4}{t^2} + \dfrac{k_2k_3L^2V}{k_1t}}}{k_2L/k_1t} \qquad (13)$$

We consider the results for a hypothetical cell for which the following constants obtain:

$V = 3$ V

$k_1 = 0.464$ A-hr g $^{-1}$ (for CuF_2 and Li electrodes)

$k_2 = 100$ ohm-cm (typical of the best non-aqueous electrolytes)

$k_3 = 2$ g cm $^{-3}$

and we calculate the Q for which the energy density will be a maximum at the 1 and 10 hr rates.

L (cm)	t (hr)	Q for max. E.D. from equation 13. (A-hr cm^{-2})	(coulombs cm^{-2})	Maximum E.D. by substituting Q into equation 12 (Watt -hr lb^{-1})
0.005	1	0.1625	584	592
0.005	10	0.5236	1880	615
0.01	1	0.158	568	560
0.01	10	0.519	1870	604
0.02	1	0.149	536	502
0.02	10	0.510	1840	585
0.04	1	0.134	482	403
0.04	10	0.492	1770	543
0.08	1	0.108	399	264
0.08	10	0.459	1610	473

For a given thickness and rate increasing the capacity will cause a decrease in energy density because of the increased iR drop. Decreasing the capacity will also cause a decrease in energy density because a smaller fraction of the cell weight will be that of the electrodes.

It is important to consider just how realistic these capacities are. The capacities of aqueous alkaline secondary electrodes are of the order of 10 mA-hr cm^{-2} for nickel-cadmium cells (36 C cm^{-2}) to 100 mA-hr cm^{-2} for silver- zinc cells (360 C cm^{-2}). In non-aqueous systems considerable difficulty has been encountered in getting satisfactory discharge of cathodes at 1-10 hr rates. The most intensive work in this area has been done by Abens and co-workers at Livingston Electronic Corporation. The most recent data available to us from this group (10) presents the results for discharge of CuF_2 electrodes in PC/1.4 M $LiClO_4$. These electrodes comprise, by weight, 100 parts of CuF_2, 14 parts of graphite, and 7 parts of paper fiber. The following data were given in Table VII of reference 10:

Capacity (C cm^{-2})	Thickness of electrode (cm)	Efficiency (2-electron reduction) for discharge at .1 mA cm^{-2}
550	0.40	20% (153 hr rate)
302	0.24	35% (84 hr rate)
175	0.16	36% (48 hr rate)
100	0.12	35% (28 hr rate)

These appear not to be maximum realizable values, as the same group has previously reported efficiencies of as much as 80% under the same general conditions.

From the data given above it seems reasonable to expect that, with further development, efficient discharge of electrodes with capacities of 100 C cm^{-2} should be obtained at the 10 hr rate.

There exists another problem which is not normally encountered in aqueous cells. This concerns the ionic content in the electrolyte. Below we calculate the energy density realizable from 100 C cm^{-2} electrodes discharging at the 10-hr rate for different thicknesses of electrolyte. We use the numerical values given above, following equation 13, and use equation 12 to calculate the energy density for different thicknesses of electrolyte. We assume the electrolyte to be 1 M in a simple binary salt. We calculate the equivalents of ions initially present in the electrolyte per unit area. In each case, for the 100 C cm^{-2} electrodes, 0.001 equivalents of ions are produced at each electrode.

(10) S. Abens, T. X. Mahy, and W. C. Mery, Livingston Electronic Corp., First Quarterly Report, NASA Contract NAS3-7632, Technical Report NASA CR-54859, Dec. 28, 1965

Electrolyte Thickness (cm)	Equivalents of ions initially present	Energy density at		
		1 hr rate	10 hr rate	100 hr rate
0.001	1×10^{-6}	665	670	670
0.003	3×10^{-6}	653	670	670
0.01	1×10^{-5}	590	645	650
0.03	3×10^{-5}	444	485	610
0.1	1×10^{-4}	37	450	491
0.3	3×10^{-4}	--	235	316

It is particularly interesting to note that the amount of ions initially present in the electrolyte is significantly less than the amount of ions produced on discharge. This means that there must be nearly total ionic transport across the electrolyte, from one electrode to another. Given the necessity for this to occur, one may make a rough calculation of the maximum current which can pass. We consider the cell to discharge by the reaction: $CuF_2 + 2\,Li = Cu + 2\,LiF$. For an order of magnitude calculation, we may consider that LiF precipitates at the CuF_2 electrode and that lithium ions produced at the lithium electrode on discharge must migrate across the electrolyte to the CuF_2 electrode. To the extent this does not happen, the cell potential will show the effects of severe concentration polarization. We assume a linear concentration gradient to exist across the electrolyte. The current is then given by:

$$i = \frac{F\ D\ (C_{Li}^{o} - C_{CuF_2})}{L} \qquad 14$$

where D is the diffusion coefficient, C_{Li} is the concentration of lithium ions at the lithium electrode, and C_{CuF_2} is the concentration of lithium ions at the CuF_2 electrode. We assume that the maximum current is attained under the conditions that C_{Li} is equal to the solubility of the lithium salt, and C_{CuF_2} is zero. We use the equation $D = RT\Lambda/F^2$ and take a value of 20 for the equivalent conductance, giving a diffusion coefficient of about 5×10^{-6} cm^2 sec^{-1}. We assume the maximum solubility of the lithium salt to be 2 M. The maximum current is then, from equation 14:

$$i = \frac{(10^5\ \mathrm{C\ M^{-1}})(5 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}})(2 \times 10^{-3}\ \mathrm{M\ cm^{-3}} - 0)}{\mathrm{L\ (cm)}} \qquad (15)$$

$$= 0.001\ \mathrm{A\ cm^{-1}/L\ (cm)}$$

For a 0.01 thickness of separator this would be 100 mA $\mathrm{cm^{-2}}$; but for a 0.1 cm thick electrolyte layer, the maximum current is only 10 mA $\mathrm{cm^{-2}}$.

Let us assume , then, that this is the maximum current which can pass before concentration polarization occurs because of the insufficient supply of lithium ions to the CuF_2 electrode. We then may calculate the iR drop at this maximum current, which is the product of the maximum current, 0.001/L (A $\mathrm{cm^{-2}}$) times the resistance, ρ (ohm-cm) x L(cm). The thickness, L, cancels out, and the maximum iR drop is 0.001 xρ . For a 100 ohm-cm electrolyte this is 0.1 V, and is independent of the electrolyte thickness.

If this is the maximum iR drop, equation 12 becomes (using the constants given on page 48):

$$\mathrm{E.D.\ (Watt - hr\ lb^{-1})} = 450\frac{(3 - 0.1)(Q)}{Q/0.464 + 2\ L}$$

where 450 is the conversion factor for grams to pounds, Q is the capacity in A-hr $\mathrm{cm^{-2}}$, and L is the electrolyte thickness in cm. From this equation one finds, that for an energy density of more than 200 watt-hr $\mathrm{lb^{-1}}$ it is necessary that: Q (A-hr $\mathrm{cm^{-2}}$) $>$ 0.46 L (cm). For a 0.1 cm thickness of electrolyte Q must be greater than 166 C $\mathrm{cm^{-2}}$; for a 0.01 cm thickness of electrolyte, Q need only be greater than 16.6 C $\mathrm{cm^{-2}}$.

These calculations, admittedly most crude, give some insight into the causes of low energy densities. It does not appear that simple ohmic losses directly related to the bulk conductivity of the electrolyte are not nearly as serious a source of energy density losses as are concentration polarization through inadequate ionic transport from one electrode to the other, charge-transfer polarization at one or both electrodes, and excessive electrolyte weight.

We now consider the data presented in table 2, p. 9; table 9, p. 36; table 10, p. 37; and table 11, p. 42. A current of 10 mA $\mathrm{cm^{-2}}$ appears to be a reasonable current or a "moderate" current in the sense that the performance shown in these tables is not particularly improved by going to lower currents, nor is there any particularly marked deterioration in performance in going to several fold larger currents. By the same token, capacities of 10 C cm^{-2} are reasonable or "moderate". Such capacities and current densities are also in line with the calculations following page 46.

Since the realization of good energy density for such capacities and current densities does demand quite thin electrolyte separation, and since the low efficiency of the lithium electrode cycling is concommitant with gassing and a deposit of poor physical form -- factors which are the more serious the thinner the electrolyte separation -- it is apparent that considerable improvement in the performance of the lithium electrode is necessary before secondary cell development, employing the lithium anode, is justified.

We propose the following research objective as demonstrative of the "feasibility" of the lithium, secondary cell anode: A substrate - electrolyte system in which lithium metal may be cathodically deposited at a current of 5 mA cm^{-2} for a total of 10,000 mC cm^{-2}, and subsequently reanodized with at least 95% efficiency; and in which such cycling may be continued for at least 10 cycles before serious losses in efficiency occur.

In the next section we shall consider some more fundamental studies we have performed, with the objective of learning more about the basic cathodic behavior observed in nonaqueous solutions of lithium salts.

II-C. Cathodization Experiments in Non-aqueous Electrolytes

1. Introduction

The data presented in the previous section II-A and II-B show that the behavior of the lithium electrode is, at present, not completely satisfactory for incorporation in secondary cells. The data are unsatisfactory in the sense that they neither indicate wherein lie the major causes for inefficient cycling or for low cycle life, nor do they suggest what appropriate modicfications may be made to improve performance.

Furthermore, the sensitivity of performance to such a large number of variables -- nature and concentration of electrolyte, current density, conditions of cycling, solvent, electrode substrate, etc. -- suggest that a satisfactory screening program, involving a consideration of each of these variables, would be unduly laborious and inefficient.

It was desirable to examine in more detail the nature of the phenomena observed during cathodization in non-aqueous electrolytes. This work is discussed in this section.

The purpose of basic electrochemical experiments is similar to that of ordinary kinetic studies. One seeks first to establish the nature of the reactants and the products -- the gross stoichiometry of the reaction. This is an analytical problem. Secondly one seeks to ascertain the stoichiometry of the slow steps in the reaction, as this will allow one to postulate a reaction mechanism. This second step is accomplished by measuring reaction rates as functions of the concentration of reactive species. This is also an analytical problem. Finally, one may study the reaction rate as a function of temperature. This will allow one to determine the "activation energy", which is of interest in that it will reflect the relative stability of the "transition complex" with respect to the entities from which it is formed. A kinetic study is complete when a model may be constructed which explains the observed facts.

Thus, in kinetic measurements one has two variables to control -- the concentration(s) of reactants, and the temperature. Electrochemical measurements are identical in principle; one controls the concentration of reactants and the potential. The potential in electrochemical measurements is completely analogous to controlling the temperature in kinetic measurements. One measures the current (the rate). It is not important to consider the operation by which the potential is fixed. When all other variables are constant, the relationship between current and potential is fixed. It is irrelevant whether the instrumentation is such that one is apparently applying a controlled potential or a controlled current. One is allowed, in electrochemical measurements, a technique which is not normally employed in ordinary kinetic measurements. That is, one may hold the rate of reaction (current) constant by varying the potential. This would be analogous to performing kinetics measurements by continuously adjusting the temperature such that the rate would remain constant. Clearly, such a technique would be most difficult; however, if the technique were convenient one might be allowed the acquisition of kinetic data with greater experimental efficiency.

While it is recognized that the analytical techniques used for kinetic studies are of critical importance, there appears, in much of the reported electrochemical work, less critical attention to the relevance of the electrochemical technique to the nature of the data sought. The analytical techniques used in kinetic measurements are, in a well-designed experiment, related to the rate of the reaction studied. The same is true in electrochemical measurements.

In our work we have considered the variety of electrochemical techniques available. These will be briefly discussed.

Fast techniques, employing perturbations with time variations of the order of 0.001 sec. or less, are extremely useful in studying surface effects where the amount of current is of the order of a monomolecular layer or less, as in double layer capacity measurements, or for studying very fast reactions, where the rate of change of undesired variables (e.g. the concentration at the electrode surface) is comparable with the rate of the reaction being studied.

We have not employed such techniques in our work to date, for two reasons. First, we do not feel that the systems are sufficiently well-defined at present to justify an attempt to obtain data of a more sophisticated nature. Secondly, the experimental complexity is rather too great to be justified at present. For example, constant current may be applied through a voltage source and a dropping resistor in series with the cell. Now, during the course of a run, the total cell potential may easily vary by at least 10V. In order to insure that the variation in current is less than 5%, the voltage supply must be at 200 V or more. This is most inconvenient using battery power sources. Alternatively, one may use electronically regulated constant current supplies. These, however, have rise times of the order of milli-seconds; in addition, the switching becomes a problem since mercury relays have switching times of the order of milli-seconds. Finally, the impedance and response time of the measuring circuit must be considered.

Slow techniques are those in which electrolysis is continued for such a period of time that significant consumption of material is realized. Such techniques are used in electrogravimetry, and find extensive application in the determination of reaction products for organic electro-reactions. It is useful to consider such techniques in more detail, as it is quite desirable that these types of measurements be more extensively employed in the future. We have, in fact, performed a number of studies using methods of this nature, as will be later discussed. We consider an electrode reaction where some electroactive material is being electrolyzed at the maximum rate, that is, at the limiting current. The maximum current is, as discussed previously:

$$i = k\,A\,C\,n \qquad (16)$$

where is is the total current, k is a constant (ca. 180 mA $cm^{-2}/M\ l^{-1}$ as discussed previously), and C is the concentration at time, t, n is the number of electrons consumed per molecule of reduction.

Finally,

$$Q = n\,C\,V\,F \qquad (17)$$

where Q is the number of coulombs of material in solution at time, t, C the concentration, V the volume, and F the Faraday.

Since $i = dQ/dt$, one combines the two equations, performs the integration and finds:

$$\ln i/i_o = \frac{-k\,A\,t}{V\,F} \tag{18}$$

where i_o is the current at $t = 0$, the initiation of electrolysis. Using the appropriate units and setting $k = 180$ m A cm^{-2}/M l^{-1}, one has:

$$\ln i/i_o = -\frac{(6.5)\ (t\ \mathrm{hr})\ (A\ \mathrm{cm}^2)}{(V\ \mathrm{cm}^3)} \tag{19}$$

For V = 100 ml, and A =1 cm^2, it is seen that almost 11 hr. are required to reduce the concentration of C by half (i.e. $\ln i/i_o = \ln 0.5$). Increasing the area to 10 cm^2, and decreasing the volume to 10 ml. allows one to decrease the amount of active material by half in about 10 min. and in 42 min. the concentration has been reduced to 1% of its initial amount. This is for stirred solution; for quiet solution k is about 1/5 the value in stirred solution, and times for a given amount of reduction are proportionately increased. In such measurements one must consider the effect of significant amounts of joulean heating across any separator between working and counter electrodes, and also the effect of a build-up reaction by-products at the counter electrode, with subsequent migration into the working electrode compartment.

Finally, having considered fast and slow techniques, we consider <u>intermediate techniques</u> -- those experiments in which the amount of electrolysis does not consume a significant amount of electroactive material in solution and where the times are greater than 0.01 sec.

The instrumentation used is normally such that one controls either the current or the potential. Either may be held constant, or may be varied as some appropriate function of time. In addition, the degree of electrolyte agitation is most important.

We have avoided using experiments involving varying potentials, such as linear sweep voltammetry. The reason for this is that the data cannot be analyzed with any rigor. The theory concerning the relationship between current and potential is based on the fact that one is able to control the potential at the "electrode surface". In fact, one is only able to control the potential between the electrode surface and the point at which the reference electrode probes the potential. In poorly conducting solutions there is a very significant difference between these two potentials as will be later discussed. Hence, though one supposes one is varying that potential which determines the rate of the electrode processes in some well-defined way, that supposition is, in fact, not true. Since the "effective potential" is varying in an erratic fashion one cannot obtain either kinetic or mass transport data. Thus such a technique as linear sweep voltammetry is, therefore, quite inadequate for obtaining useful data in poorly conducting solutions unless considerable instrumental elaboration is used so that, after prior calibration, automatic corrections to the applied potential may be effected. Otherwise the technique is analogous to attempting to make kinetic rate measurements, with inadequate temperature control. Even if the temperature variation is known, the rate equations become exceedingly complex.

Periodic or continuously varying current measurements may be used with more facility. Although the measured potential must be corrected as discussed below, and although this correction would be tedious if performed manually, the instrumental complexity involved in making an automatic correction is not too great. Again, prior calibration of the system is necessary.

In our work we have only used measurements at constant potential or at constant current. We next consider the degree of agitation. Measurements are made either in quiet solution, or in agitated solution--with or without control of agitation. In quiet solution, convective effects occur under normal laboratory conditions after about 40-60 sec., and the theory is not valid thereafter. The theory concerning processes occurring with convection is too involved to be useful to us at this time. In agitated solution, the degree of agitation may be controlled as with a rotating disc electrode or at the dropping mercury electrode (which, for convenience, we here consider as a type of agitated solution). The theory does not in principle involve empirical constants. In agitation without control we consider such techniques as the use of a rotating wire electrode, streaming electrodes, or stationary electrodes in stirred solutions. In none of these cases is the theory exact because of the ill-defined hydrodynamic conditions, and one must resort to the determination of empirical constants. In the subsequent discussion of Section II-C-3a, we will consider what theory has to say about each of these conditions.

Having discussed briefly the basic electrochemical techniques available, we consider the conditions under which our experiments are performed, which complicate the attempt to interpret the data in a simple fashion. These conditions differ from those which normally obtain in electrochemical studies in aqueous media in the following respects.

1. No supporting electrolyte.
2. Low conductivity.
3. High impurity content (ca. 0.01 to 0.001 M).
4. Solvents are markedly different from water.
5. Solid electrode substrates not well-defined.
6. Extremely negative potentials across the electrical double layer.

We first consider the general question of electrochemical measurements in the absence of supporting electrolyte, in solutions of low conductivity. This work constitutes the discussion of "background experiments" in Section II-C-3-a.

We then have studied the behavior observed in a variety of lithium salt solutions. This work is discussed in Section II-C-3-b. It will be shown that, to the degree the formalism normally used to describe electrochemical processes is valid, the behavior observed during cathodization in lithium salt solutions does not reflect the occurrence of a simple., one-electron electrode process. It will be shown that there is evidence for extensive meso-reduction; that is, reduction of materials other than the lithium ion concurrently with lithium reduction, and, in lithium salt solutions, occurring only when lithium is also deposited.

Finally, we discuss, in Section II-C-3-c, the results of cathodization experiments performed in other, non-lithium containing, electrolytes to establish a broader picture of cathodic behavior in general.

II -C-2. Experimental. The experimental procedures were identical to those described in Section II-B-2. Working electrodes, shown in Figure 5, and the circuitry, shown in Figure 6, were used. Other experimental modifications will be described in conjunction with particular experiments.

II-C- 3. Results and discussion

II-C-3a. These experiments were designed to study the effects observed when electrochemical measurements are performed in the absence of supporting electrolyte in poorly conducting solutions. In particular, we are concerned with the mass transport properties and the significance of potential measurements in such media. For brevity, we shall restrict our discussion to the reduction of the lithium ion, and consider the case when the reduction is reversible and when totally irreversible.

If the reduction, $Li^+ + e^- = Li^o$, is "reversible" the measured potential, E_M, is given by:

$$E_M = E_O + E_R + E_D + E_L \tag{19}$$

These will be discussed below:

E_O = The open circuit potential of a lithium electrode in the same solution versus an appropriate reference electrode. The choice of a reference electrode is, of course, most important. The reference electrode must be well-poised; that is, its potential must be invariant during the course of electrolysis, and not subject to variation because of small amount of current which flows through the measuring circuit. (Note: with the use of electrometers and vacuum tube voltmeters this current is negligible). It is desirable that the potential of the electrode have thermodynamic significance. In our work, we have found that the potential of silver metal assumes a well-poised potential in many solutions in which silver ions are absent. Although the potential of the silver wire may vary ± 0.1 V from solution to solution (in the case of propylene carbonate), its potential in a given solution has been observed to be constant to within the accuracy with which the iR drop can be corrected. In propylene carbonate, the potential of the silver is about -0.7 V vs. a $Ag/(0.01\ M\ Ag^+)$ electrode, and is about +3.1 ± 0.1 V vs. that of a lithium electrode in a lithium salt solution. This is quite satisfactory for most purposes. However, when a more accurate definition of the reference electrode is desired, we have either made measurements versus an electrode comprising a dilute (0.01 M) solution of $AgClO_4$ in a more concentrated lithium salt solution (ca. 0.5M) and a silver wire, or versus an electrodeposited lithium electrode. In the latter case, lithium is simply electrodeposited on the center silver disc R.E. (see figure 5). Preliminary measurements are made to insure that the potential of this electrodeposited lithium electrode remains constant over the period of time required for the measurement.

E_R= the potential across the double layer during cathodization.

This is the potential which would be measured in the ideal case that an electrode probe were positioned at the outer extent of the diffuse double layer without perturbing the current flux on the electrode surface. The measurement of this potential is in principle possible, but in practice is not possible since the diameter of a Luggin capillary probe would have to be of the order of Angstroms.

The potential, E_R, for a reversible system is defined by the Nernst equation:

$$E_R = \frac{RT}{Z_1F} \ln(Li^+)/(Li^+)_o \qquad (20)$$

where (Li^+) is the concentration of lithium at the electrode "surface" and $(Li^+)_o$ is the bulk concentration. (Note: we continue to use concentrations instead of activities.) When activity coefficients are unity, this potential should be the same regardless of whether or not supporting electrolyte is present.

E_D = the potential across the diffusion layer. This potential is negligible in the presence of supporting electrolyte. In the absence of supporting electrolyte it is significant. It is approximated by:

$$E_D = \frac{RT}{z_2F} \ln(Li^+)/(Li^+)_o \qquad (21)$$

where z_2 is not the charge of the lithium ion but that of the counter, non-electroactive ion. Its derivation is discussed by Vetter(12), and is based on the assumption that the equilibrium exists between the diffusion layer and the bulk of solution; that is, that the electrochemical potentials of ionic species are equal throughout the region between the electrode surface and the bulk of solution. Under these conditions the following relationship exists:

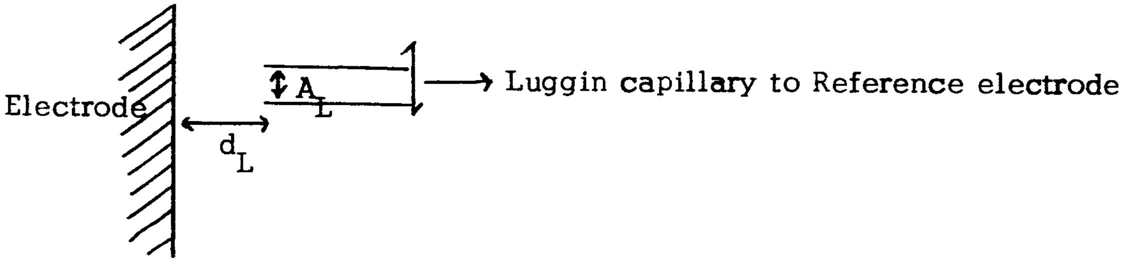
$$\frac{(C_2)}{(C_{2,o})} = \exp(-z_2F\, E_D/RT) \qquad (22)$$

where C_2 and $C_{2,o}$ are the concentrations of the counter ion at the electrode surface and in the bulk of solution respectively. The principle of electroneutrality dictates that $(z_{Li^+})(Li^+) = (z_2)(C_2)$ at all points, and equation (21) is therefore easily derived. It is convenient to think of this potential, E_D, as reflecting an iR drop across the diffusion layer through ionic depletion during electrolysis. Vetter terms this potential the WIDERSTANDSPOLARISATION.

E_L = the potential between the tip of the Luggin capillary probe and the outer extent of the diffusion layer. This distance will, of course, decrease as the diffusion layer penetrates into the bulk of solution. However, as will be discussed later, we believe that the effective distance between the probe and the electrode surface is about 0.16 cm, while the diffusion layer thickness grows to about 0.005 cm. For the present purposes, we will assume that the effect is negligible. In the diagram below, the source of E_L is shown. Ideally, it represents the product of current and resistance in that cylinder of

(12) Vetter, op. cit., p. 295-297.

solution prescribed by the radius of the Luggin Capillary. It is not related to any current flowing in the measuring circuit, nor is it the ohmic drop between the working and counter electrodes.



One has:

$$E_L = \frac{i_T}{A_E} \cdot A_L \cdot \frac{\rho\, d_L}{A_L} = (i \text{ A cm}^{-2})(\rho \text{ ohm-cm})(d_L \text{ cm}) \qquad (23)$$

where i_T is the total current on an electrode of area A_E; A_L is the area of the tip of the Luggin capillary, ρ is the specific resistance of the solution, and d_L is the distance between the tip and, approximately, the electrode surface.

Combining equations 19-23, one writes for a reversible process

$$E_M = E_O + \frac{RT}{F}(1/z_1 + 1/z_2) \ln (Li^+)/(Li^+)_o + i\, \rho d_L{}^* \qquad (24)$$

For a totally irreversible process:

$$E_M = E_K + E_D + E_L \qquad (25)$$

E_D, and E_L are the same as in equations 21 and 23.

E_K = the potential for a process in which the current is kinetically controlled. A totally irreversible process is defined as one which the relationship between current and potential is given by an equation of the form:

$$i = Fk\,(Li^+)\;e^{-B\,E_k} \qquad (26)$$

where F is the faraday, k a heterogeneous rate constant in cm sec^{-1}, and B a constant in V^{-1}.

---

* The sign conventions used in this report are such that for increasing cathodic current, the potentials become more negative. Thus, for cathodic reduction the iR term should be negative; for anodic oxidation it should be positive.

One writes:

$$E_K = 1/B \ \ln \frac{F\,k\,(Li^+)}{i} \tag{27}$$

Therefore, for a totally irreversible process, one has

$$E_M = E_O + 1/B \ln \frac{F\,k\,(Li+)}{i} + RT/z_2F \ln (Li^+)/(Li^+)_o + i\ \rho d_L \tag{28}$$

This equation is usually written using, instead of the constant B and k, the exchange current density, i_o, and the transfer coefficient, α. These quantities, which have a <u>purely formal</u> significance in this discussion, are obtained by making measurements of E_M at decreasing currents. In the limit $E_M \dashrightarrow E_O$, the latter two terms vanish, $(Li^+) = (Li^+)_o$, and $i \dashrightarrow i_o$ by definition. Since the third term is equal to zero, $i_o = F\,k\,(Li+)_o$. The slope, 1/B, is defined: $1/B = RT/\alpha F$ and equation 28 becomes for a totally irreversible process:

$$E_M = E_O + \frac{RT}{\alpha F} \ln i_o + \frac{RT}{F} (1/\alpha + 1/z_2) \ln (Li^+)/(Li^+)_o + i\,\rho\,d_L \tag{29}$$

and, for comparison, we again write the equation for the reversible process.

$$E_M = E_O \qquad\qquad + \frac{RT}{F} (1/z_1 + 1/z_2) \ln (Li^+)/(Li^+)_o + i\,\rho d_L \tag{30}$$

If these equations are to be used one must make corrections for (Li^+), the concentration of lithium at the electrode surface, and for the last term, the iR drop.

We first consider the corrections which may be made for the concentration of lithium ion at the electrode surface. We consider five situations each denoted by their more common names:

1. Chronoamperometry. In quiet solution, the potential is held constant at a sufficiently negative value that the concentration at the electrode surface is zero throughout the time of interest: (13)

(13) Delahay, *op. cit.*, pp. 49-52.

$$C = 0 ; \qquad i = \frac{D_1^{1/2} C_o n F}{t^{1/2} \pi^{1/2}} \tag{31}$$

2. Polarography. The potential is held constant while the drop grows in size as the mercury flows through a capillary at rate, m (mg sec^{-1}) and t is the age of the drop. In our work we do not measure, as is customarily done, the limiting current as the "average current", but rather use the current at the instant before the drop falls and a new drop begins growing. In this case t is the "drop time", and the limiting current and concentration relationships are(14):

$$C = C_o(1 - i/i_L) ; \qquad i_L = D_1^{1/2} C_o n \, (708 \, m^{2/3} t^{1/6}) \tag{32}$$

3. Rotating Disc Electrode. Either current or potential held constant and steady state situation measured.(15)

$$C = C_o(1 - i/i_L) ; \qquad i_L = D_1^{2/3} C_o n \, F(\omega^{1/2}/1.61 \, \nu^{1/6}) \tag{33}$$

where ω = angular velocity in sec^{-1}; and ν = kinematic viscosity in $cm^2 \, sec^{-1}$.

4. Voltammetry in Agitated Solution. Either current or potential held constant in stirred or otherwise agitated solution and steady state situation measured. Either the electrode or solution may be moved mechanically.(16)

$$C = C_o(1 - i/i_L); \qquad i_L = D_1 C_o n \, k \tag{34}$$

where k is empirically determined.

5. Chronopotentiometry. In quiet solution, the current is held constant and the potential measured with time.(17)

$$C = C_o\left(1 - \frac{it^{1/2}}{iT^{1/2}}\right); \; iT^{1/2} = D_1^{1/2} C_o n \, (\pi^{1/2} F/2) \tag{35}$$

where t is the time elapsed since the initiation of current, and T is the "transition time", defined as the time at which the concentration at the electrode surface goes to zero.

All of these techniques are well-known. It seems less widely appreciated that equations, identical in form, exist in the total absence of supporting electrolyte. While we have not encountered any theoretical

---

(14) Delahay, *op. cit.*, pp. 63-65.
(15) Delahay, *ibid.*, p. 230
(16) Delahay, *ibid.*, p. 219
(17) Delahay, *ibid.*, p. 180, 184

expression for case 1, chronoamperometry, in the absence of supporting electrolyte, the other four cases have been treated. In each of these cases the form of the equation for i_L or $iT^{1/2}$ is identical to that in the preceding equations 32-35, if one substitutes for D_1 an effective diffusion coefficient D_{eff}.

To our knowledge the equations for i_L and $iT^{1/2}$ for the four cases shown on page 64 have not been tabulated together, and for the convenience of other workers who find it necessary to work in the total absence of supporting electrolyte, such a tabulation is made at this time.

The derivation of the equations of course follows from Fick's first and second laws for mass transport. The expression for the first law is that given by equation (1), p. 23, and, in the absence of supporting electrolyte involves a term, $\partial \phi / \partial x$, the potential gradient. The second law is $\partial C/\partial t = \partial f/\partial x$ (f, again, is the flux). The main difference between the solution of the equations in the total absence ofsupporting electrolyte and that which obtains in the presence of excess supporting electrolyte is that one must take account of this potential gradient.

The equations presented in the literature are often given in terms of the diffusion coefficient of the salt, D_s, given by:(18)

$$D_s = (z_1 + z_2)(D_1 D_2)/(z_1 D_1 + z_2 D_2) \quad * \qquad (36)$$

In the solution of the equations the relationship between the diffusion coefficient and the equivalent conductance is assumed to obtain as shown in equation (4), p. 24:

$$D = RT\lambda/zF^2 \qquad (4)$$

---

(18) V. G. Levich, Physicochemical Hydrodynamics, Prentice-Hall, Inc. Englewood Cliffs, N. J., 1962, p. 281 (eqn. 51.10)

* Note: Levich uses the term D_{eff} for the diffusion coefficient of the salt; whereas we, and most other writers, use the term D_s. The term we call D_{eff} or its equivalent does not appear in the literature. It is merely the term which must be substituted for D_1 in equations 32 - 35, to give the right value for i_L or $iT^{1/2}$. It is not the same for each case -- the D_{eff} to be used for polarography is not the same as that which should be used for the rotating disc electrode.

therefore, it is proper to express the various diffusion coefficients, D_1, D_2, D_s, and D_{eff} in terms of the independently measurable quantities, t_+, the transference number of the cation, and Λ, the equivalent conductance of the salt. These calculations are completely straightforward and will not be reproduced here.

	D_{eff} for a 1:1 univalent electrolyte when $t_+ = 0.5$		
	In total absence of supporting electrolyte	in presence of excess supporting electrolyte	
Polarography(19)			
$D_{eff} = \dfrac{RT\ (z_1 + z_2)\ t_+ \Lambda}{F^2\ (z_1 z_2)\ (1 - t_+)}$	$\dfrac{2RT\Lambda}{F^2}$	$\dfrac{0.5\,RT\Lambda}{F^2}$	(37)
Rotating Disc Electrode(20)			
$D_{eff} = \dfrac{RT\ (z_1 + z_2)\ t_+ \Lambda}{F^2\ (z_1 z_2)\ (1 - t_+)^{1/2}}$	$\dfrac{2^{1/2}\,RT\Lambda}{F^2}$	$\dfrac{0.5\,RT\Lambda}{F^2}$	(38)
Voltammetry in Agitated Solution(21)			
$D_{eff} = \dfrac{RT\ (z_1 + z_2)\ t_+ \Lambda}{F^2\ (z_1 z_2)}$	$\dfrac{RT\Lambda}{F^2}$	$\dfrac{0.5\,RT\Lambda}{F^2}$	(39)
Chronopotentiometry(22)			
$D_{eff} = \dfrac{RT\ (z_1 + z_2)\ t_+ \Lambda}{F^2\ (z_1 z_2)\ (1 - t_+)}$	$\dfrac{2RT\Lambda}{F^2}$	$\dfrac{0.5\,RT\Lambda}{F^2}$	(40)

---

(19) Levich, ibid., p. 560 (equation 110.17). Note: in Levich's equation c_I = molar concentration (pp. 557, 245 - equation 46.7), D_{eff} is the salt diffusion coefficient, and the first z_1 is actually the number of electrons involved in the reaction, normally, n.

(20) Levich, ibid., p. 293 (equation 52.25), p. 296 (equation 53.11).

(21) Levich, ibid., p. 247 (equation 46.18 - 46.20)
Vetter, op. cit., p. 149 (equation 2.110)

(22) P. Bro, J. Electrochemical Soc. 111, 1104 (1964)
M. D. Morris and J. J. Lingane, J. Electroanal. Chem. 6, 300 (1964)

We again recall, the effective diffusion coefficients, D_{eff}, given on the preceding page are those quantities which should appear in place of D_1 in the equations given on page 64. On page 66 are also given the effective D_{eff}'s for a 1:1 univalent electrolyte when $t_+ = 0.5$. Comparing the ratios of these and the power to which the diffusion coefficient is raised in equations 32-35, it is apparent that the measured quantity, i_L or $iT^{1/2}$, is, in the total absence of supporting electrolyte, exactly <u>twice</u> that ideally expected in the presence of supporting electrolyte.

We continue this discussion of electrochemical measurements in the total absence of supporting electrolyte in poorly conducting solutions by going back to equation (24), p. 62, which is the expression for the measured potential observed during a reversible electrode process:

$$E_M = E_O + \frac{RT}{F}(1/z_1 + 1/z_2)\ln (Li^+)/(Li^+)_o + i\rho d_L \qquad (24)$$

where (Li^+) = the concentration at the electrode surface, and $(Li^+)_o$ = the concentration in the bulk of solution. Now, from equations 32-35 one observes that in each case the concentration at the electrode surface is related to the bulk concentration by an equation of the form:

$$C/C_o = 1 - x/x_L \qquad (41)$$

where x_L is the limiting quantity, i_L or $iT^{1/2}$. Therefore, equation (24) above may be generally expressed:

$$E_M = E_O + \frac{RT}{F}\left(\frac{1}{z_1} + \frac{1}{z_2}\right)\ln\left(1 - \frac{x}{x_L}\right) + i\rho d_L \qquad (42)$$

For a totally irreversible process, as described by equation (29), p. 63, we may make the identical substitution, and obtain:

$$E_M = E_O + \frac{RT}{F}\left(\frac{1}{\alpha} + \frac{1}{z_2}\right)\ln\left(1 - \frac{x}{x_L}\right) + i\rho d_L + \frac{RT}{\alpha F}\ln\frac{i_o}{i} \qquad (43)$$

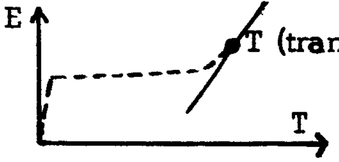
To determine whether a reaction is "reversible" or "irreversible" it is necessary to see which equation is followed by the current-potential curve. It shall be shown in the following discussion that, for the deposition of lithium, this is difficult to do because any apparent deviations from the reversible behavior expressed by equation (42), p. 67, may as easily be ascribed to other causes than a measurable exchange current or transfer coefficient.

In poorly conducting electrolytes, one of the most important corrections, of course, is for the iR drop. We consider this term, $i \rho d_L$. In addition, we consider the validity of the mass transport equations given on pages 64 and 66; in particular those for chronopotentiometry, which is the type of measurement most easily made and is described by equation (35), p. 64, and equation (40), p. 66.

For these preliminary experiments, silver perchlorate was selected as the best salt. It is similar to the simple lithium salts in being a 1:1 uni-univalent salt; it is soluble in a number of organic solvents, it is expected to undergo "reversible" reduction, and the problem of a reference electrode is conveniently dispatched by simply using a piece of metallic silver in the same solution as the reference electrode.

Initial experiments were conducted in aqueous solution. Dilute solutions of $AgClO_4$ were prepared and measurements made using the working electrode described in figure 5, p. 17. Chronopotentiograms were run at several current densities in each solution, to give transition times of from 5 to 20 seconds. The chronopotentiograms were run on polished silver electrodes. There were no serious problems in obtaining reproducible results; and there were no indications of serious adsorption of silver ions on the electrode, which would augment the transition time.

At the lower concentrations, the transition times were rather ill-defined. There are various methods of selecting the transition time; these are discussed by Russell and Peterson(23). We used an extrapolation method termed by them the "method of Kuwana". This procedure is illustrated below.



(23) C. D. Russell and J. M. Peterson, J. Electroanal. Chem. 5, 471 (1963)

After the initial potential plateau, the potential enters a region where the potential increases linearly with time. The point at which this occurs is picked as the transition time, T. At the higher concentrations this region of linear potential increase with time becomes steeper and there is less arbitrariness in selecting the transition time.

It was assumed that the reduction was reversible, and equation (42), p. 67, was applied. In this case, chronopotentiometry, the term $(1 - x/x_L)$ becomes $(1 - t^{1/2}/T^{1/2})$. Plots were made at various currents of the potential versus this term, using, in each case, the measured transition time for the particular current density. The slope of this plot gives the term: $(1/z_1 + 1/z_2)RT/F$. This term has been multiplied by 2.303 to give the coefficient applicable for Briggsian logarithms.

The second correction to be made in equation (42) is for the iR drop . Clearly, the term, $i \rho d_L$, is not applicable, since the geometry of the system, shown in figure 5, p. 17, is not that described by the figure at the top of page 62, from which the term is derived. Nevertheless, we assumed that there might exist an "effective" d_L. To calculate the value of the effective d_L we again go back to equation (42). At $t = 0$, the logarithm term is zero $(\ln(1 - 0) = 0)$. Therefore the initial potential should be:

$$E_{M(t=0)} = E_O + i \rho d_L$$

Since the potential is measured against a silver metal reference electrode in the same solution, and deposition is performed on silver electrodes, E_O should also be zero. Hence, the effective d_L is calculated from:

$$d_L = E_{M(t=0)}/i \rho$$

In each solution ρ was measured, and the effective d_L calculated.

The results of these measurements are shown in table 13 on the next page. From equation 35, p. 64, we calculate from a value for $iT^{1/2}/C = 620$ mA cm sec$^{1/2}$ mM^{-1}, an effective diffusion coefficient:

$$D_{eff} \text{ (observed)} = 5.4 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$$

Using equation (40), p. 66, and calculating the transference number of the silver ion and the equivalent conductance of the salt from the ionic equivalent conductances (in ohm^{-1} cm^2 M^{-1})at infinite dilution of 61.9 for Ag^+ and 67.3 for ClO_4^- we obtain:

$$D_{eff} \text{ (calculated)} = 6.4 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}.$$

Table 13

CHRONOPOTENTIOMETRY IN AQUEOUS UNSUPPORTED $AgClO_4$

Concentration of $AgClO_4$ ($M\ l^{-1}$)	$\frac{iT^{1/2}}{C}$ (mA cm $sec^{1/2}$ mM^{-1})	$2.303\ (1/z_1 + 1/z_2)RT/F$ (V)	effective d_L (cm)
0.0001	630	0.12	0.153
0.000295	620	0.11	0.152
0.000583	610	0.11	0.157
0.00113	620	0.11	0.154
0.0049	620	0.11	0.168
0.00962	630	0.11	0.165
0.0293	630	0.11	0.170
0.100	640	0.12	0.170

The validity of the concept of an effective d_L appears plausible from this data. The apparent value is, ave. $d_L = 0.161 \pm 0.009$ cm. Thus, the chronopotentiograms are quite satisfactorily described by the equation:

$$E_M = 0.059(2)\log(1 - \frac{it^{1/2}}{620C_o}) - i\,\rho\,(0.161)$$

The validity of which "proves" the reversibility of the reduction.

As expected, the addition of supporting electrolyte decreases the value for $iT^{1/2}$, since the silver ions are no longer impelled toward the electrode by a potential gradient as well as a concentration gradient. This is shown in table 14 below. These chronopotentiometric measurements were made in a solution, initially 0.021 M in $AgClO_4$, to which were added successive amounts of $LiClO_4$ to give the concentration indicated. The transference number was calculated from the concentrations of the several ions and their equivalent conductances at infinite dilution:

Table 14

CHRONOPOTENTIOMETRY IN AQUEOUS $AgClO_4$
WITH SUPPORTING ELECTROLYTE

Conc. of $LiClO_4$ ($M\ l^{-1}$)	$1/1 - t_+$ (t_+ = transference no. of Ag^+)	$iT^{1/2}/C$ (mA cm $sec^{1/2}$ mM^{-1})
0.000	1.925	630
0.005	1.67	550
0.010	1.52	502
0.0175	1.39	469
0.040	1.22	418
0.090	1.11	384
1.09	1.00	369

Similar studies were in other aqueous systems. The purpose was to see how good the general agreement was between theory and observation for mass transport properties in the total absence of supporting electrolyte.

A variety of aqueous solutions were prepared, as shown in table 15 below. Chronopotentiograms were run at various current densities. For the results given in table 15, the chronopotentiograms gave sufficiently well-defined and current independent values of $iT^{1/2}$ to justify comparison with theory. To make this comparison we used equation (35), p. 64, substituting for D_1, the value for D_{eff} given by equation (40), p. 66. One obtains:

$$\frac{i\,T^{1/2}}{n\,C} = \frac{(\pi R\,T)^{1/2}}{2} \cdot \left[\frac{(z_1 + z_2)t_1\Lambda}{(z_1 z_2)(1 - t_1)}\right]^{1/2} \qquad (44)$$

In this equation the first T is the transition time, the second T, on the right hand side of the equation is the temperature. The subscript 1 refers to the electroactive species. The values for $iT^{1/2}/nC$ were experimentally measured. These values were divided by the term in brackets which was calculated from the literature values for the equivalent ionic conductances at infinite dilution. This quotient should equal $(\pi R\,T)^{1/2}/2$, which, at room temperature, is 44 $\text{Joules}^{1/2}\ M^{-1/2}$. The agreement between theory and observation is remarkably good.

Table 15

CHRONOPOTENTIOMETRY IN THE ABSENCE OF SUPPORTING ELECTROLYTE

Salt	Concentration ($M\ l^{-1}$)	Reaction studied	Quotient observed (Theory = 44)
$AgClO_4$	0.0021	$Ag^+ + e^- = Ag^o$	40
$AgNO_3$	0.002	$Ag^+ + e^- = Ag^o$	43
$Pb(NO_3)_2$	0.002	$Pb^{++} + 2\,e^- = Pb^o$	45
$Cu(NO_3)_2$	0.002	$Cu^{++} + 2\,e^- = Cu^o$	43
$CuSO_4$	0.0018	$Cu^{++} + 2\,e^- = Cu^o$	47
$CuCl_2$	0.002	$Cu^{++} + 2\,e^- = Cu^o$	39
$CuCl_2$	0.002	$Ag + Cl^- = AgCl + e^-$	48
KI	0.002	$Ag + I^- = AgI + e^-$	43
HCl	0.001	$H^+ + e^- = 1/2\ H_2$	42
HCl	0.001	$Ag + Cl^- = AgCl + e^-$	42

The agreement is certainly remarkably good. We conclude that useful electrochemical measurements may be made in the absence of supporting electrolyte and that, when the experimental results do not agree with theory, this fact is significant in reflecting important mass transport properties.

Having discussed the mass transport properties in the absence of supporting electrolyte, we next consider the proper correction for the iR drop. We assume that, for an electrode system of the geometry shown in Figure 5, there exists an effective d_L, which, when multiplied by the specific resistance and the current density, will give the iR drop which must be subtracted from the measured potential. There is, to our knowledge, no theoretical justification for this assumption.

The effective d_L may be calculated as shown on p. 69. Most simply measurements should be made at t = 0, since the logarithm term then vanishes and $E_{M(t=0)} = E_O + i\rho d_L$. It is desirable that the system be reversible, otherwise equation 43 will obtain and at t = 0, $E_M = \frac{RT}{\alpha F} \ln (i/i_o) + i\rho d_L$, and one cannot separate these two terms. We again chose the $AgClO_4$ aqueous system, since it is known to be reversible, the mass transport properties are similar to those of $LiClO_4$, and the one-electron reduction is the same as one would hope to find for the lithium reduction.

Since the recorder has a time lag of about 0.5 sec. per full scale deflection, the best data were obtained by recording the potential with an oscilloscope, set at 0.02 sec. per full sweep. The voltage scales were so adjusted that the visual error in the potential reading of the photographically recorded oscillographs was less than 5%. An aqueous, 0.0021 M $AgClO_4$ solution was used. The measured specific resistance was 3770 ohm-cm. The measurements were performed using the polished silver disc electrodes (0.196 cm^2) and measuring the potential versus the silver disc reference electrode in the center of the structure shown in Figure 5. The results are shown below both for cathodization and anodization (oxidation of silver metal).

Table 16

DETERMINATION OF EFFECTIVE d_L

Current Density ($mA\ cm^{-2}$)	Initial Potential (V)	Effective d_L from $E_{M(t=0)} = i(3770)d_L$ (cm)
Cathodization:		
0.153	-0.09	0.156
0.306	-0.17	0.147
0.459	-0.26	0.150
0.765	-0.45	0.156
0.918	-0.54	0.156
		Average = 0.153 ± 0.008
Anodization:		
0.153	+0.09	0.156
0.306	+0.18	0.156
0.459	+0.27	0.156
0.613	+0.37	0.160
0.765	+0.46	0.159
		Average = 0.157 ± 0.003

The magnitude of the corrections involved is seen by the following results obtained under steady state conditions. The data were obtained in stirred solution on polished silver electrodes. Equation (42), p. 67, again was used. In this case the term $(1 - x/x_L)$ derives from equation (34), p. 64, and is $(1 - i/i_L)$. The limiting current was measured and found to be $1.15\ mA\ cm^{-2}$. As shown in table 13, p. 70, the coefficient before the logarithm term is 0.12 V. Therefore, since $E_O = 0$, we write, for equation (42):

Cathodization:

$$E_M = 0.12 \log (1 - i/1.15) - i \rho d_L$$

Anodization:

$$E_M = 0.12 \log (1 + i/1.15) + i \rho d_L$$

The results are shown in table 17 on the next page.

TABLE 17

DETERMINATION OF EFFECTIVE d_L

Current Density (mA cm^{-2})	E_M	0.12 log (1 - i/1.15)	Effective d_L
Cathodization:			
0.087	0.055	0.005	0.153
0.163	0.105	0.007	0.159
0.240	0.150	0.012	0.158
0.360	0.205	0.014	0.160
0.398	0.255	0.020	0.156
0.469	0.305	0.023	0.159
		Average =	0.157 ± 0.004 cm
Anodization:			
0.153	0.113	0.006	0.154
0.306	0.218	0.012	0.163
0.459	0.323	0.018	0.155
0.613	0.418	0.022	0.164
0.765	0.528	0.026	0.164
		Average =	0.162 ± 0.008 cm

Taking the average of all the results in Tables 16 and 17 we estimate an effective d_L of 0.157 ± 0.007 cm (5% variation). It was also noted that the results did not vary from one electrode to another as much as did the estimated error in measurement.

There remain other procedures for calibrating an electrode with respect to an effective d_L. From the chronopotentiograms obtained by the recorder one can extrapolate to t = 0 by plotting the potential versus the ln $(1 - it^{1/2}/iT^{1/2})$ to $it^{1/2} = 0$. These tended to give high results for d_L in the aqueous, 0.0021 M $AgClO_4$ system, from 0.183 cm at 0.25 mA cm^{-2} to 0.170 cm at 0.5 cm. If the silver disc electrode was anodically etched (50 mC cm^{-2}) or silver was initially deposited (50 mC cm^{-2}), the calculated d_L in both cases was than 0.163 cm.

A number of other aqueous solutions were investigated. Besides those shown in Table 15, the following were examined with respect to determining an effective d_L: 0.001 M NH_4Cl, 0.002 M K_2SO_4, 0.002 M KOH, and 0.003 M $K_2Cr_2O_7$.

In the dilute $Pb(NO_3)_2$ solution the results were in excellent agreement with those obtained on silver. Lead was first deposited on the center silver disc R.E., to give the Pb/Pb^{++} reference electrode. Cathodic voltammetry in stirred solution was performed. Using Equation 48 to correct for the mass transport properties, and using Equation 48 together with the measured limiting current for reduction of the silver ion under the same conditions of 1.15 mA cm^{-2} to calculate the effective k in Equation 48, one calculates a limiting current for the two electron reduction of Pb^{++} of 3.75 mA cm^{-2}. Current-potential measurements were made at currents up to 0.95 mA cm^{-2}. The correction for mass transport properties was made and the resultant potential-current plot was linear and extrapolated to i = E at E_M(corrected = 0, with a slope corresponding to an effective d_L of 0.157 cm. From cathodic chronopotentiograms, extrapolations were made to t = 0 and the effective d_L was 0.155 cm. Finally, the initial potential during galvanostatic cathodization was measured oscillographically and the effective d_L was 0.156 cm.

In the KI solution the results were also in agreement with the previous results. Anodic voltammetry performed on the silver electrode gave an effective d_L of 0.156 cm. Evidently the oxidation of silver to silver iodide for solutions of this concentration (0.002) proceeds without either passivation or significant electrokinetic irreversibility.

In KOH solutions an effective d_L of 0.161 cm was obtained when the silver electrode, after first being anodized potentiostatically to Ag_2O, was then cathodized galvanostatically with the initial potential measured oscillographically.

In K_2SO_4 solution an effective d_L of 0.161 cm was also obtained when the platinum electrode was anodized potentiostatically for several minutes at +1.2 V vs. the silver disc reference electrode, to form the platinum oxide film, and then cathodized galvanostatically with the initial potential measured oscillographically.

Finally, in a 0.002 M $AgNO_3$ solution, a value of 0.159 cm was obtained for galvanostatic cathodization with the initial potential recorded oscillographically.

In the other solutions, the Cu^{++}, HCl, NH_4Cl, and $K_2Cr_2O_7$ solutions the results were not satisfactory. Apparent values for d_L of from 0.144 to 0.166 cam could be obtained under certain conditions but a reanalysis of the data indicates that the processes were too irreversible to allow the use of Equation 42, or satisfactory corrections for the mass transport properties could not be made since the data were incomplete.

At this point it is useful to digress a bit and point out that when one hopes to use an electrochemical system for calibration purposes of any kind, be it calculation of an effective d_L or an effective surface area, great caution must be experted. Very few systems, in fact, are sufficiently well-behaved or sufficiently independent of a variety of surface effects to allow complete reliance on the data. Other systems which could be used are those employing complex iron redox couples (simple iron salts are too subject to hydrolysis), cadmium systems (it is difficult to define a limiting current for the reduction of cadmium on solid electrodes because of its activity), and mercury couples (the problem of amalgamation of the solid electrode presents complications which are experimentally inconvenient).

II.C-3-b. Cathodic Behavior in Nonaqueous Solutions of Lithium Salts.

II-C-3-b-(1). Voltammetry

We now consider the data obtained in non-aqueous systems. We first consider the results of voltammetric experiments in dilute $LiClO_4$ solutions. In table 18 below are shown the results obtained in PC/0.01 M $LiClO_4$. The measurements were performed in stirred solution on platinum disc working electrodes as shown in figure 5. The potential was measured against that of a silver disc in the same solution. The potential of the disc was measured versus the open circuit potential of an electrodeposited lithium electrode in the same solution both before and after the runs and was +3.10 V. The specific resistance of the solution was 4340-ohm-cm. From the data given earlier following table 7, we calculate a limiting current for the 0.01 M solution to be about 1.44 mA cm^{-2} -- one-fifth of that for the 0.05 M solution. We use equation (42), p. 67, to calculate the expected E_M if the reduction were a simple, reversible one-electron reduction. Using , for the logarithm expression, $(1 - i/1.44)$, and for the effective d_L, 0.156 cm, we write, from equation (42)

$$E_M \text{ (calculated)} = -3.10 + 0.118 \log \left(1 - \frac{i}{1.44}\right) - i\,(4340)\,(0.156)$$

In table 18 we show the measured current and potential, and the calculated potential.

Table 18

VOLTAMMETRY IN PC/0.01 M $LiClO_4$

E_M	i	E (calculated)				
		$0.118 \log (1 - i/1.44)$	$- i\,(680)$	-3.10	=	E (calculated)
(V)	(mA cm^{-2})	(V)	(V)	(V)		(V)
-2.50	0.05*	-0.002	-0.034	-3.10	=	*
-2.70	0.05*	-0.002	-0.034	-3.10	=	*
-2.90	0.05*	-0.002	-0.034	-3.10	=	*
-3.10	0.085	-0.004	-0.058	-3.10	=	-3.16
-3.30	0.165	-0.006	-0.112	-3.10	=	-3.22
-3.50	0.28	-0.011	-0.190	-3.10	=	-3.30
-3.70	0.40	-0.017	-0.272	-3.10	=	=3.34
-4.00	0.60	-0.026	-0.408	-3.10	=	-3.53
-4.40	0.89	-0.049	-0.544	-3.10	=	-3.69
-4.60	1.03	-0.064	-0.700	-3.10	=	-3.86
-4.80	1.17	-0.086	-0.795	-3.10	=	-3.98

*(See subsequent discussion)

The measured potential, appearing in the first column of table 18 is considerably more negative than the calculated potential, appearing in the last column of table 18. This latter potential was calculated assuming the process to be a reversible, one-electron reduction. The disagreement would normally constitute proof that the process is not a reversible, one-electron reduction.

It can be seen that the correction for iR drop, appearing in the fourth column, is quite large. Nevertheless, an error of even 10% in the iR correction would not effect a marked change in the calculated potential. It is useful at this point to discuss the procedures for correcting for iR drop. The well-known methods have been discussed by Barnartt(24) and many others. The basic methods are: interruption techniques, measurement of d_L and various distances and extrapolation of the measured potential versus d_L to the potential at $d_L = 0$, and the direct method used in our work.

Each of these methods has advantages and disadvantages in accuracy and experimental convenience. One point should be emphasized which is general to all methods. It is generally accepted that the distance of the tip of the Luggin capillary from the electrode surface must be at least three to four times the radius of the capillary to prevent shielding of the electrode surface by the capillary. The iR correction calculated in table 18 is based on an effective distance of 0.156 cm. It can be seen that reducing this distance to 0.05 cm, requires the use of a capillary tip with a radius of not more than about 0.02 cm. Even then, the iR correction will be quite large. The problem then becomes one of the accuracy with which the correction can be made. We doubt that any of the three methods described above has any particular advantages over any other in the relative accuracy of measurement.

It might also be noted that, in the absence of supporting electrolyte, measurements made at currents which are some fraction, f, of the limiting current will include the same iR drop, regardless of the concentration of electrolyte. Thus, if the limiting current = kC, and the iR correction $=(i/C\Lambda)d_L$, the iR drop at $i = f\, i_L$, is: $iR = f\, k\, d_L/\Lambda$; and is independent of the specific resistance.

(24) S. Barnartt, J. Electrochem. Soc., 99, 549-553 (1952)

The three initial data given in table 18 were not steady state values. The currents slowly diminished with time, nor do they change when the solution is agitated or unstirred. In general we find this to be the case for currents less than about 0.1 mA cm^{-2}; this then gives a lower limit to the current range which can be studied.

Since, at higher currents than 0.1 mA cm^{-2} one is approaching the limiting current in the example shown in table 18, it is necessary to work with more concentrated solutions. Voltammetric measurements were made in such solutions. The experiments were modified in two ways. First, an amount of lithium was initially deposited on the center silver disc R.E. and this then served as the reference electrode. The open circuit potential of this electrodeposited lithium R.E. remained constant over the period of time, several minutes, required for a given run. Secondly, following the measurement of the steady state current at a given potentiostat setting, the amount of lithium which had been deposited was determined by anodization. Anodization was performed potentiostatically. This potentiostatic anodization will be discussed in more detail in conjunction with the presentation of the current-potential data.

In these measurements the potentiostat was set at a pre-set value and the resultant current recorded. In some cases, steady state currents were not attained. It may be of interest to see just how this current variation looked, and we report the current after various periods of time following the initiation of electrolysis. Since the current varies, the effective potential also varies and must be corrected for. Finally, the anodic recoveries of lithium were performed at the indicated potential versus the electrodeposited lithium electrode and the current-time plots integrated to give the coulombs of lithium recovered.

The results are shown in tables 19, 20 and 21.

TABLE 19

VOLTAMMETRY IN PC/0.1 M Li ClO$_4$

tentiostat etting (V vs. Li^{O})		Measured Current at Indicated Time (Min.) after Commencement of Cathodization (mA cm^{-2}) Corrected Potential for Solution iR Drop (In parentheses) (V vs. Li^{O})					Total Amount of Cathodization (mC cm^{-2})	Anodic Utilization
	min. =	0	0.5	1	2	3		
-0.30	i=	3.0	--------	--------	--------	3.0	540	76%
	V=	(-0.05)	--------	--------	--------	(-0.05)		
-0.60	i=	6.5	--------	--------	--------	6.5	1170	61%
	V=	(-0.07)	--------	--------	--------	(-0.07)		
-1.00	i=	11.0	--------	--------	--------	11.0	1980	57%
	V=	(-0.10	--------	--------	--------	(-0.10)		
-1.30	i=	15.5	--------	--------	--------	15.5	3050	32%
	V=	(-0.08)	--------	--------	--------	(-0.08)		
-1.80	i=	20.5	--------	--------	--------	20.5	3700	37%
	V=	(-0.12)	--------	--------	--------	(-0.12)		
-2.00	i=	20.0	18.5	18.5	18.0	18.0		
	V=	(-0.36)	(-0.48)	(-0.48)	(-0.52)	(-0.52)		
..40	i=	26.0	25.5	25.0	--------	25.0	4500	19%
	V=	(-0.67)	(-0.71)	(-0.75)	--------	(-0.75		
-3.0	i=	30.0	25.0	--------	25.0	24.5	4500	5%
	V=	(-0.54)	(-0.95)	--------	(-0.95)	(-0.99)		
-4.0	i=	30.0	27.0	25.5	23.5	20.5	4500	1%
	V=	(-1.54)	(-1.79)	(-1.91)	(-2.08)	(-2.32)		
-5.0	i=	25.0	19.0	17.5	15.0	12.5	2900	1%
	V=	(-2.95)	(-3.44)	(-3.57)	(3.62)	(-3.97		

TABLE 20

VOLTAMMETRY IN PC/ 0.2 M $LiClO_4$

Potentiostat Setting (V vs. Li^{o})		Measured Current at Indicated Time (Min.) after Commencement of Cathodization (mA cm^{-2}) Corrected Potential for Solution iR Drop (In parentheses) (V vs. Li^{o})					Total Amount of Cathodization (mC cm^{-2})	Anodic Utilization
	min. =	0	0.5	1	2	3		
-0.30	i =	6.0	5.5	5.0	4.0	4.0	810	66%
	V =	(-0.03)	(-0.06)	(-0.08)	(-0.12)	(-0.12)		
-0.60	i =	13.0	12.0	11.5	10.5	10.0	1860	54%
	V =	(-0.02)	(-0.07)	(-0.09)	(-0.13)	(-0.16)		
-0.90	i =	17.5	---	---	---	17.5	2930	71%
	V =	(-0.12)	---	---	---	(-0.12)		
-1.20	i =	23.5	21.0	20.5	19.5	19.5	3350	44%
	V =	(-0.16)	(-0.27)	(-0.29)	(-0.33)	(-0.33)		
-1.50	i =	30.0	28.5	---	---	28.5	4750	43%
	V =	(-0.17)	(-0.23)	---	---	(-0.23)		
-1.80	i =	35.0	34.5	---	---	34.5	5850	38%
	V=	(-0.25)	(-0.27)	---	---	(-0.27)		
-2.00	i =	41.0	39.5	39.0	38.0	38.0	6380	39%
	V=	(-0.18)	(-0.25)	(-0.27)	(-0. 32)	(-0.32)		
-3.00	i =	51.0	49.5	47.5	46.5	45.5	7350	33%
	V=	(-0.74)	(-0.80)	(-0.89)	(-0.93)	(-0.98)		
-4.00	i =	49.5	48.5	48.0	46.5	45.5	8100	16%
	V =	(-1.80)	(-1.85)	(-1.87)	(-1.93)	(-1.98)		
-5.00	i =	49.0	47.5	47.0	---	47.0	7300	2%
	V =	(-2.82)	(-2.89)	(-2.91)	---	(-2.91)		

TABLE 21

VOLTAMMETRY IN PC/0.3 M LiClO$_4$

Potentiostat Setting (V vs. Li^{o})		Measured Current at Indicated Time (Min.) after Commencement of Cathodization ($mA\ cm^{-2}$) Corrected Potential for Solution iR drop (in Parentheses)					Total Amount of Cathodization ($mC\ cm^{-2}$)	Anodic Utilization
	min.=	0	0.5	1	2	3		
-0.02	i=	0.055	0.115	0.145	0.160	0.165	42	83%
	V=	(-0.18)	(-0.015)	(-0.014)	(-0.013)	(-0.013)		
-0.04	i=	0.290	0.225	0.245	---------	0.245	60	86%
	V=	(-.028)	(-0.030)	--------	--------	(-0.030)		
-0.06	i=	0.475	0.380	0.340	0.300	0.275	125	72%
	V=	(-0.039)	(-0.044)	(-0.046)	(-0.047)	(-0.048)		
-0.08	i=	0.640	0.465	0.410	0.355	0.320	75	66%
	V=	(-0.053)	(-0.060)	(-0.063)	(-0.065)	(-0.067)		
-0.15	i=	1.85	1.65	1.45	1.10	1.00		
	V=	(-0.072)	(-0.081)	(-0.089)	(-0.104)	(-0.108)		
-0.20	i =	3.25	--------	--------	--------	3.25	585	56%
	V=	(-0.06)	--------	--------	--------	(-0.06)		
-0.25	i=	3.45	3.80	3.90	3.85	3.70	675	69%
	V=	(-0.11)	(-0.09)	--------	--------	(-0.09)		
-0.30	i=	5.00	5.50	5.60	5.35	5.15	1000	70%
	V=	(-0.09)	(-0.07)	(-0.06)	(-0.08)	(-0.09)		
-0.60	i=	11.2	--------	--------	--------	11.2	4220	71%
	V=	(-0.11	--------	--------	--------	(-0.11)		

The data in tables 19-21 are not particularly enlightening except insofar as they indicate the nature of the problems to be encountered in making voltammetric measurements for lithium deposition on solid electrodes. First of all, non-steady state conditions are apparent even though the amount of deposit is many atomic layers thick. In the absence of supporting electrolyte this results in a change in both potential and current, which makes the measurements difficult to interpret. Secondly, the data are not concordant with those shown in table 5 for cathodizations performed at constant current. In particular, apparent limiting currents are obtained which are about double those found for the 0.1 and 0.2 M solutions discussed in table 5.

II-C-3-b-(2) Polarography.

The polarographic behavior was also examined in nonaqueous lithium salt solutions. In figure 10 is shown a polarogram obtained in 0.01 M $LiClO_4$ in propylene carbonate. This is the same concentration for which the data shown in table 18, p. 77, were obtained. The potential was measured with respect to a strip of lithium metal in the same solution. A silver wire served as the counter electrode. The apparent half-wave potential is +0.9 V vs. the Li/Li^+(0.01 M) reference electrode. The expected half-wave potential versus this reference electrode should be about +0.98 V, since this is equal to the free energy of formation for the reaction Li + Hg = Li(Hg); for a 0.005 M amalgam(25) this is -22.84 kcal M^{-1}, or +0.98 V. We assume the difference of less than 0.1 V is due to the iR drop encompassed in the measurement. We have made no attempt to make iR drop corrections for the polarographic measurements. It should be noted that a simple correction for iR drop cannot be made with this three electrode system in the usual fashion by simply measuring the resistance between the working and counter electrodes, using this counter electrode as the reference electrode also, and calculating the iR drop by multiplying the measured current by the measured resistance.

(25) O. Kubaschewski and J. A. Catterall, Thermochemical Data of Alloys, Pergamon Press, London, 1956, p. 14.

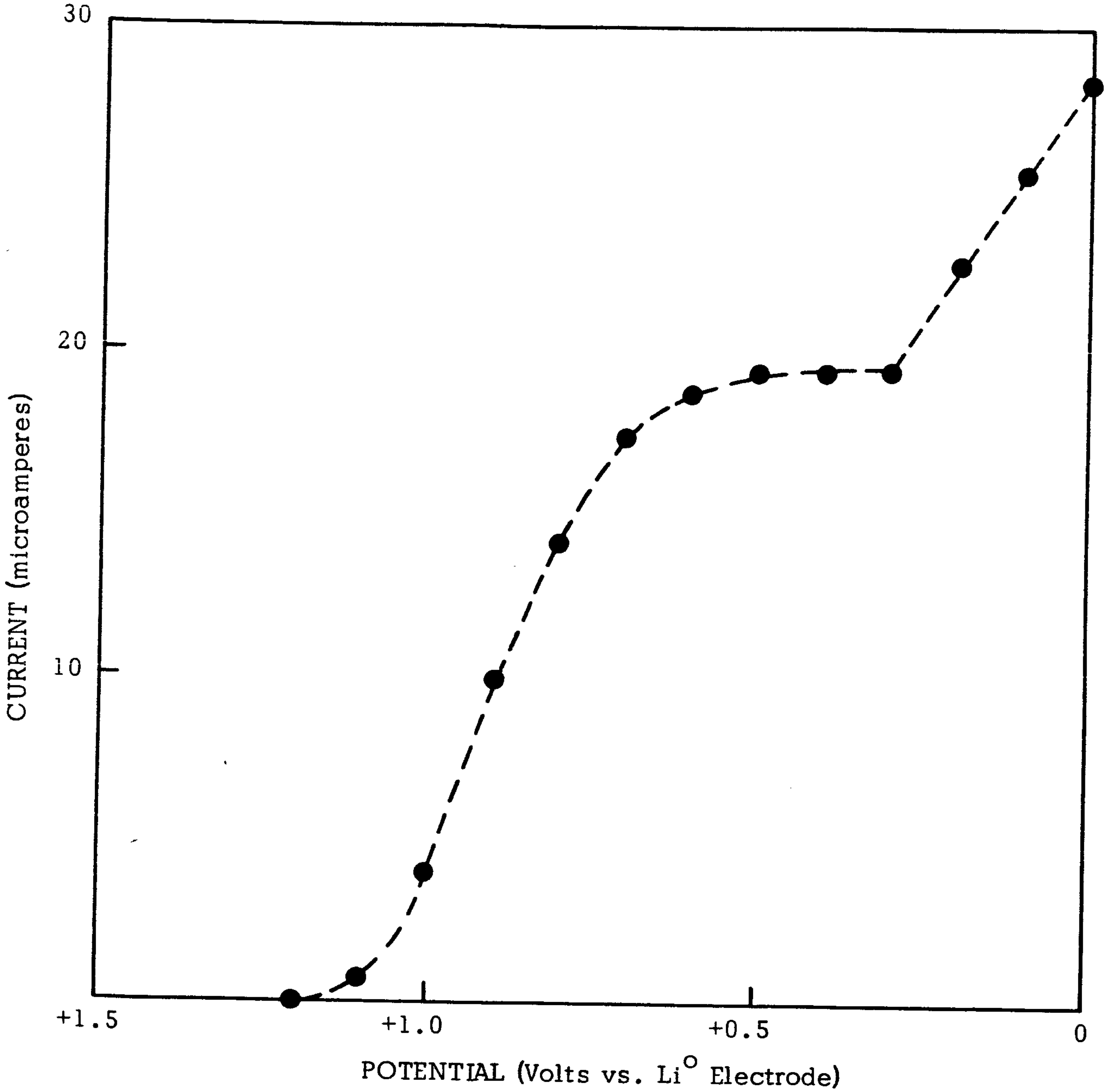


Figure 10: DROPPING ELECTRODE POLAROGRAPHY OF LITHIUM ION

Obtained in propylene carbonate, 0.01 M in $LiClO_4$. Drop characteristics were: m = 0.683 mg sec^{-1}; t = 5.25 sec. The currents in the figure were those recorded at the end of the drop.

Quite well-defined limiting currents were observed. The effective diffusion coefficient was calculated from equation (32), p. 64. This is the equation for the current at the end of the drop, with a drop time of t sec. We did not use the normal equation for average current, since the recorder was not highly damped. The head of mercury was varied and the following data were obtained:

Mercury head = 67 cm	Mercury head = 35 cm
$m = 0.683$ mg sec^{-1}	$m = 0.347$ mg sec^{-1}
$t = 5.25$ sec	$t = 10.96$ sec
$i = 19.4$ microamps	$i = 14.0$ microamps
$D_{eff} = 7.23 \times 10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$	$D_{eff} = 7.25 \times 10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$

We have also calculated the D_{eff} from equation (37), p. 66. The measured equivalent conductance in this 0.01 M solution was 23.0 $\text{ohm}^{-1}\ \text{cm}^2\ \text{M}^{-1}$. To do this one must assume a value for the transference number. The following are calculated:

for $t_+ = 0.5$ $D_{eff} = 12 \times 10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$
for $t_+ = 0.4$ $D_{eff} = 8 \times 10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$
for $t_+ = 0.3$ $D_{eff} = 5 \times 10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$

(Note: the transference number of Li^+ in aqueous $LiClO_4$ is 0.37)

One must also consider the fact that the lithium salt may not be completely dissociated. Harris(26) reports from conductivity data in propylene carbonate that NaBr, NaI, $NaBF_4$, KCl, KBr, KI, and KBF_4 are highly ionized in propylene carbonate. On this basis we assume that the 0.01 M $LiClO_4$ solution is also probably completely dissociated, and that the polarographically determined D_{eff} agrees with theory, it being assumed that the transference number of the lithium ion is about 0.4. It may be noted that conductance theory in non-aqueous solution suffers from the lack of data on transference numbers. Perhaps such mass transport measurements in the absence of supporting electrolyte may be useful in such determination.

(26) W. S. Harris, Electrochemical Studies in Cyclic Esters, AEC Report, UCRL 8381, 1958, p. 50.

The polarogram shown in figure 10 is also of interest in showing that evident electrolyte decomposition occurs at potentials significantly positive to that of the lithium electrode. Thus, if lithium did not form an amalgam with mercury, one would not expect to obtain a polarogram for lithium reduction, since the lithium wave would be preceded by extensive electrolyte decomposition.

The polarograms present a question of great concern: Does electrolyte decomposition occur at potentials positive to that of the lithium electrode on solid electrode substrates? It would be most surprising if, based on the polarographic evidence, this did not occur. This is because the reduction of organic materials normally proceeds with a larger "overpotential" on mercury than on metals such as silver or platinum. If any reduction is observed on mercury at potentials positive to that of lithium, one would expect even more extensive reduction to occur on the solid metal electrodes.

Polarograms allow better mass transport analysis than is possible on the solid electrodes in stirred solution. They do not tell us much about the processes expected on solid electrodes, and it is desirable to undertake such measurements on solid electrodes under conditions in which the mass transport properties are more rigorously defined. In the next section we shall review three of these techniques.

II-C-3-b-(3) Mass transport Measurements on Solid Electrodes.

We consider those three techniques which currently receive widest use for studies on solid electrodes: linear sweep voltammetry, rotating electrode voltammetry, and chronopotentiometry. In each case a quantity is measured with is related to the mass transport properties -- i_L or $iT^{1/2}$ or i_p (the peak current). In each case a parameter can be varied which will give different values for the mass transport related quantity. And, finally, in each case the measured potential at the point where the mass transport related quantity is measured will include a substantial iR drop in the absence of supporting electrolyte. A few calculations are shown on the next page which may be of use in considering the relative merits of these techniques.

In these calculations we will consider the reduction of lithium from the 0.01 M $LiClO_4$ solutions, the polarography of which was previously described. We shall, in each case use the polarographically measured effective diffusion coefficient of 7.25×10^{-6} cm^2 sec^{-1}. The measured specific resistance of the solution was 4340 ohm-cm and we shall calculate the iR drop from this value, the current, and an assumed distance between the tip of the Luggin capillary probe and the electrode surface of 0.1 cm. For the calculations we use the equations from Delahay's monograph, reference 2, p. 25.

Linear Sweep Voltammetry (equation 6-24, p. 124, Ref. 22)

$$i_p = (3.67 \times 10^5) n^{3/2} A\, C\, D^{1/2} v^{1/2}$$

or, for n = 1, $A = 1\ cm^2$, $C = 0.01\ M$, $D = 7.25 \times 10^{-6} cm^2 sec^{-1}$

$$i_p\ (mA\ cm^{-2}) = (9.9)\ (v\ V\ sec^{-1})^{1/2}$$

for rotating electrode voltammetry (equation 9-30, p. 230, Ref. 22)

$$i_L = n\ F\ A\ C\ D^{2/3} \quad \omega^{1/2}/1.62\ \nu^{1/2}$$

or, for n = 1, $A = 1\ cm^2$, $C = 0.01\ M$, $D = 7.25 \times 10^{-6} cm^2\ sec^{-1}$

ω (angular velocity) $= 2\pi N$(N = rotations per second) and
ν (kinematic viscosity) $= 10^{-2} cm^2\ sec^{-1}$

$$i_L (mA\ cm^{-2}) = 1.91\ (N\ \text{rotations per sec.})^{1/2}$$

for chronopotentiometry (equation 8-12, p. 184, Ref. 22)

$$T^{1/2} = \pi^{1/2} nAF\ C\ D^{1/2}/2\ i$$

or, for n = 1, $A = 1\ cm^2$, $C = 0.01\ M$, $D = 7.25 \times 10^{-6} cm^2 sec^{-1}$

$$T(sec) = 5.55/(i\ mA\ cm^{-2})^2$$

We calculate for each technique the following:

Technique	Varied parameter	Quantity of interest	Calculated iR drop
Linear Sweep Voltammetry	$v = 0.05\ V\ sec^{-1}$	$i_p = 2.21\ mA\ cm^{-2}$	0.96 V
"	$v = 0.001\ V\ sec^{-1}$	$i_p = 0.28\ mA\ cm^{-2}$	0.12 V
Rotating disc Voltammetry	N = 20	$i_L = 8.5\ mA\ cm^{-2}$	3.7 V
	N = 1	$i_L = 1.91\ mA\ cm^{-2}$	0.40 V
Chrono-potentiometry	$i = 5.55\ mA\ cm^{-2}$	T = 1 sec.	2.41 V
	$i = 0.53\ mA\ cm^{-2}$	T = 20 sec.	0.23 V

We immediately discard linear sweep voltammetry, since the mass transport properties are not, in fact those given by theory when a significant fraction of the potential is iR drop. This point is well discussed by Delahay (Ref. 2, p. 132). In the absence of supporting electrolyte or in poorly conducting solutions it is doubtful that any useful information can ever be achieved with this technique. Most measurements will, if interpreted in conventional fashion, indicate that a process is "irreversible"; such a conclusion would be quite specious.

Again, we chose not to use rotating disc voltammetry because our previously described measurements on flat electrodes in stirred solution indicated serious problems at low current densities. These problems would exist on rotating electrodes as well. It may be of interest to note that the limiting currents calculated above for the rotating disc at 1 revolution are comparable with those obtained in stirred solution (e.g. 3.60 mA cm^{-2} for a 0.02 M $AgClO_4$ solution see Table 7), suggesting that laminar flow prevails under the geometry in which our measurements are made in stirred solution. Secondly, the necessity of performing each run on a fresh electrode surface would have been experimentally inconvenient at this time. We do believe work with rotating disc electrodes will be of future interest, however.

Thus, chronopotentiometric measurements were resorted to. In the subsequent discussion we shall discuss the results of such work, and indicate the major problems encountered. Such information will be of use to other workers in considering other techniques of measurement.

II-C-3-b-(4) Chronopotentiometry

The chronopotentiometric results observed in lithium salt solutions are considered to be real by virtue of the fact that excellent reproducibility and consistency have been observed throughout the course of almost two and a half years. We shall focus attention on $LiClO_4$ and $LiBF_4$ solutions. Any differences observed between these solutions are no greater than the differences observed over the course of time for the particular salt.

The following procedure is used. The cells in which the experiments shall be performed are oven dried. Immediately upon removal they are stoppered and cooled under a stream of argon. After 15-20 min. the requisite amount of salt was added to the cell, and then an appropriate volume of solvent. The cell was marked so that the solvent could be poured directly from the storage vessel into the cell. Needless to say, all operations were performed as rapidly as possible to avoid undue contact with the atmosphere.

The electrodes again were the disc structures shown in Figure 5. Potentials were normally measured with respect to the center disc silver R.E. Potentials could also be measured with respect to a lithium electrode, by electrodepositing lithium on the center disc. When this was done, appropriate care was taken to be sure that the potential of the lithium electrode did, in fact, remain constant over the course of time required for the subsequent measurements. Typically, 2500-5000 m C cm^{-2} would be deposited at currents of from 5 to 10 mA cm^{-2} in stirred solution. Before immersion in the cell the electrode was polished on a wheel with 1 micron alumina. The electrodes were then thoroughly rinsed with water, wiped with ordinary tissue, rinsed again with acetone, placed under a stream of warm air, and wiped again before immersion in the cell. While the discs were mirror bright after this treatment, it is obvious that the actual surface roughness is probably quite large.

We consider the following variations in chronopotentiometric measurements.

a. variation with time of contact with electrolyte.
b. variation with current
c. variation with concentration
d. variation with anion
e. variation with electrode substrate
f. variation with impurities

a. Variation with time of contact with electrolyte.

A variation in the appearance of a chronopotentiogram is often observed as a function of the time the electrode has been allowed to sit in the solution before doing the run. There are a number of reasons for this; two of the most common are the adsorption of material from solution at a rate commensurate with the concentration, rate of mass transport, and kinetics of adsorption of the material, and, secondly, the chemical reaction of the electrode substrate with the electrolyte or impurities. We have not found such an effect on platinum electrodes in most electrolytes at least for periods of up to about three hours.

b. Variation with current.

It is normal to find a significant variation with current density, since few processes are so simple that mass transport is the only determining factor. We again consider the basic chronopotentiometric equation for a solution of a given concentration: $iT^{1/2} = K$. It is fairly common practice to investigate this by plotting iT vs. $1/i$. Ideally, the plot should extrapolate to $iT = 0$ at $i \dashrightarrow \infty$, $1/i = 0$. In practice, one often finds that a linear plot is obtained, but extrapolation to $1/i =$ yields a value for iT of the order of 0.1 to 1 mC cm^{-2}, which is commensurate with the magnitude expected for specific surface effects. At sufficiently low currents, for which one would predict transition times of 40 or more seconds, one also finds a positive deviation of the plot. This is because, for such long transition times, convective effects set in, which disturb the mass transport process and increase the transition time. In general, one should not expect a constancy of $iT^{1/2}$ for currents such that iT is less than about 1 mC cm^{-2}, or for currents such that the expected transition time is more than about 40 sec.

The effect of varying the current is seen from the chronopotentiograms shown in Figure 11. These are, in each case, an actual size trace of the curves.

Ideally, the shape of a chronopotentiogram should tell one something about the process. We refer to Equations 42 and 43 for reversible and totally irreversible processes. From these equations we may calculate what the chronopotentiograms should look like, assuming certain values for the various parameters, and show in what respect the actual chronopotentiogram shown in Figure 11-b is different. We use $E_o = 0$, since the potential is measured versus a lithium electrode in the same solution, $z_1 = 1$, $z_2 = 1$, $iT^{1/2} = 21.5$ mA cm^{-2} $sec^{1/2}$, $\rho = 510$ ohm-cm, $d_L = 0.157$ cm, and assume $\alpha = 0.5$. We then write, for a reversible process at i = 6.5 mA cm^{-2}

$$E_M = 0.12 \log (1 - it^{1/2}/21.5) + 0.53$$

and for a totally irreversible process at i = 6.5 mA cm^{-2}

$$E_M = 0.18 \log (1 - it^{1/2}/21.5) + 0.53 + 0.12 \log i_o/6.5$$

The actual plot of log $(1 - it^{1/2}/21.5)$ vs. E_M gives a slope for $\Delta E_M / \Delta \log (1 - it^{1/2}/21.5)$ of 0.483 V, considerably larger than either of the slopes predicted above. Assuming the process were totally irreversible, we would then calculate an apparent transfer coefficient, α, of only 0.14. The extrapolated potential at t = 0 is -0.71 V. If the process were totally irreversible, one would calculate from the term $0.12 \log i_o/6.5 = -0.71 + 0.53$ (iR drop), that $\log i_o = 0.21$ mA cm^{-2}. Alternatively, from the discussion immediately preceding Equation 29, one calculates a heterogeneous rate constant for an expression of the form $i_o = F k (Li^+)$ of $k = 2.2 \times 10^{-5}$ cm sec^{-1}. Again, we re-emphasize the point that this data is meant merely to give a preliminary statement about the magnitude of the apparent kinetic parameters, since this will be of value to other workers in considering more definite kinetic studies.

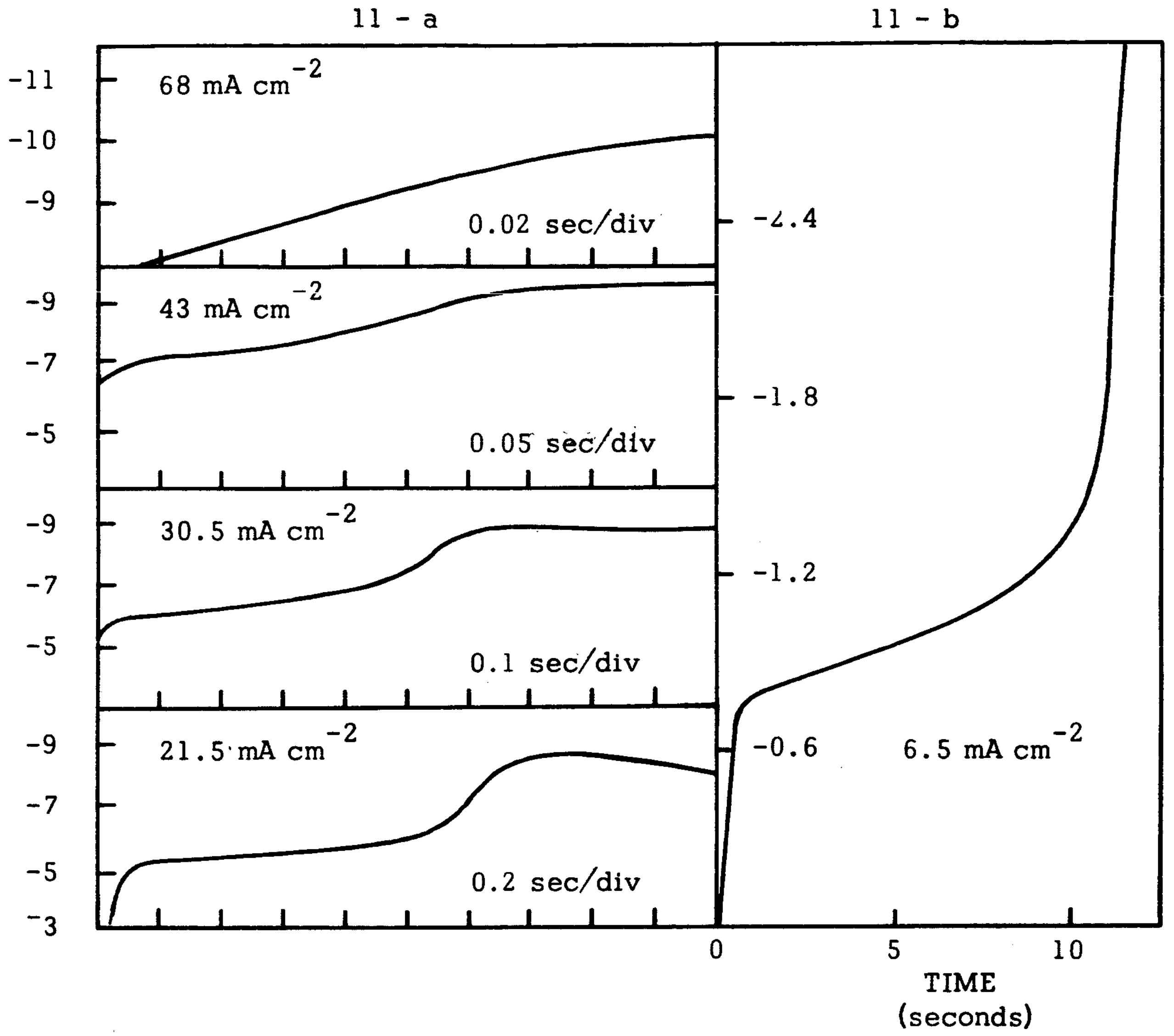


Figure 11: CHRONOPOTENTIOMETRY OF LITHIUM ION

On platinum electrode in PC/0.1 M $LiClO_4$, no supporting electrolyte

At higher currents, as shown in the four chronopotentiograms in Figure 11-a, the curves become increasingly ill-defined with increasing current. If plots are made of the log ($1 - it^{1/2}/i\tau^{1/2}$) term versus the potential, one will observe that the slope, given by the coefficient preceding the log term, becomes larger with increasing current. This is conveniently summarized by stating that the apparent transfer coefficient, α , is a function of the current, decreasing with increasing current. Actually, as will be later discussed, we believe this reflects the concurrent growth of a resistive film along with lithium deposition, and one is, in reality, measuring an increasing iR drop through this film.

It will be noted that the variation in $i\tau^{1/2}$ with current is not serious. How serious such an effect can be will be seen later in discussing the behavior in dimethylsulfoxide.

At lower currents, one cannot obtain transition times because of convective effects. However, at lower currents the appearance of the initial knee of the chronopotentiograms is magnified. This is shown in Figure 12. These curves have been corrected for iR drop. A plot of E vs. log ($1 - it^{1/2}/i\tau^{1/2}$) using the value of 18.7 mA $cm^{-2}sec^{1/2}$ for the chronopotentiogram obtained at 5 mA cm^{-2} gives a value for the coefficient of the log term of 0.65, or an apparent transfer coefficient of 0.1. The extrapolated potential (vs. an Ag disc R.E.) is -3.31 V which, considering that the open circuit potential of a lithium electrode versus this electrode is -3.1 ± 0.1 V gives values of the exchange current of 0.016 to 5 mA cm^{-2}. The uncertainty arises from the use of the silver disc R.E. rather than a lithium reference electrode. The major differences between chronopotentiograms performed on different electrodes lies in the appearance of this knee at lower currents, as will be discussed in a later section on the variations with electrode substrate.

c. Variation with concentration.

Conclusions regarding the degree to which the transition time does reflect concentration polarization cannot be established without measurements

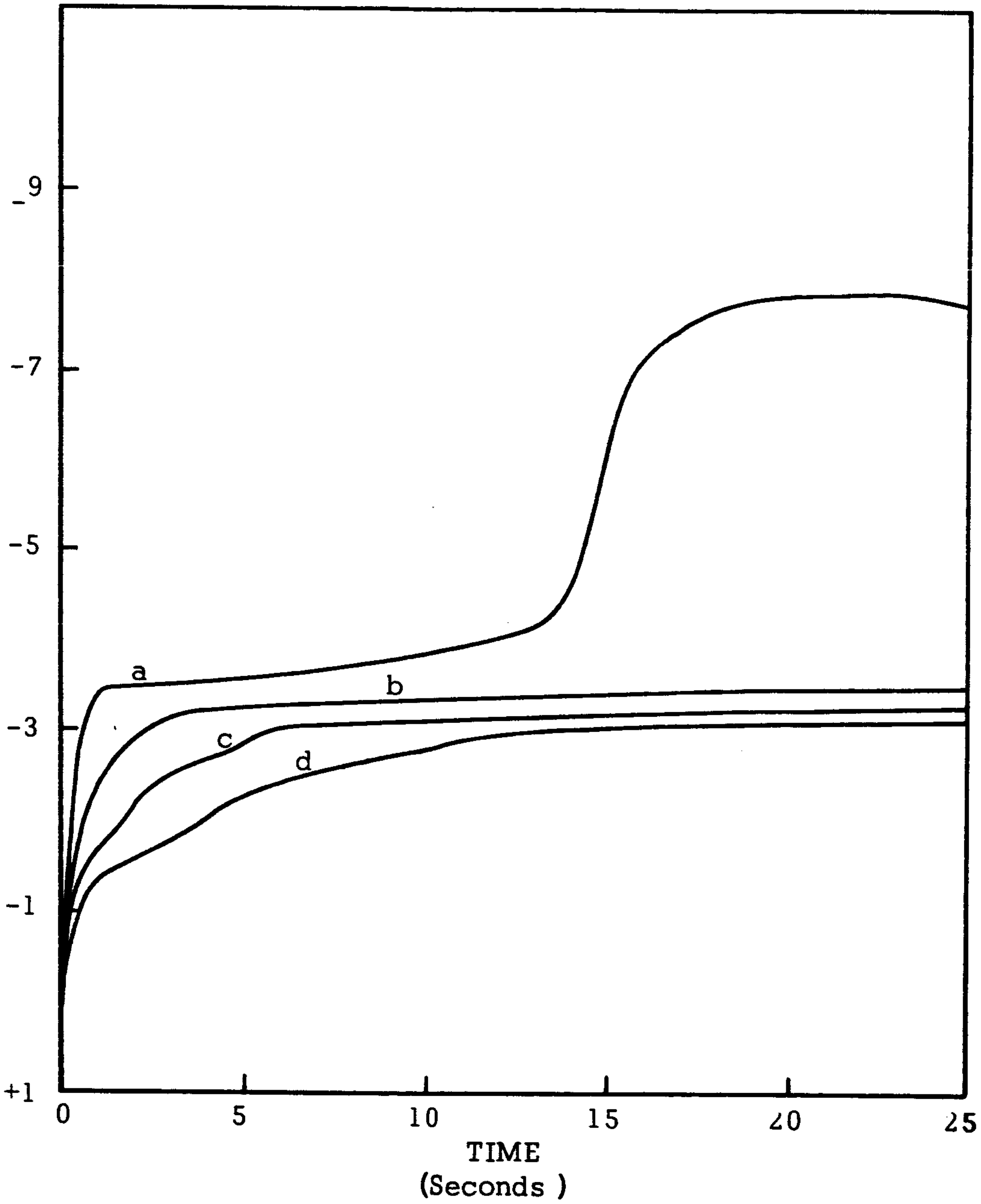


Figure 12: CHRONOPOTENTIOMETRY OF LITHIUM ION

On platinum electrode in PC/0.1 M $LiClO_4$, no supporting electrolyte. Potentials corrected for iR drop. Potentials measured vs. silver disc R.E. against which the open circuit potential of the lithium electrode was -3.1 ± 0.1 V. Currents as indicated:

a - 5 mA cm^{-2}; b - 2 mA cm^{-2}; c - 1 mA cm^{-2}; d - 0.5 mA cm^{-2}

in solutions with different concentrations of reducible material.

Measurements have been made in propylene carbonate solutions at concentrations of $LiClO_4$ from 0.01 M to 1.0 M. In the range of concentration 0.05 to 0.3 M the results are essentially identical to those shown in Figure 11 and are thus:

$i\,T^{1/2}$ (mA $cm^{-2}sec^{1/2}$) = (200 ± 15) x (Concentration in M l^{-1})
Effective transfer coefficient = 0.1 - 0.2
Effective heterogeneous rate constant = 10^{-4} - 10^{-5} cm sec^{-1}.

Very few chronopotentiometric measurements have been made at higher concentrations. In only one case could a reasonably well - defined transition time be observed. This was in propylene carbonate, 1 M in $LiBF_4$ where, at i = 50 mA cm^{-2}, a transition time of 12.5 sec. was observed, giving a value for $iT^{1/2}$ of 177 mA cm^{-2} $sec^{1/2}$. The inability to obtain satisfactory chronopotentiograms for higher concentrations is the result of the fact that a large density gradient develops and pronounced convection is expected. In general, it is probably wise to work with solute concentrations of about 0.1 M.

At lower concentrations, the chronopotentiograms become less well-defined because, at the low currents necessary to obtain a transition time, the knee referred to above becomes relatively more pronounced. This is shown in Figures 13 and 14. It is noteworthy that transition times giving values for $iT^{1/2}$ (mA cm^{-2} $sec^{1/2}$) = 200(concentration in moles per liter) are still obtained, just as with the more concentrated solutions.

From the value for the transition time we calculate an apparent diffusion coefficient and compare this with that obtained polarographically in the 0.01 M $LiClO_4$ solution. From Equation 35 we calculate, for $iT^{1/2}/C$ = 200 mA cm $sec^{1/2}$ nM^{-1}, we find, $D_{eff} = 5.5 \times 10^{-6}$ $cm^2 sec^{-1}$.

Using the polarographically determined value, we would have calculated $iT^{1/2}/C$ = 230 mA cm $sec^{1/2}$ nM^{-1}. While the agreement is not as good as would be desired, it is sufficiently good to say that the reductions observed

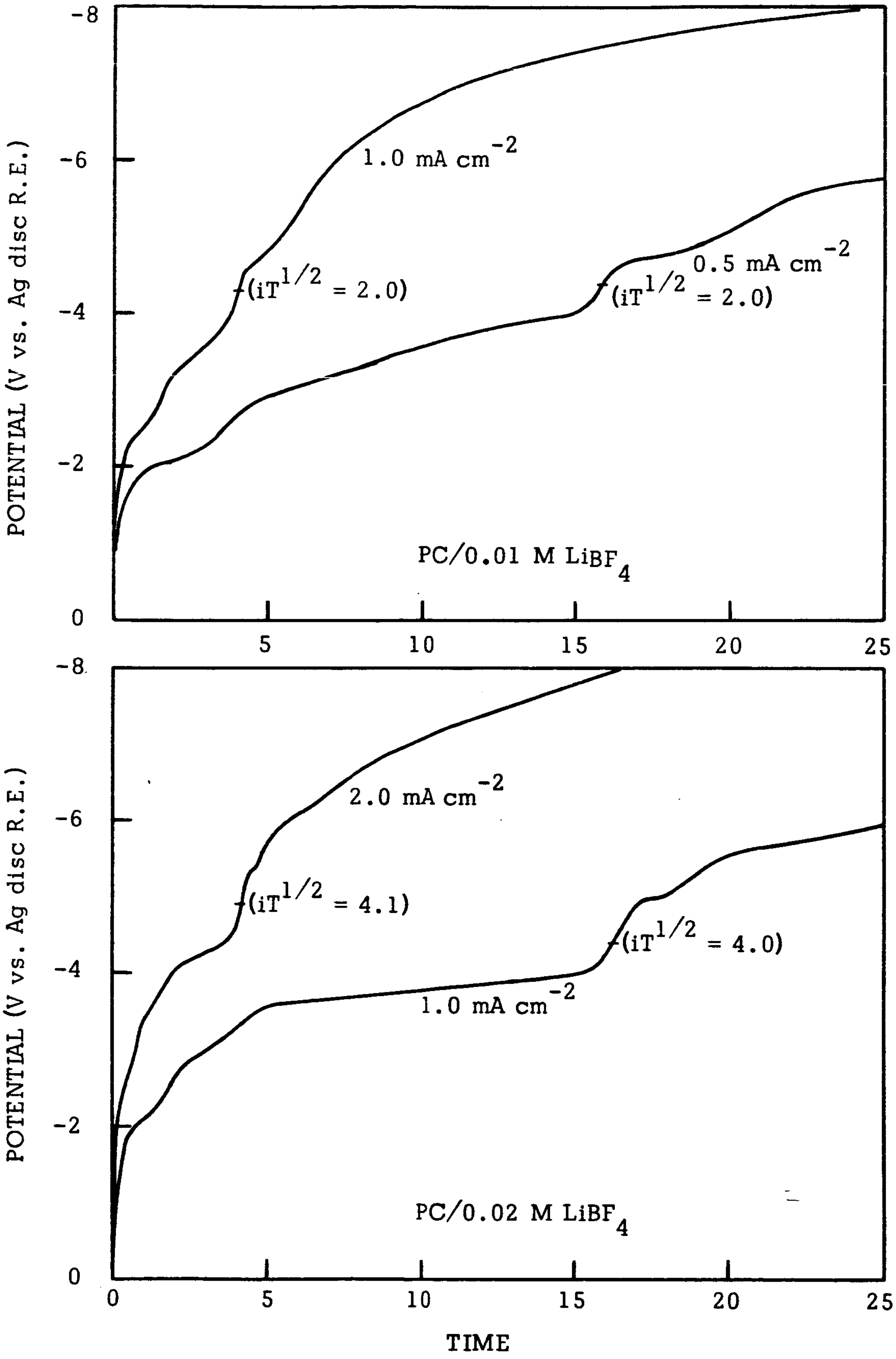


Figure 13: CHRONOPOTENTIOMETRY OF LITHIUM ION

On platinum electrode in solution indicated. Values for $iT^{1/2}$ in mA cm^{-2} $sec^{1/2}$.

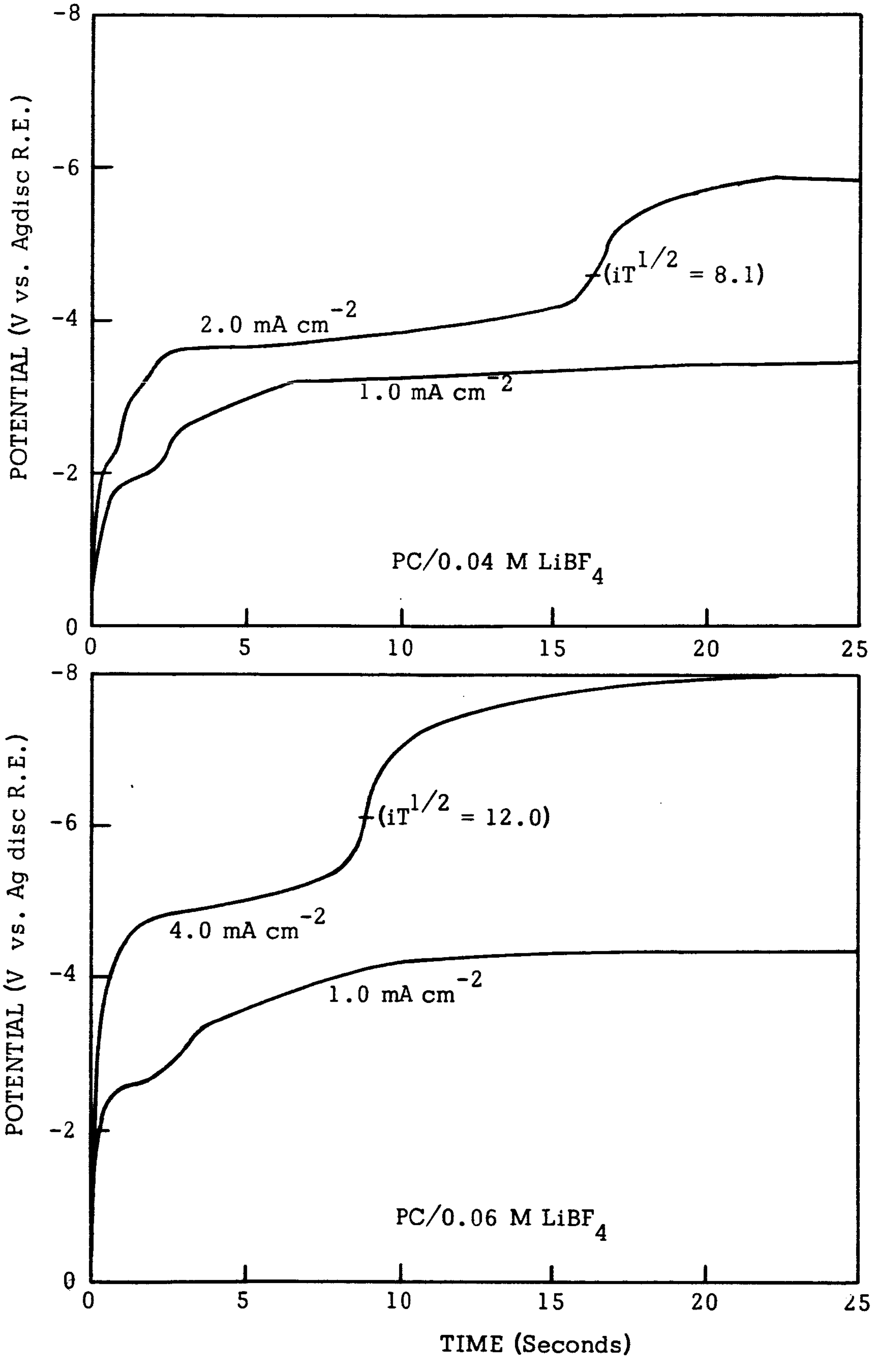


Figure 14: CHRONOPOTENTIOMETRY OF LITHIUM ION

On platinum electrode in solution indicated. Values for $iT^{1/2}$ in mA cm^{-2} $sec^{1/2}$.

in the lithium salt solution are, indeed, limited by the mass transport of the lithium ion.

d. Variation with anion.

In propylene carbonate solutions, we have observed no significant variations depending on the nature of the anion. Solutions, 0.1 M in $LiClO_4$, $LiBF_4$, LiBr, LiI, and $LiAlCl_4$ have been examined chronopotentiometrically, on platinum electrodes. The chronopotentiograms have similar shapes as those previously described; that is, apparent transfer coefficients of 0.1 to 0.2 are observed, and the extrapolated potential at $t = 0$, when correction is made for iR drop is a few tenths of a volt. Since these measurements in all but $LiClO_4$ and $LiBF_4$ solutions were not made against lithium reference electrodes, more detailed examination is not appropriate. The equivalent conductances in all five salt solutions, for the 0.1 M solutions, were about the same (ca. 18 ohm^{-1} $cm^2 M^{-1}$), and measured values of $i\tau^{1/2}/C$ were all sufficiently close to 200 mA cm $sec^{1/2}$ mM^{-1} as to indicate no significant differences in the transport properties.

e. Variation with electrode substrate.

In the course of the chronopotentiometric work only platinum and silver electrodes were used to any great extent, and on these two metals the behavior was essentially identical. In one case, other substrates were also used; this was PC/0.1 M LiBr. This salt was used because the silver R.E. could be oxidized anodically (7.5 mA cm^{-2}, 100 sec.) to form an insoluble AgBr reference electrode. Chronopotentiograms were performed at 7.0 mA cm^{-2}. The shapes were similar as is seen by the data below. The knee was observed for $t < 1$ sec. Thus data taken at times less than 1 sec. do not fall on the linear plot of E vs. $\log (1 - it^{1/2}/i\tau^{1/2})$. Except for the knee the chronopotentiograms are described by the following equations for each electrode:

Silver: $E = -2.60 + 0.66 \log (1 - it^{1/2}/19.2)$

Platinum: $E = -2.60 + 0.70 \log (1 - it^{1/2}/19.8$

Cobalt $E = -2.58 + 0.47 \log (1 - it^{1/2}/20.1)$

Nickel: $E = -2.58 + 0.47 \log (1 - it^{1/2}/20.6)$

Copper: $E = -2.48 + 0.44 \log (1 - it^{1/2}/18.9)$

Aluminum: $E = -2.67 + 0.55 \log (1 - it^{1/2}/19.2)$

The open circuit potential of a deposited lithium electrode vs. the Ag/AgBr reference electrode was -2.55V.

The chronopotentiograms were run on a chart scale such that the actual potential was probably not more accurate than ± 0.05 V, though the relative potential variation was better than ± 0.02 V. Thus we do not attach too much importance to the potentials at extrapolated t = 0, given by the first number in the above equation (i.e. - 2.60 for silver). The similarity of $iT^{1/2}$ was extremely good, 19.6 ± 1mA $cm^{-2} sec^{1/2}$, and is essentially identical with that obtained in the $LiClO_4$ and $LiBF_4$ solutions, 20 ± 1.5 mA $cm^{-2} sec^{1/2}$. Measurements were made at lower currents and there was a significant difference in the appearance of the knee. These are shown in Figures 15 and 16.

Some speculation is in order concerning the processes taking place before the lithium deposition potential is reached. These are the processes earlier termed proto-reduction. Reference was made to alloy formation of lithium with the metal, double layer charging, reduction of adsorbed material, reduction of oxide films, and coverage of active sites by reduction products for surface limited proto-reduction. The reductions observed during the knee of the chronopotentiograms are, indeed, surface limited proto-reductions and not mass-transport limited processes. This is readily seen by polarizing the electrode at a potential slightly positive to the open circuit potential of the lithium electrode. As was observed in the $LiClO_4$ solutions, the potential rapidly decays to negligible values, independent of the stirring rate. We will not speculate concerning the actual process occurring. The measurements do not distinguish clearly whether the process consumes lithium ions or not.

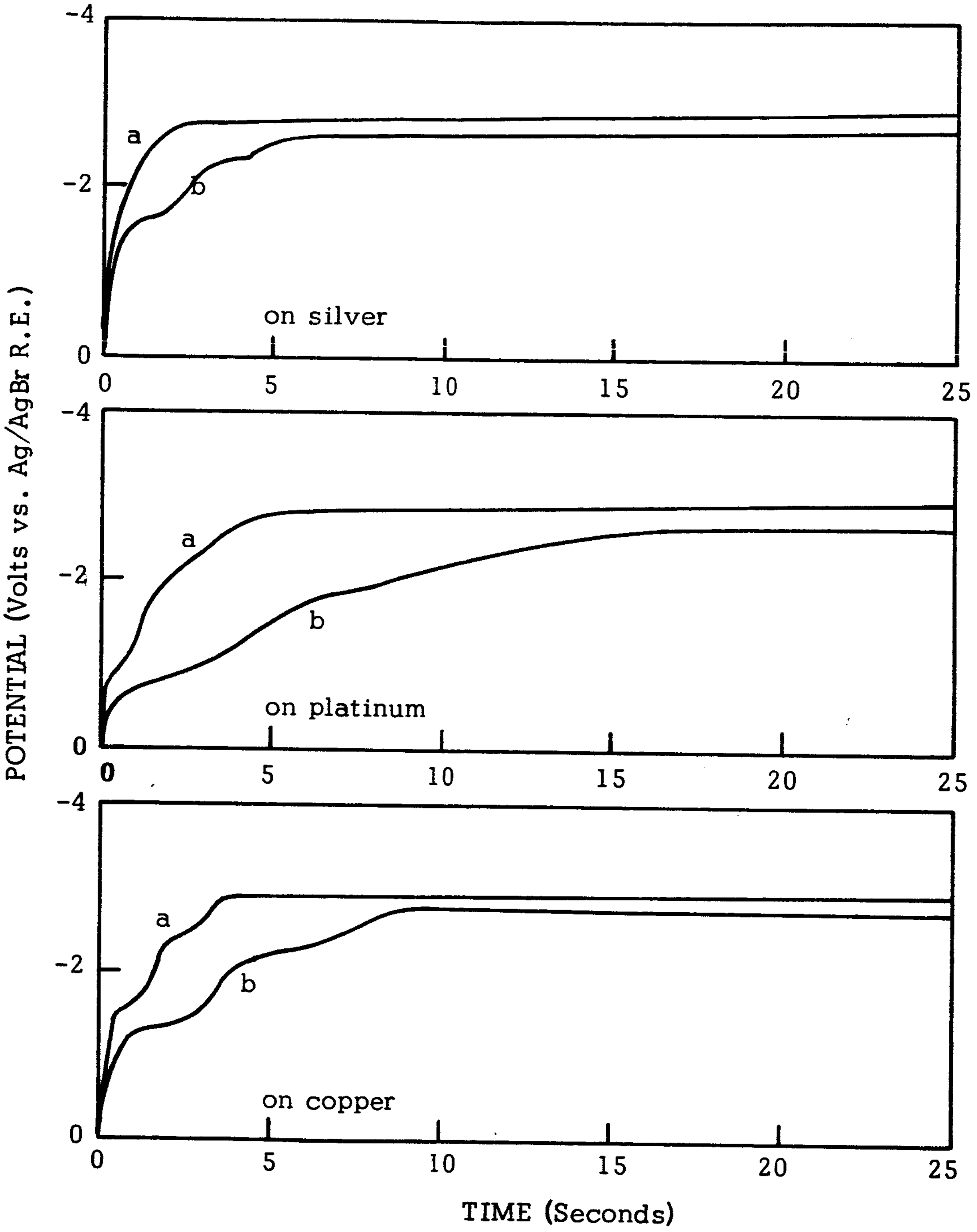


Figure 15: CHRONOPOTENTIOMETRIC SURFACE EFFECTS IN PC/LiBr

On substrate indicated, in PC/0.1 M LiBr.
a = 2 mA cm^{-2}; b = 0.8 mA cm^{-2}

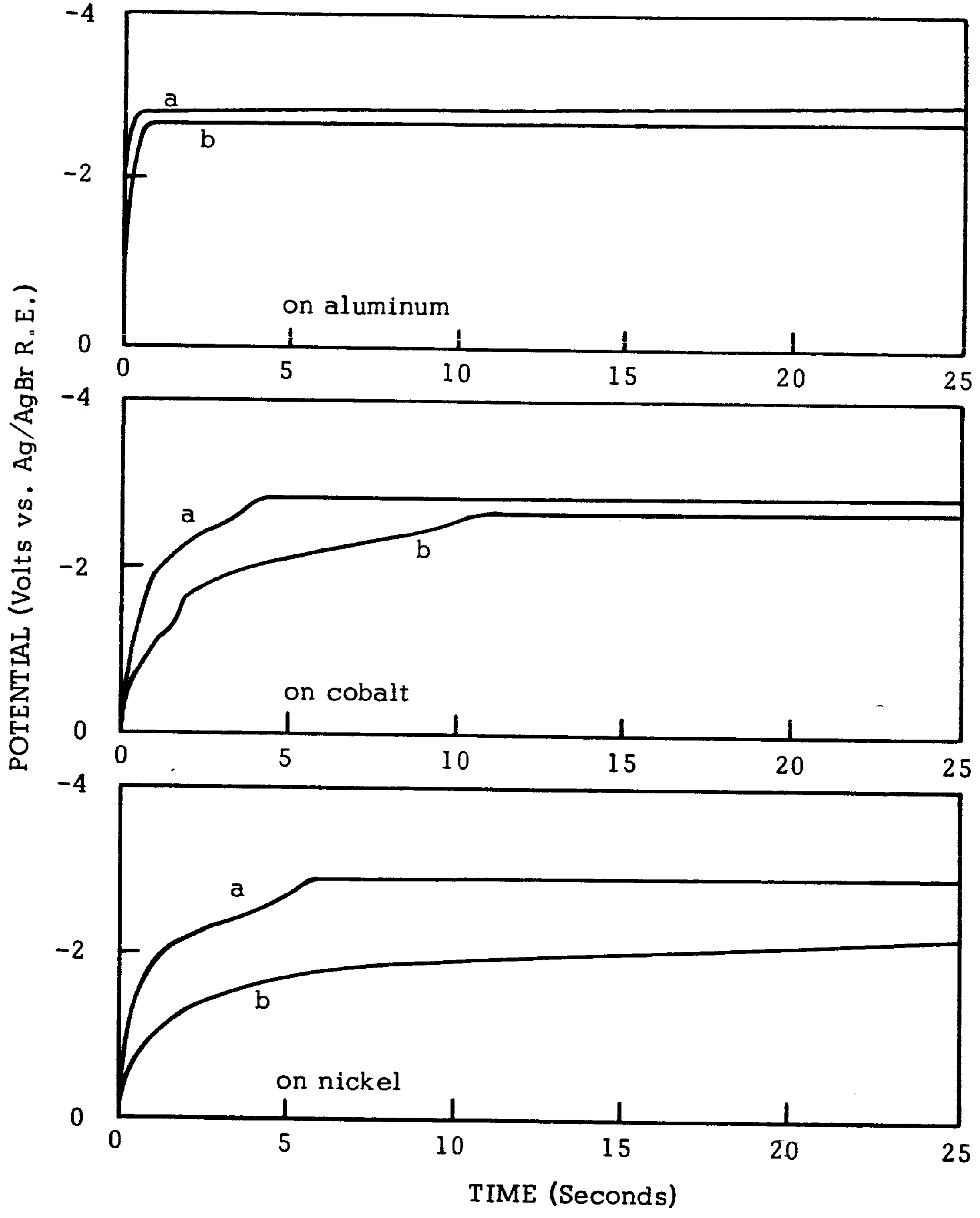


Figure 16: CHRONOPOTENTIOMETRIC SURFACE EFFECTS IN PC/LiBr

On substrate indicated, in PC/0.1 M LiBr.
a = 2 mA cm^{-2}; b = 0.8 mA cm^{-2}

For example, we consider cobalt, where the leveling off to the lithium potential is particularly sharp at 0.8 mA cm^{-2}, after 10.7 sec. Now, if we take the expected transition time at 7 mA to be 7.85 sec $(19.6/7)^2$, the measured transition time, of 8.6 mC cm^{-2} (10.7 x 0.8) are first passed before lithium consumption occurs, should be $8.6/7 + 7.85 = 9.1$ sec, or $iT^{1/2}$ of 21.1.

This is not significantly different from the expected value for $iT^{1/2}$ to allow determination of whether lithium consumption occurs or not. It is unlikely that the knee reflects significant double layer charging as the total current consumed is too large. On mercury, for example, the charge on the electrode at a potential 1.3 V negative to the point of zero charge is about 0.025 mC cm^{-2}. It is unlikely that a quantity of current, 400 times this on platinum for example, would be required for double layer charging. This would mean an enormous roughness factor and a marked deviation from double layer theory at these more negative potentials. One would probably also expect a more marked difference between the different electrode materials. Again, however, we only state that it is "unlikely", and the question does deserve further examination, and will, indeed, be quite critical if more definite kinetic studies are to be attempted.

Attempts were made to obtain chronopotentiograms on bulk lithium. This was not possible. Typical results are shown in Figure 17. First, no transition times could be obtained; secondly the initial potential is negative to the open circuit potential by more than 1 V. We believe these results reflect the growth of a resistive film on the lithium metal by direct reaction with the electrolyte.

f. Variation with Impurities.

The appearance of the chronopotentiograms are expected to differ depending on the impurity content of the media. One of the major troubles would be expected to arise from the presence of water. In Figure 18 are shown chronopotentiograms obtained in PC/0.1 M $LiBF_4$ for two water concentrations. The solid line chronopotentiogram was obtained in a solution,

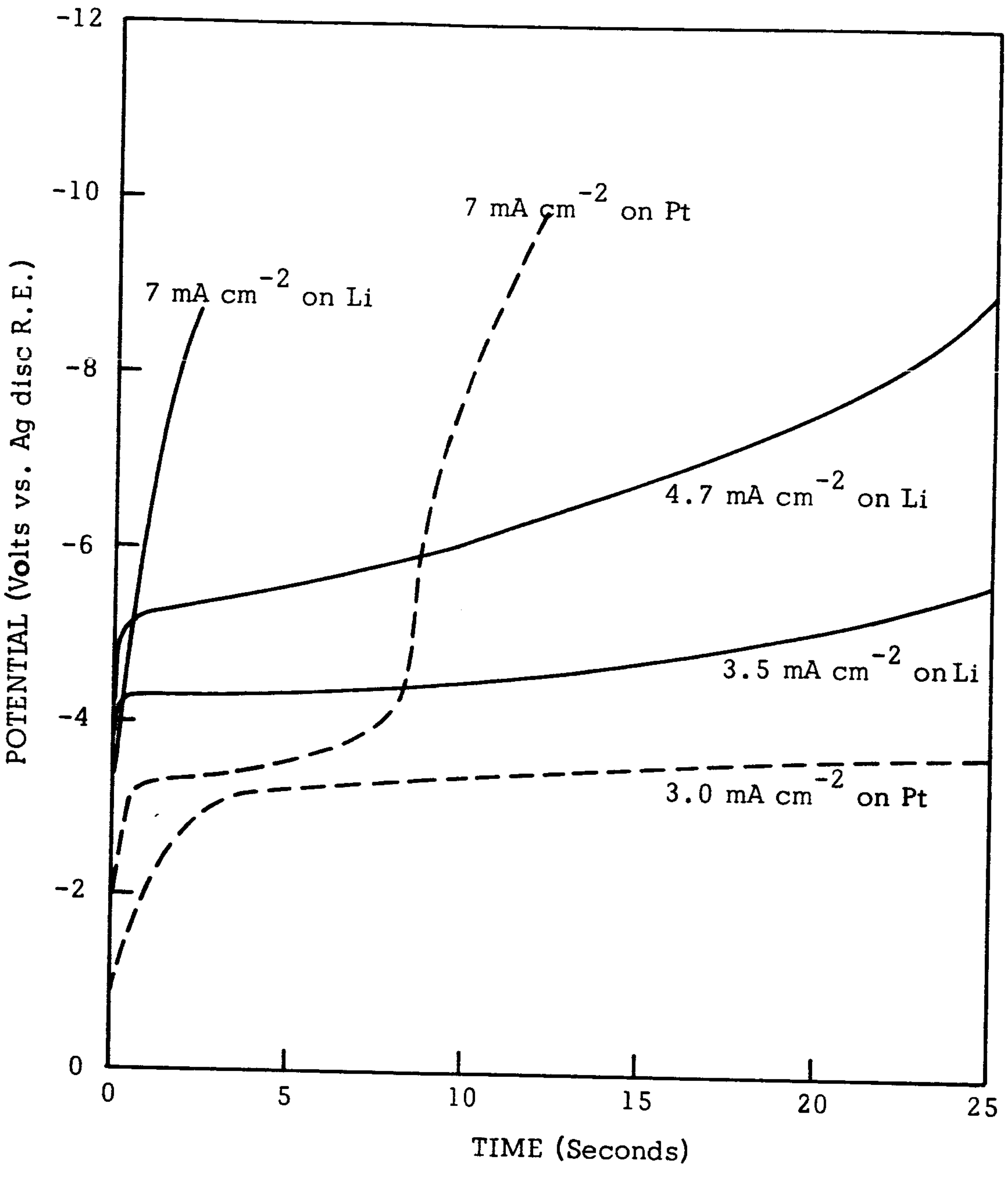


Figure 17: CHRONOPOTENTIOMETRY OF LITHIUM ION ON LITHIUM AND PLATINUM SUBSTRATES.

In propylene carbonate, 0.1 M $LiBF_4$. Chronopotentiograms are the observed curves corrected for iR drop.

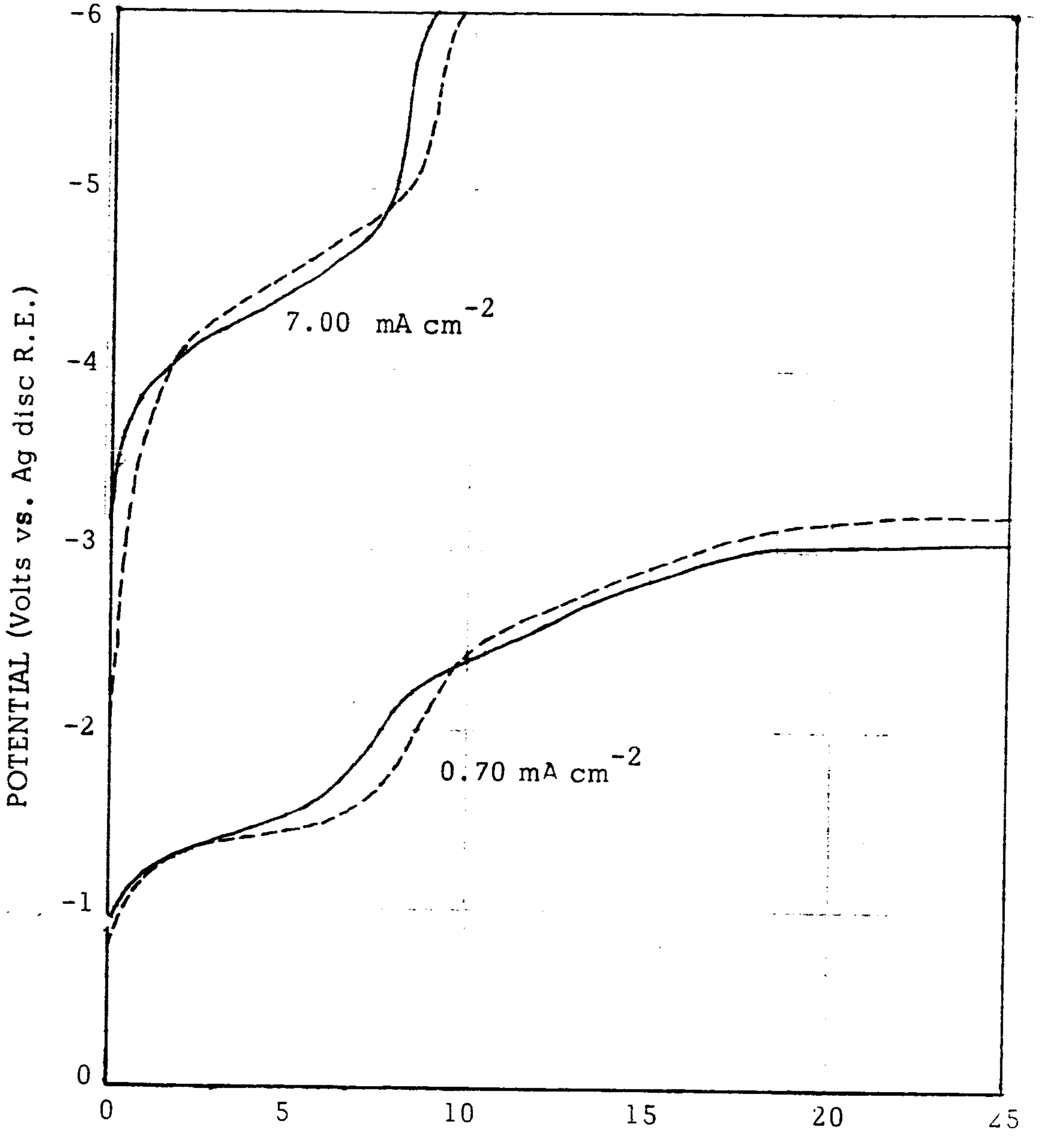


Figure 18: CHRONOPOTENTIOMETRY OF LITHIUM ION -- EFFECT OF WATER

On polished platinum electrodes at current indicated, in PC/0.1 M $LiBF_4$. Solid line in solution, 0.02 M in water; dashed line in solution, 0.1 M in water. Water concentration determined by vapor phase chromatography.

the water content of which was measured by V.P.C. to be 0.02 M. The dashed line chronopotentiogram was obtained in a solution, 0.1 M in water, a concentration equal to that of the lithium salt.

The primary difference is merely a change in the shape of the chronopotentiograms, in particular a more gradual rounding off of the knee and an increased slope for log $(1 - it^{1/2}/iT^{1/2})$. The magnitude of $iT^{1/2}$ does not change significantly (e.g. in Figure 18 from 20 to 21 mA $cm^{-2} sec^{1/2}$) in comparison with the amount of added water. The extrapolated potential at $t = 0$ does not change significantly either. From the fact that the transition time does not change, we must assume that whatever other processes occur in the presence of water also consume lithium ions. Thus, reaction such as the following: $H_2O + e^- + Li^+ = 1/2\ H_2 + LiOH$ should also show a transition time, since one would expect, for this reaction, that the chronopotentiogram should follow an equation of the form:

$$E_M = E_K + k \log C/C_o$$

where E_K is, ideally, the potential for water reduction and the second term reflects the fact that the potential drop across the diffusion layer will increase as lithium ions are exhausted by precipitation and a transition time will be observed when $C = 0$, at the electrode surface.

The possible effect of other impurities was also studied by vacuum distilling propylene carbonate and taking off successive 100 ml. fractions. The following results were obtained for chronopotentiograms at 5 mA cm^{-2}:

Fraction 1: Potential constant at - 1.8 V vs. Ag R.E.
Fraction 2: E (vs. Ag) $= -3.44 + 2.9 \log (1 - it^{1/2}/17.7)$
Fraction 3: E (vs. Ag) $= -3.26 + 0.59 \log (1 - it^{1/2}/19.0)$

Fractions 4 - 7 were essentially identical to Fraction 3. Again we note that the transition times are about the same, the major change is in the coefficient of the log term, and apparently a somewhat increased extrapolated potential.

The major points concerning the chronopotentiometry in propylene carbonate have been described. Before discussing the behavior in other solvents, it is of interest to compare the apparent kinetic data obtained from chronopotentiometric measurements with those obtained by voltammetry in stirred solution. We do this by going back to equation 43, p. 67, and note that the only difference between measurements by the two techniques lies in the logarithm term, $(1 - \frac{Li^+}{Li_0^+})$. For chronopotentiometry this is $(1 - it^{1/2}/i\tau^{1/2})$, for voltammetry in stirred solution it is $(1 - i/i_L)$.

Only the data in Table 21 were obtained at a sufficiently larger number of currents below the limiting current. It will be noted that the plot of the initial potential - log current from Table 21 gives a reasonably straight plot with the exception of the points made at the -0.02, -0.20 and -0.25 V settings. The slope, $\Delta E/\Delta \log i = 0.05$, and the current, extrapolated to $E = 0$, is 0.068 mA cm^{-2}. From the term, $i (E = 0) = i_o = F k_o C_o$, we calculate a heterogeneous rate constant of 2.3×10^{-6} cm sec^{-1}, which, for the present, is sufficiently close to the value of $10^{-4} - 10^{-5}$ obtained chronopotentiometrically.

A significant difference appears to exist in the term containing the mass transport properties, $\{1/\alpha + 1/z_2\}\ 0.059 \log (1 - x/x_L)$. As discussed before, in chronopotentiometry the term in brackets has a value of about 0.5 at currents necessary to give transition times of about 10 sec. Were the same coefficient to prevail in the voltammetric measurements one would expect, at a current half the limiting current, a potential due to concentration polarization of about 0.15 V. Comparing the limiting currents calculated following Table 7 with the data in Tables 19 - 21, this does not seem to be the case.

In the preceding discussion we have given but little consideration to the double layer. If we assume, as is normally done, that the potential which is actually effective in determining the rate of an "irreversible" process is that which exists across the compact double layer, it is clear that one must also consider the magnitude of the diffuse double layer potential, since this will be a quantity which must also be subtracted from the measured potential. Now, for solutions as dilute as 0.1 M, and in the absence of supporting electrolyte, this contribution of the diffuse double layer will, indeed, be substantial. From the well-known and extensive work which exists for the mercury electrode, some appreciation of the magnitude of the diffuse double layer contribution can be obtained with reference to data on the mercury electrode. We use the Gouy-Chapman equation:

$$E_{\psi} = \frac{2\,R\,T}{z\,F}\ \sinh^{-1}\left(\frac{q^{2}}{2\,\varepsilon\,k\,T\,C}\right)^{1/2}$$

Where E is the potential across the diffuse double layer, and q is the electrode surface charge density. At room temperature, one calculates:

$$\sinh 19.4\,E_{\psi} = \frac{0.756\,q}{\varepsilon^{1/2}C^{1/2}}$$

Where E is the diffuse double layer potential in volts, q is the surface charge density in microcoulombs cm^{-2}, and C is the concentration in $M\,l^{-1}$. From Russell's tables(27) we note that the rate of increase of surface charge density with applied potential is about 18 microcoulombs $cm^{-2}\,V^{-1}$. If lithium is deposited on platinum at about 3 V negative to the point of zero charge on platinum, from a 0.1 M solution with a dielectric constant of 80, one would calculate the potential of the diffuse double layer to be about 0.18 V. Similar calculations for other experimental conditions will show that, in general, the diffuse double layer potential will not be negligible.

Thus, the problems attending the attempt to measure kinetic parameters are most complex. We summarize:

1. The apparent exchange current for the Li^{o}/Li^{+} system appears to be, in mA cm^{-2}, of the order of theconcentration, in $M\,l^{-1}$.

2. At currents less than about 0.5 mA cm^{-2} there is evidence of surface limited proto-reduction, and satisfactory steady state measurements could not be made.

3. For voltammetric measurements or chronopotentiometric measurements under such conditions that the concentration of electroactive species at the electrode surface is less than about 25% of the bulk concentration, it is

(27) C. D. Russell, J. Electroanal. Chem., 6, 486-490, (1963).

difficult to evaluate the data with respect to kinetic parameters since large corrections must be made for (a) concentration polarization, (b) the potential across the diffusion layer, (c) the potential across the diffuse double layer, and (d) the iR drop is considerable, regardless of the concentration of solute.

4. The efficiency of lithium deposition is not 100%, thus account must be taken of side reactions (meso-reduction) in interpreting the data. In particular, account must be taken of the concurrent formation of resistive films. Also, in correcting for concentration dependent terms, account must be taken of the fact that these meso-reductions may also consume lithium ions through precipitation of lithium salts.

The above conclusions are summarized through the following calculations. We consider, again, the reduction: $Li^+ + e^- = Li^o$.
We assume the reaction is not reversible and is described by the equation:

$$i = k_r C e^{-bE} - k_o e^{bE} \tag{45}$$

where C is the concentration at the electrode surface, and E (without subscript) is the potential across the compact double layer. The quantities k_r, k_o, and b are constants for the process. At $E = E_o$, the open circuit potential of the Li^o/Li^+ electrode, $i = 0$, and $i_o = k_r C_o \exp(-bE_o) = k_o \exp(bE_o)$. We then may write equation (45) in terms of i_o and E_K ($E_K = E - E_o$) as:

$$i = i_o \frac{C}{C_o} e^{-bE_k} - i_o e^{bE_k} \tag{46}$$

The measured potential, E_M, will be the sum of E_k and the other potential terms:

$$E_M = E_k + E_D + E_R + E_\psi$$

Where E_D is the potential across the diffusion layer, E_R is the included iR drop, and E_ψ is the potential across the diffuse double layer. We shall calculate these four terms, assuming they are independent, and using the indicated numerical values.

E_k: Weconsider a 0.3 M $LiClO_4$ solution. Assume the limiting current is 60 mA cm^{-2}, and the concentration at the electrode surface is given by $C = 0.3(1 - i/60)$. Assume the exchange current is 0.3 mA cm^{-2}. Assume the transfer coefficient is 0.5. Equation 46 then becomes:

$$i = 0.3(1 - i/60)e^{-19.3\ E_k} - 0.3\ e^{+19.3\ E_k} \qquad (47)$$

E_D: The potential across the diffusion layer is given by:

$$E_D = 0.059 \log (1 - i/60) \qquad (48)$$

E_R: The iR drop is the product of the current density, the specific resistance, and the distance between the electrode "surface" and the tip of the Luggin capillary. We assume a solution specific resistance of 200 ohm-cm, and a distance of 0.1 cm between the Luggin capillary and the electrode. Therefore

$$E_R = i\ (0.02) \qquad (49)$$

E_ψ: We use the second equation given on page 107. We shall suppose the point of zero charge to be the open circuit potential of the Li/Li$^+$ electrode. We shall assume that $q = (18 \text{ microcoulombs cm}^{-2})(E_k\ V)$. This, together with the relation between C and the current gives the following expression for the potential across the diffuse double layer, assuming the solution to have a dielectric constant of 40:

$$E_\psi = 0.0516\ \sinh^{-1} \frac{7.2\ E_k}{(1 - i/6)^{1/2}} \qquad (50)$$

For a given value of i, we calculate E_k from equation 47; this, together with the current are used in equation 50. Equations 48 and 49 are also solved for the given current. These values are shown below:

i (mA cm^{-2})	E_k (eqn. 47)	E_D (eqn. 48)	E_R (eqn. 49)	E_ψ (eqn. 50)	E_{total}
0.06	0.005	0.000	0.001	0.002	0.008
0.2	0.018	0.000	0.004	0.007	0.029
0.6	0.048	0.001	0.012	0.018	0.079
2.0	0.098	0.002	0.040	0.034	0.174
6.0	0.156	0.006	0.120	0.052	0.334
20.0	0.219	0.022	0.400	0.073	0.714

Since the exchange current is, clearly, quite large, the potentials for which corrections must be made assume great importance. It is doubtful, in fact, whether there is really much point in trying to make electrokinetic measurements of the lithium electrode. The primary problem with the lithium electrode is the inefficiency of deposition -- conventional electrokinetic measurements will probably not provide much insight into the causes of this. A more direct phenomenological approach is desired, in which reasonable variations in the experimental parameters are made and the effects on the deposition efficiency noted. Some of these approaches are discussed in the next section.

II-C-3-c. Other Cathodic Phenomena.

The experiments described in this section were performed to obtain some more insight into cathodic phenomena occurring in non-aqueous electrolytes. The following are considered in this section:

(1) Effects on highly active surfaces.
(2) Effects on other metal substrates
(3) Effect of lithium ion surface concentration.
(4) Deposition of lithium in other solvents.
(5) Cathodic behavior with non-lithium solutes.
(6) Effects of long term cathodization (pre-electrolysis).

II-C-3-c-(1) Effects on highly active surfaces. When lithium is electrodeposited, the deposit is far from smooth. It is therefore of interest to see what happens when one attempts cathodization in lithium salt solutions on electrodes with large active surface areas.

Active silver electrodes were used in this study. They were prepared quite simply by anodizing a polished silver electrode in aqueous chloride media, whereon a film of AgCl is formed. One then reduces this film of AgCl cathodically in the same solution, and obtains a surface of finely divided silver metal. The effect of this increased surface area has been previously discussed by us(28). It was noted, for example, that, though only about 50 mC cm^{-2} of Ag_2O could be formed by potentiostatic anodization of polished silver

(28) K. R. Hill and R. G. Selim, Final Report, NASA Contract No. NAS 3-2780, August 1965, pp. 24-26.

electrodes, increasing the active area by the above described treatment results in a proportionate increase in the amount of Ag_2O which can be formed. For example, 1500 mC cm^{-2} of Ag_2O can be formed on 2000 mC cm^{-2} of active silver. Apparently this reflects about a thirty-fold increase in active area.

In figure 20 are shown the variations in the extent of proto-reduction on polished and active silver electrodes. Preliminary studies had indicated that it was necessary to pre-reduce the active silver electrodes at -0.9 V vs. the Ag disc R.E. in the lithium salt solutions to insure complete reduction of all AgCl. As seen in figure 20 about 10 mC cm^{-2} of proto-reduction occur on the polished silver electrode. On the electrode with 1500mC cm^{-2} of active silver, this increases to 100 mC cm^{-2} of proto-reduction.

That the proto-reductions were not mass transport limited is unequivocally demonstrated by cathodizing the electrodes potentiostatically. Typical results are shown below, where an active silver electrode was cathodized at -2.8 V vs. the Ag disc R.E. (ca. + 0.3 V vs. the lithium electrode). The solution was stirred during the run. The current decayed smoothly, without oscillations.

Time after Commencement of Cathodization	Current Density
0	ca. 5 mA cm^{-2}
0.1 min.	3.0 "
0.5 min.	1.0 "
1.0 min.	0.6 "
2.0 min.	0.4 "
4.0 min.	0.3 "

The rate of current decay on the polished electrodes is more rapid, and the total amount of current passed markedly less on the polished electrodes after a few minutes. (Note: under the conditions which prevail in our work, steady state conditions for true mass transport limited processes are attained within a few seconds after the commencement of electrolysis.) It is generally observed that limiting currents (in mA cm^{-2}) are of the same order of magnitude as the values for $iT^{1/2}$ (in mA cm^{-2} sec$^{1/2}$); a value for $iT^{1/2}$ of 22, calculated from the solid line curve in figure 20, would give a limiting current of almost 100 times that observed from the above data after four minutes.

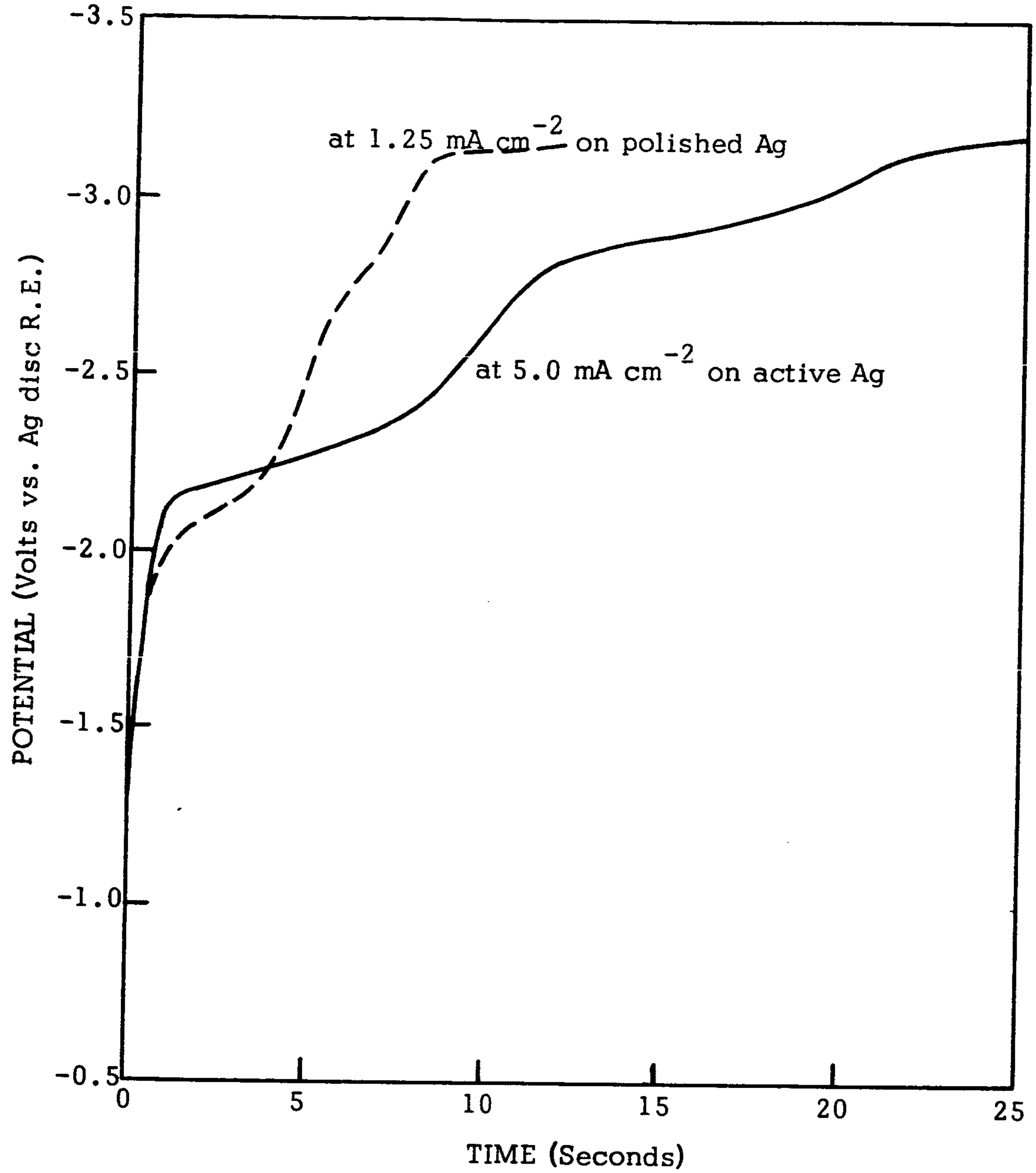


Figure 20: PROTO-REDUCTION ON POLISHED AND ACTIVE SILVER ELECTRODES

Obtained in quiet solution, PC, 0.2 M $LiClO_4$, under conditions indicated. Active silver electrode formed by anodic oxidation in aqueous HCl at 5 mA cm^{-2} for 300 sec. followed by completely cathodic reduction to finely divided silver metal.

The effect of this proto-reduction on the lithium chronopotentiograms is typically that shown in figure 21. Proto-reduction is obviously much more extensive on the electrode which had not been pre-cathodized at -2.8 V. A comparison of the values for $iT^{1/2}$ with those found in 0.1 M $LiClO_4$ solutions on polished electrodes (20 mA cm^{-2} sec$^{1/2}$) proves that proto-reduction does not consume lithium ions. It is also clear that proto-reduction is neither double layer charging nor mass transport limited processes, or successive runs should all look like curve b in figure 21.

Reductions were performed on active silver electrodes in stirred PC/0.2 M $LiClO_4$. The data are compared with selected data from table 20:

On active Ag			On polished Pt		
Measured Current (mA cm^{-2})	Corrected Potential (V vs. Li^{o})	Anodic Utilization	Measured Current (mA cm^{-2})	Corrected Potential (V vs. Li^{o})	Anodic Utilization
11	-0.01	64%	13.0	-0.02	54%
21.5	-0.05	70%	23.5	-0.16	44%
35	-0.10	65%	35	-0.25	38%
40	-0.23	60%	41	-0.18	39%
45	-1.0	3%	51	-0.74	33%

Surprisingly, the results show the efficiency to be even better on the active silver than on the polished platinum.

II-C-3-c-(2) Effects on other metal substrates.

The effect of the substrate on lithium deposition was also examined for polished metal substrates of other metals. Typical results are shown in figure 22. These were obtain in the same solution -- PC/0.1 M $LiBF_4$. Single cycle experiments were performed in stirred solution (Note: the limiting current for lithium ion reduction is about 10 mA cm^{-2} in this solution). The high efficiencies noted on beryllium were surprising, but particularly noteworthy was the fact that the efficiencies remained high even at the lowest currents; this is contrary to the behavior normally observed on platinum (compare also with table 5). Behavior similar to platinum was observed, as

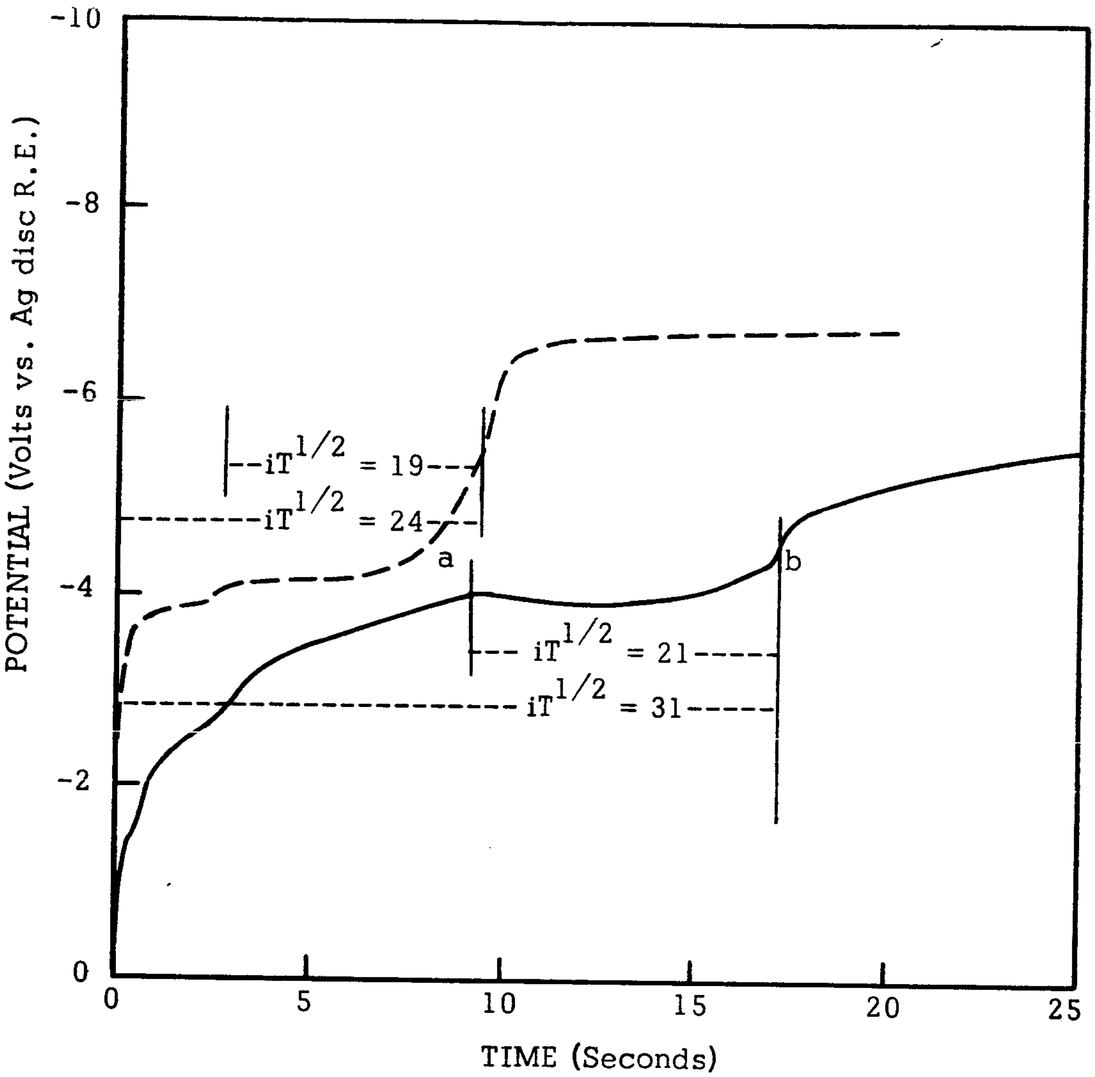


Figure 21: EFFECT OF PROTO-REDUCTION ON CHRONOPOTENTIOMETRY OF LITHIUM ION.

Obtained on active silver electrodes (100 mC cm^{-2}) at 7.5 mA cm^{-2}, in PC/0.1 M LiClO$_4$. Curve a was obtained following prolonged potentiostatic cathodization at -2.8 V. Curve b was obtained without preliminary cathodization.

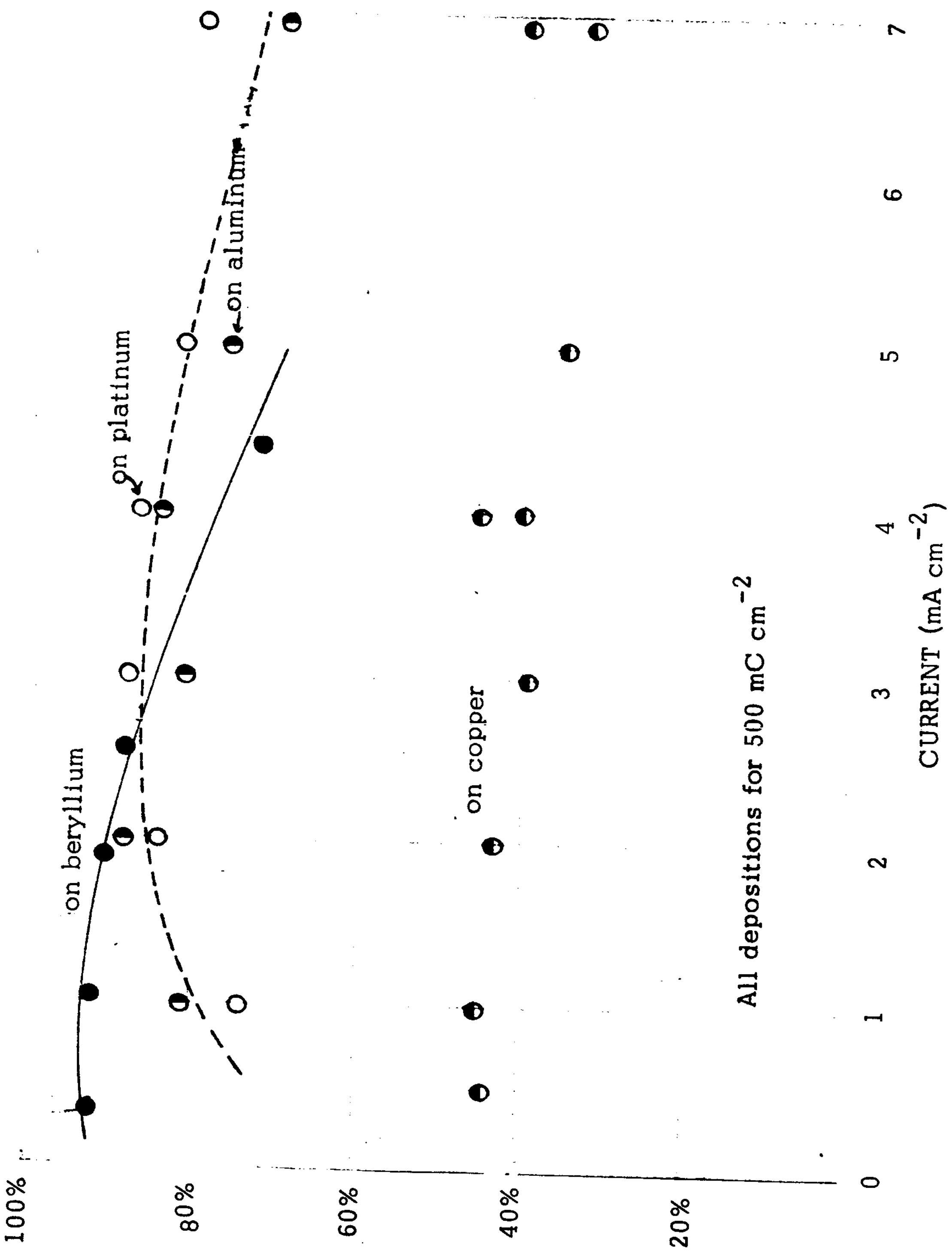


Figure 22: LITHIUM DEPOSITION EFFICIENCY ON VARIOUS METALS

shown in Figure 22, on aluminum. The nature of the deposit on beryllium was also markedly different. A light colored, striated deposit formed, whereas on platinum a uniform light gray deposit normally forms at these current densities. The variation of efficiency with amount of deposit was also examined. A current of 2 mA cm^{-2} was used. On beryllium the anodic utilization remained at 92± 2% for deposits of from 150 to 1900 mC cm^{-2}. On platinum, on the other hand the efficiency decreased from 83% for 250 mC cm^{-2} of deposition to 64% for the 2000 mC cm^{-2} deposition.

Other solutions were examined, using the same batch of propylene carbonate. The results were as follows:

PC/0.1 M $LiClO_4$: On Be, anodic utilizations of 61± 2 % for depositions at 300 mC cm^{-2} at currents of from 0.6 to 3.2 mA cm^{-2}. For depositions at 1.26 mA cm^{-2} utilizations showed a good deal of scatter, 60 ± 10% for from 15 to 1200 mC cm^{-2} of deposition.

PC/0.1 M $LiAlCl_4$: at 1 mA cm^{-2}, utlizations were very low, 25 -50% for depositions up to 1000 mC cm^{-2}.

BL/0.1 M $LiBF_4$: On Be, anodic utilizations showed much scatter for depositions at 1.26 mA cm^{-2} from 60 - 95% for depositions of from 15 to 2000 mC cm^{-2}.

Clearly, there is a marked dependence on the electrode substrate and on beryllium, even on the solute. Now these depositions were performed at rather low currents, and, as seen in Table 5, it is characteristically observed that there is a decrease in efficiency at the lower currents. More experiments are required over a range of both current densities and total amount of cathodization before a clear assessment of the effect of the electrode substrate can be made. However, it is interesting to note the significant differences shown in Figure 22 for a constant amount of deposition. This amount of deposition corresponds to many hundred atomic layers and it is clear that even these relatively thick lithium deposits must reflect processes occuring shortly after the initiation of electrolysis which carry through as cathodization is continued. The results simply re-emphasize the necessity for more critical basic studies on the lithium deposition process.

II-C-3-c-(3). Effects with Surface Concentration of Lithium Ions.

As can be seen in the preceding discussions, a significant change in the potential which exists across the compact and diffuse double layers, and across the diffusion layer, develops as the concentration of lithium ions at the "electrode" surface is significantly less than in the bulk of solution. This is the type of situation which occurs when electrolyses are performed close to the limiting current.

It will be recalled that the surface concentration, ideally, is given by, $C = C_o\ (1 - i/i_L)$ for voltammetry, and $C = C_o(1 - it^{1/2}/iT^{1/2})$ for chronopotentiometry. Since the longer term voltammetric measurements are more tedious to perform, and steady state conditions rarely observed, it was felt that chronopotentiometric measurements might give a more rapid assessment of any effects resulting from variations in the surface concentration of lithium ions. For voltammetric measurements the best initial evaluation of a system is in terms of i vs. anodic utilization curves; the equivalent for chronopotentiometric measurements would then be $it^{1/2}$ vs. anodic utilization curves.

Some typical results are shown in Table 22. The data were collected as follows. Constant current was applied at various currents and for various periods of time; after the pre-determined period of the time the current was reversed, and the anodic utilization determined. The times were from 4 - 25 sec. If the system behaves ideally, then the actual current used for a given value of $it^{1/2}$ should be immaterial. Thus, for an $it^{1/2}$ of 5 mA cm^{-2} $sec^{1/2}$ one may use either a current of 1 mA cm^{-2} for 25 sec. or a current of 2.5 mA cm^{-2} for 4 sec. We have not found there to be much difference; this is not surprising in view of the fact that the current does not change by much more than a factor of 2 in going from the two extremes of time used (4 - 25 sec.). Nevertheless, we show in Table 22 the currents used. These are shown in parentheses, so as to focus attention on the $it^{1/2}$ rather than the current.

Table 22

ANODIC UTILIZATION VS. $it^{1/2}$

Measurements performed as described on p. 117 in propylene carbonate solutions of $LiBF_4$ in indicated concentration.
$it^{1/2}$ in mA cm^{-2} $sec^{1/2}$
i in mA cm^{-2}

0.04 M
($iT^{1/2} = 8.0$)

$it^{1/2}$	i	Efficiency
2.0	(0.40)	33%
3.0	(0.60)	40%
4.5	(1.50)	45%
6.0	(1.50)	50%
6.0	(2.00)	50%
8.0	(2.00)	63%
9.0	(1.80)	61%
11.0	(2.20)	55%

0.06 M
($iT^{1/2} = 12.0$)

$it^{1/2}$	i	Efficiency
1.5	(0.30)	ca. 16%
2.5	(0.50)	33%
4.2	(0.84)	40%
5.0	(1.00)	53%
6.3	(1.25)	60%
8.3	(1.65)	62%
11.0	(2.00)	69%
12.5	(2.50)	70%
15.0	(3.00)	63%
17.0	(3.40)	58%
20.0	(4.00)	45%
25.0	(5.00)	31%

0.266 M
($iT^{1/2} = 64$)

10	(2.00)	54%
20	(4.00)	72%
25	(5.00)	74%
30	(6.00)	68%
40	(8.00)	77%
50	(10.0)	73%
60	(12.0)	68%

1.0 M
($iT^{1/2}$ ill-defined, ca. 180)

7.5	(1.5)	37%
10.0	(2.0)	53%
15.0	(5.0)	50%
20.0	(5.0)	69%
25.0	(5.0)	75%
37.5	(7.5)	78%
50.0	(7.5)	81%
62.5	(7.5)	82%
75	(25.0)	83%
125	(25.0)	85%
150	(50.0)	72%
200	(50.0)	47%
250	(50.0)	30%

We note that the data are quite consistent with the voltammetric i vs. anodic utilization curves shown earlier. It is noted that the utilization actually increases as one gets closer to $it^{1/2} = iT^{1/2}$.

II-C-3-c-(4). Effects in other solvents.

In figures 23, 24, and 25 we show the chronopotentiometric behavior observed in DMF, DMSO, and AN. In each case the results were not as satisfactory as in PC. In DMF and DMSO the chronopotentiograms were so ill-defined that it was difficult to establish the transition time; the slope of E vs. $\log (1 - it^{1/2}/iT^{1/2})$ was much larger than in PC. Nevertheless, mass transport limitation is still indicated as shown below where we compare the lithium chronopotentiograms with those obtained in solutions of $AgClO_4$ in each solvent. The latter were quite well-defined in all cases and allowed unambiguous determination of transition times. Comparison is made in a manner similar to that shown on page 71. From equation (44), p. 71, the ratio of $iT^{1/2}/C\Lambda^{1/2}$ for a 1:1 uni-univalent, completely dissociated electrolyte, should be 62.

Electrolyte	$iT^{1/2}/C$	Measured Equivalent Conductance	$iT^{1/2}/C\Lambda^{1/2}$
PC/0.03 M $AgClO_4$	260	25	52
PC/0.1 M $LiClO_4$	200	18	47
DMF/0.1 M $AgClO_4$	500	66	62
DMF/0.1 M $LiBF_4$	370-420	52	51 - 58
DMSO/0.1 M $AgClO_4$	338	30	62
DMSO/0.1 M $LiClO_4$	260-300	26	51 - 59
AN/0.05 M $AgClO_4$	702	128	62
AN/0.05 M $LiBF_4$	633	100	63

Again the results show that the processes, being limited by the mass transport of the lithium ion, must involve the consumption of lithium ions. As was earlier discussed in connection with the PC solutions, this does not mean that the lithium ions must be consumed by reduction to the metal, but may merely be precipitated at the electrode surface as lithium salts.

A further examination of these other solvents was undertaken by making $it^{1/2}$ vs. anodic utilization measurements. Those systems in which the largest

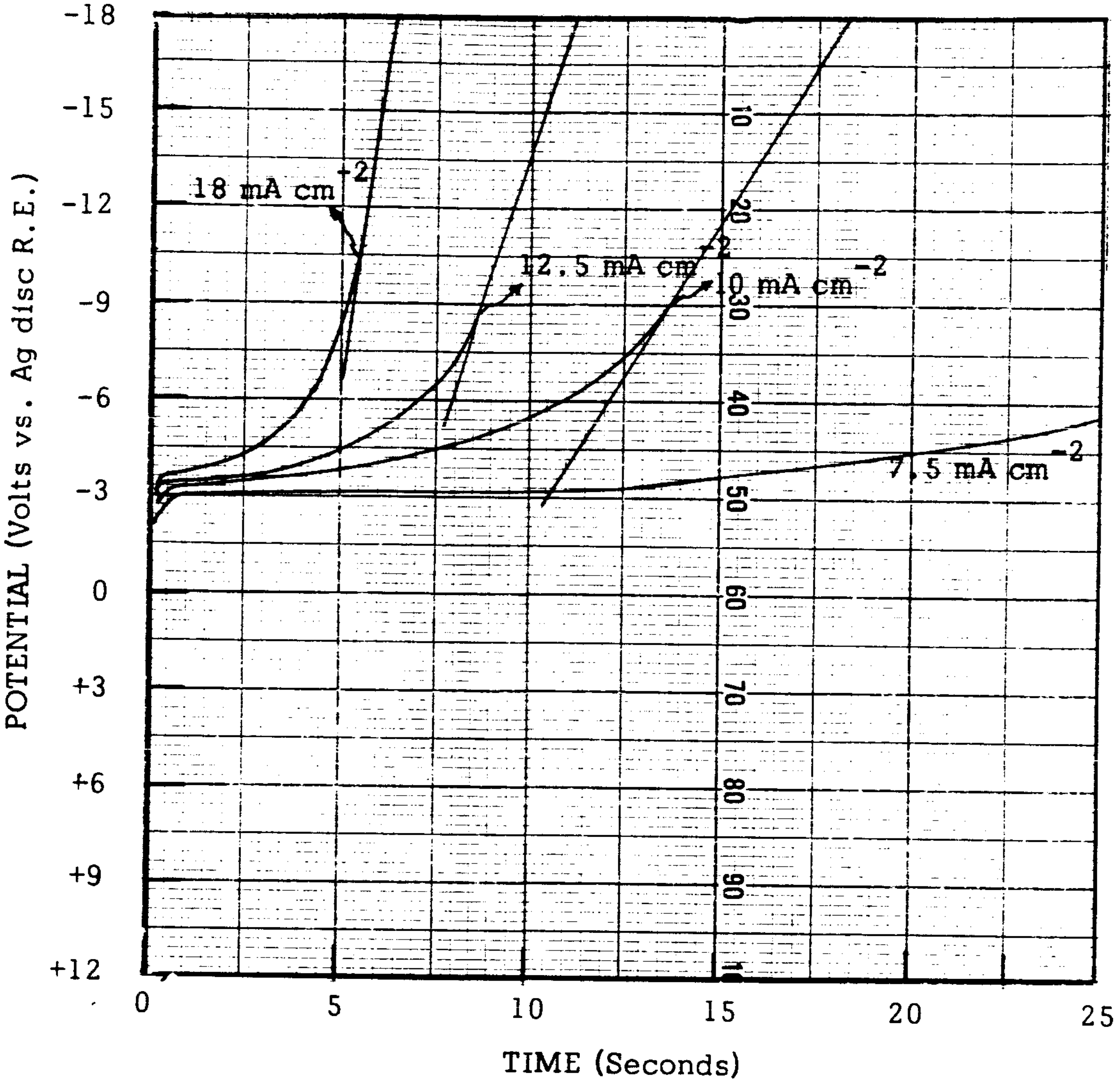


Figure 23: CHRONOPOTENTIOMETRY OF LITHIUM ION IN DIMETHYLFORMAMIDE.

On polished platinum in DMF/0.1 M $LiBF_4$ at current indicated. Since the chronopotentiograms were recorded on such a wide scale it was not useful to make corrections for iR drop, but the calculated values are shown below, along with the values for $iT^{1/2}$ determined as discussed on page 68.

i (mA cm^{-2})	Calculated iR (V)	$iT^{1/2}$ (mA cm^{-2} $sec^{1/2}$)
18	0.54	42
12.5	0.38	38
10	0.30	37

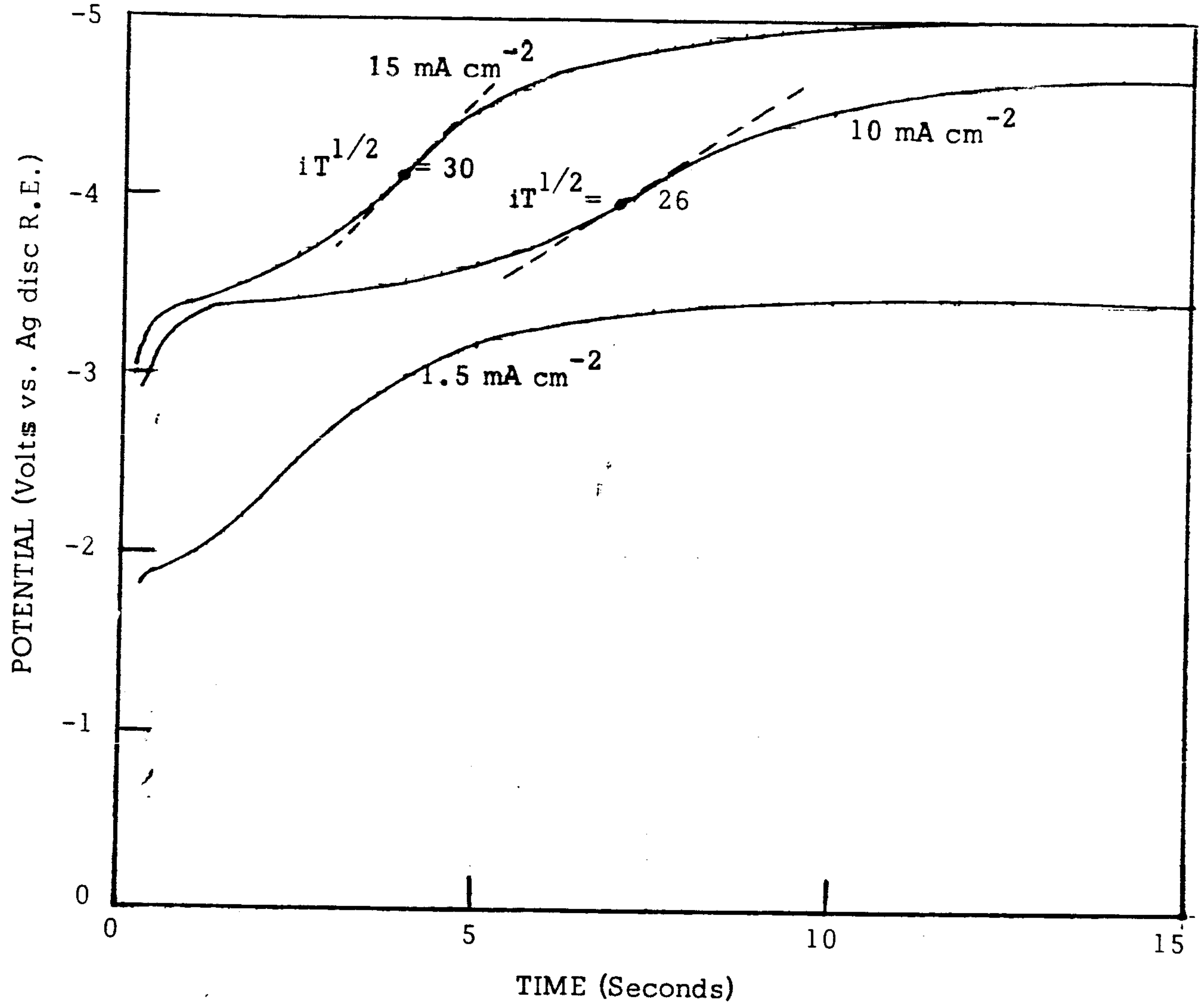


Figure 24: CHRONOPOTENTIOMETRY OF LITHIUM ION IN DIMETHYLSULFOXIDE.

On polished platinum in DMSO/0.1 M $LiBF_4$, at current indicated. The chronopotentiograms have been corrected for iR drop. The open circuit potential of a deposited lithium electrode in this solution was -3.4 V vs. the silver disc R.E.

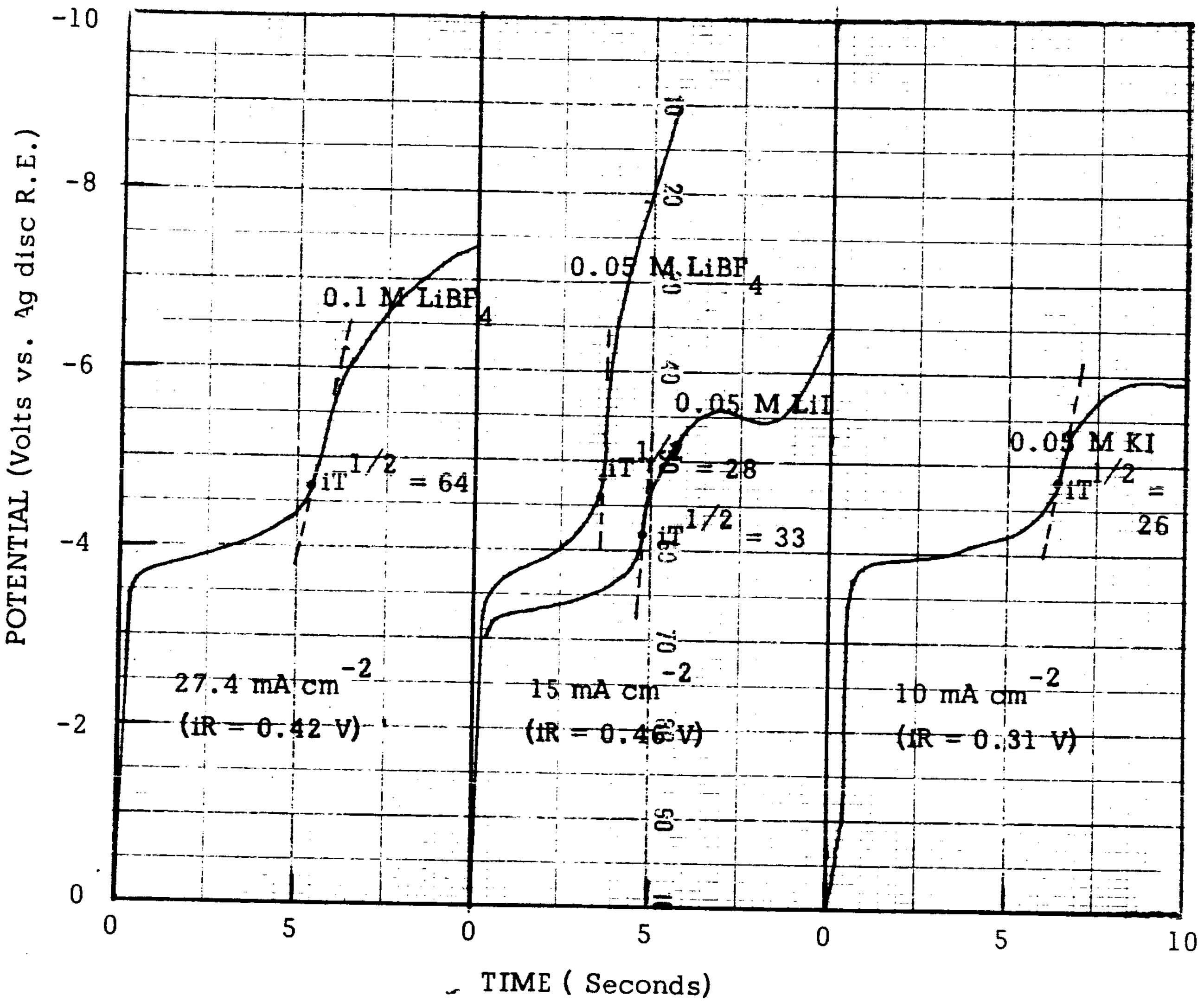


Figure 25: CHRONOPOTENTIOMETRY IN ACETONITRILE.

On polished platinum in solution indicated at current indicated. The chronopotentiograms were not corrected for iR drop. The calculated correction is given in parentheses in the figure.

number of measurements were taken are shown in table 23. We have not shown the actual current used, in order to avoid confusion. The approximate value of the current is easily calculated by dividing $it^{1/2}$ by 3.5, since, in all cases, the times were from 4 to 25 seconds ($t^{1/2}$ = 2 to 5).

II-C-3-c-(5). Effects in Propylene carbonate with other solutes.

Brief studies have been made from time to time in propylene carbonate solutions of other solutes. These are summarized below. In preliminary examination of new systems either or both of the following are employed.

Chronopotentiometry. Chronopotentiograms are measured over a fairly wide range of currents which bracket the value of 6.3 mA cm^{-2}. This is the current density which, in 0.1 M $LiClO_4$ or $LiBF_4$ solutions, would give a transition time of 10 seconds. The objective is to see whether a transition time can be observed in the new solution which would give evidence of the existence of a process limited by the mass transport of the solute species.

Voltammetry. Steady state current-potential curves were measured in stirred solution. For comparison, it will be recalled that the limiting current for a one-electron change in stirred propylene carbonate is about 18 mA cm^{-2} for a concentration of electroactive material of 0.1 M.

The potentials are reported versus the open circuit potential of the lithium electrode in a 0.1 M solution of a lithium salt in PC. This is done indirectly, as follows. We consider the potentials of five electrodes:

E_1 = the potential of a lithium electrode in a PC solution, 0.1 M in Li^+

E_2 = the potential of a silver electrode in a PC solution, 0.1 M in Li^+ and 0.01 M in Ag^+.

E_3 = the potential of a silver electrode in a PC solution, 0.1 M in supporting electrolyte not containing silver ions. (This is the electrode referred to in this report as simply the Ag disc R.E.).

E_4 = the open circuit potential measured in a PC solution, 0.1 M in supporting electrolyte not containing silver ions, and measured 0.5 sec. after the silver electrode has been anodically oxidized at a current and time such that $it^{1/2}$ = 1.0 mA cm^{-2} $sec^{1/2}$.

E_5 = the potential which one seeks to relate to that of the lithium electrode. We desire the value, $E = E_5 - E_1$, and consider how this can be done conveniently.

TABLE 23

ANODIC UTILIZATION VS. $it^{1/2}$

DMF/0.1 M LiCl		DMSO/0.1 M $LiClO_4$		AN/0.1 M $LiBF_4$		BL/0.2MLiAlC$_4$	
$it^{1/2}$	Eff	$it^{1/2}$	Eff	$it^{1/2}$	Eff		
2.5	10%	7.5	56%	25	58%	5.5	16%
5.0	20%	15.0	68%	50	67%	11.0	45%
7.5	44%	22.5	69%	75	54%	16.5	50%
10.0	60%	30.0	51%	100	36%	22.3	62%
12.5	68%	37.5	38%	125	25%	28.0	66%
15.0	69%	45.0	29%	$iT^{1/2}$ = 64		32.5	66%
17.5	67%	$iT^{1/2}$ = ca. 27		AN/0.05 M $LiBF_4$		46.0	68%
20.0	60%			12.5	64%	56.0	57%
22.5	70%			25.0	71%	65.0	52%
25.0	70%			37.5	63%	90.0	27%
27.5	70%			50.0	50%	$iT^{1/2}$ = 57	
30.5	68%			62.5	28%		
32.5	44%			$iT^{1/2}$ = 28			
35.0	30%						
42.5	20%						
$iT^{1/2}$ = 35.0							

In the "unknown" solution we measure two quantities with respect to the silver disc R.E.:

$$E_M = E_5 - E_3 \qquad \text{or} \qquad E_5 = E_M + E_3$$

and $E_R = E_4 - E_3$

We have learned, experimentally, and this is discussed in more detail in Section III of this report that:

$$E_1 - E_2 = -3.67 \text{ V}$$

and $E_4 = E_2$

therefore: $E_1 - E_4 = -3.67$ V

or $E_1 - E_3 - (E_4 - E_3) = -3.67$ V

which is $E_1 - E_3 - E_R = -3.67$ V or $E_1 = -3.67 + E_R + E_3$

Therefore: $E = E_5 - E_1 = E_M + 3.67 - E_R$

The procedure involves nothing more than an internal standardization of the silver disc reference electrode (E_3) against a known electrode, E_4. The potentials given below are calculated by this procedure.

(a) 0.1 M KI/PC. Chronopotentiograms were completely irreproducible on both silver and platinum, and further examination was not made.

(b) 0.1 M KPF_6/PC. Chronopotentiograms were too ill-defined to obtain satisfactory results on active silver electrodes. In one run, at 7.5 mA cm^{-2}, a reasonably well-defined transition time was obtained after 12.5 sec., giving an apparent $iT^{1/2}$ of 27 mA cm^{-2} $sec^{1/2}$, which is about the same as in the 0.1 M Li^+ and Ag^+ solutions; however, during the plateau preceding the transition time there was vigorous gassing.

(c) 0.25 M morpholinium hexafluophosphate/PC. The chronopotentiograms all showed flat potential plateaus and no transition times or other irregularities were observed. Good steady state voltammograms could be obtained. At currents of from 2.5 to 37.5 mA cm^{-2}, the potential of cathodization was, when corrected for iR drop, was +2.18 to +2.28 V vs. the Li^+/Li^0 electrode. The morpholinium ion is obviously reduced with considerable more ease than is the lithium ion.

(d) 0.1 M tetra n-propyl ammonium hexafluophosphate/PC. Reduction occurred at potentials positive to the lithium electrode. There was present in the salt an electro-reducible impurity, which underwent cathodic reduction at about +1.5 V vs. the $Li+/Li^{o}$ electrode. The observed limiting current for this reduction was 1.5 mA cm^{-2}, corresponding to a concentration of 0.005 to 0.01 M. At higher currents the reduction was still positive to the lithium electrode, being, for example, +0.27 V at 5 mA cm^{-2}.

(e) 0.1 M tetra n-propyl ammonium tetrafluoborate/PC. The material appeared free of electrochemically reducible impurities. Voltammetry was performed. The current-potential curves varied regularly from +0.84 V at 0.075 mA cm^{-2} to -0.13 V at 5 mA cm^{-2} vs. the Li^{+}/Li^{o} electrode.

(f) 0.1 M tetra n-propyl ammonium iodide/PC. There was evidence of a small amount of electrochemically reducible impurities present to the extent of about 0.001 to 0.002 M. Extensive cathodic measurements were not performed. Anodic chronopotentiograms on platinum gave reasonably well-defined transition times, with $i\tau^{1/2}$ = 43 mA cm^{-2} $sec^{1/2}$. This is about double that expected for a one electron change in a 0.1 M solution, and may reflect the greater mobility of the iodide ion.

(g) 0.1 M tetra n-butyl ammonium iodide/PC. Voltammetry was performed on platinum electrodes. The potential varied from +1.34 V at 0.05 mA cm^{-2} to +0.10 V at 6.5 mA cm^{-2} vs. the Li^{+}/Li^{o} electrode.

(h) 0.05 M $MgCl_2$/PC. No chronopotentiometric transition times could be obtained. On cathodization in both stirred and quiet solution the potential rose to extremely negative values. In a typical result, at 0.25 mA cm^{-2}, the potential gradually increased from +1.8 V to -24 V vs. the Li^{+}/Li^{o} electrode after nine minutes (135 mC cm^{-2} of cathodization). We ascribe this to the formation of resistive films on the electrode.

It can be seen that in none of the above examples does reduction occur at potentials sufficiently negative to the lithium electrode to allow the use of these materials in systems where they will be in prolonged contact with lithium metal; nor is their use as "supporting electrolytes" for the study of the lithium electrode indicated.

II-C-3-c-(6) Effects on long term cathodization.

The objective of this work was to determine what changes in solution composition can be detected by vapor phase chromatography following extended electrolysis. Of immediate interest was the degree to which water is electrolytically reduced in competition with the deposition of lithium.

The experiments were conducted in the same H-cell as shown later in figure 27, with the addition of two stopcocks to facilitate draining the solution. Fifty ml. of total electrolyte were used and, when level, the anode compartment contained 23 ml. of solution and the cathode compartment, 27 ml. In all the experiments here described the electrolyte was PC/0.1 M $LiClO_4$. Thus the cathode compartment contained 2.5 meq (milliequivalents) of the salt, and the anode compartment, 2.3 meq.

The cathode consisted of a platinum foil, 6 cm^2 in total surface area. After each electrolysis the cathode was immersed in water, supposedly to remove the lithium metal and deposits of lithium salts. An extremely tenacious black film remained on the electrode after immersion in water. To remove this film it was necessary to flame the electrode in a Meeker burner for several minutes. The red flame color, typical of lithium salts, was observed. Flaming was stopped when the red color was no longer apparent.

The anode consisted of a piece of lithium foil, about 10 cm^2 in total area. The reference electrode was simply a silver wire immersed in the cathode compartment. The potential of the cathode was continuously recorded with time against this reference electrode.

All electrolyses were conducted for a total of 120 coulombs. This is a total of about 1.24 meq-- about half the number of meq salt initially present in each compartment. It was the specific purpose of these experiments to continue electrolyses for such an amount that a significant fraction of the ions initially present shoudbe affected.

After electrolysis, vapor phase chromatograms were obtained, and were compared to those which were obtained for the same solution before electrolysis. The procedures used in vapor phase chromatography are subsequently described in Section IV.

The results are shown in Table 24 . In several cases the concentration of $LiClO_4$ in each compartment was determined, after electrolysis, by the following method. Five ml. aliquots were diluted to 100 ml. with water. The conductance of the solution was measured and compared with that of a standard 0.005 M $LiClO_4$ aqueous solution, containing 5% by volume of propylene carbonate. The accuracy of this method depends upon the truth of the assumption that the only ionic species are lithium and perchlorate ions, and that their equivalent conductance does not significantly vary for concentration changes in this range, ± 50%.

Some comment should be made regarding the potential observed at the working electrode during electrolysis. For all but the last four solutions, those with a water content of 0.456 M, the results were similar. On commencing cathodization, the potential immediately rose to -3.5 to -7.0 V vs. the silver wire, depending on the current. The difference between this initial potential and the expected open circuit potential of about -3.1 V is almost all iR drop. As electrolysis continued, the potential steadily, but slowly, became more negative, by as much as 5 V. We ascribe this both to the formation of resistive lithium salt films on the electrode and to the lowered conductance of the solution due to the depletion of ions as a result of electrolysis.

The potential-time behavior in the 0.456 M water solution was dramatically different. On the commencement of cathodization the potential immediately rose to a value positive to the open circuit potential of the lithium electrode, typically about -2 V vs. the silver wire reference electrode. The potential remained constant at this value for a period of time depending on the current. For example, for cathodization at 2 mA cm^{-2} , the potential remained at this lower value for about 16 min, or 1920 mC cm^{-2} of total deposition. Thereafter, there was an extremely sharp, almost vertical jump in potential to more negative values, typically - 10 V vs. the Ag wire reference electrode, and the potential change thereafter was linear with time. Potentials reached values of more than -50 V vs. the Ag wire reference electrode before the completion of electrolysis.

TABLE 24

PROLONGED CATHODICATION IN PC

Initial Water Concentration (M l^{-1})	Cathode Current Density (mA cm^{-2})	Estimated Limiting Current** (mA cm^{-2})	Final Water Concentration (M l^{-1})		Millimoles of water consumed in cathode Compartment
			Cathode Compartment	Anode Compartment	
0.007	1	0.14	0.011	0.011	none
0.012	1	0.24	0.014	0.014	none
0.014	1	0.28	0.014	0.016	none
0.010	2	0.20	0.006	0.009	0.11
0.014	4	0.28	0.006	0.011	0.24
0.082	0.3	1.6	0.060	0.076	0.59
0.082	1	1.6	0.074	0.064	0.22
0.082	2	1.6	0.057	0.074	0.67
0.082	4	1.6	0.052	0.064	0.81
0.168	0.3	3.4	0.135	0.106	0.89
0.168	1	3.4	0.137	0.141	0.84
0.168	4	3.4	0.124	0.151	1.08
0.168	4	3.4	0.111	---	1.54
0.456	1	9.1	0.436	0.402	0.54
0.456	1	9.1	0.409	0.302	1.27
0.456	2	9.1	0.436	0.409	0.54
0.456	4	9.1	0.402	0.402	1.46

** See page 27. For the one electron reduction of a univalent ion in the absence of supporting electrolyte we estimate a limiting current in PC of:
i_L(mA cm^{-2}) = 40 (C M l^{-1})

assuming the migration of water to the electrode is via an uncharged species the limiting current should be half this, since there is not electrical migration hence, we estimate a limiting current for water in m cm^{-2} = 20 (C M l^{-1})

The fact that this striking change in the potential - time behavior does not occur until over 4 moles of water have been added per mole of $LiClO_4$ may indicate that the initial water is preferentially bound by the perchlorate ion. One may imagine the hydrogen end of the water molecule to be oriented toward the perchlorate ion, and suppose this hydrogen to be kinetically inactive towards electrochemical reduction. Up to four moles of water may be bound by the perchlorate ion. Thereafter, the excess water combines with the lithium ions or exists as "free" or solvated water, and can be reduced electrochemically at the lower potentials. As reduction occurs, however, something happens either with the solution composition or on the electrode surface, by which this reduction becomes inhibited, and the potential immediately becomes more negative.

II-B. CONCLUSIONS. The Lithium Anode.

In order to justify secondary cell development, certain minimal performance requirements must be met by a system, operating in excess electrolyte. For the lithium electrode we have proposed that the performance objective in such initial screening should be 95% current efficiency for lithium deposition at 5 mA cm^{-2} to a capacity of 10,000 mC cm^{-2}, and that such performance persist for at least 10 cycles.

These objectives have not been realized in any of the five polar organic solvents examined in this work -- propylene carbonate, butyrolactone, dimethylformamide, dimethylsulfoxide, and acetonitrile. This is not surprising since lithium, or any "active metal", is thermodynamically unstable in contact with any polar organic compound, whether aprotic or not. The fact that one can obtain cycling behavior which approaches the objectives give in the preceding paragraph is most encouraging, since this indicates that the extent of parasitic processes is kinetically rather than thermodynamically determined. The fact that the rate of parasitic reaction is a function of so many variables -- the substrate, the solvent, the solute, the impurities, etc. -- is even more encouraging since one may then legitimately anticipate the discovery of systems in which parasitic reaction rates may be totally inhibited.

The work discussed in this section has led to the following conclusions. First, further research should be done in the construction and study of "experimental cells". These experimental cells should, in no sense, be considered "prototype cells", but rather as laboratory devices for determining what processes are, indeed, limiting in non-aqueous cell operation. In particular it is important to learn just how important is the conductivity of bulk electrolyte, and to obtain a clearer idea of reasonable parameters for electrode operation in non-aqueous cells. There is, to date, no assurance that non-aqueous cells will be any more similar in construction to present, conventional aqueous cells than are, for example, fuel cells.

Secondly, if a study of laboratory cell operation indicates that conductivity is not a principal problem, one is then confrOnted with a tremendous number of other systems which should be examined. As a result of the work described in this report, one may anticipate the kind of "screening experiments" which should be done. Basically, these experiments should involve accurate measurements of the current efficiency for lithium deposition over a range of current densities -- from the limiting current for lithium ion mass transport down to 1% of the limiting current. There should also be concurrent analysis for other reaction products arising from solvent decomposition. The basic number which should be obtained from such measurements is the rate of solvent decomposition in the strongly reducing environments which prevail at the anode. "Screening experiments" based on the apparent reactivity of bulk lithium with the solvent, or on cathodization at potentials positive to that of the lithium electrode, have little relevance to the determination of an accurate measure of the meaningful rate of solvent decomposition.

Third, a more detailed analysis of the processes occurring during lithium deposition is required. The objective of such experiments should be to determine whether there exist procedures by which the rate of concurrent solvent decomposition can be inhibited or the efficiency of lithium deposition enhanced. A better understanding of the processes which occur when a lithium ion,in the electrode - solution interface,accepts an electron would be useful. It may be that the process is not analogous to that which occurs in the electrodeposition of metals in aqueous solution, and that the poor form of the lithium deposit is a necessary result of a wholly different mechanism of electro-reduction.

III. CATHODES.

III-A. Introduction

Secondary cell cathodes are normally salts of metallic elements. Because of weight considerations salts other than oxides, chlorides, and fluorides can be eliminated from further discussion with respect to high energy density cells. Now oxides, chlorides, and fluorides are non-conductors if stoichiometrically and crystallographically perfect. Therefore, if cathodes were made of perfect salts there would be no satisfactory discharge behavior.

In fact, however, the salts from which cathodes are constructed are quite imperfect, and sufficient ionic conductivity is realized to allow incorporation of the salt in an appropriate structure. There is normally not too much useful information to be got from an examination of the properties of the salt as such, and one must resort to an empirical approach in which the variety of materials which ultimately form the "cathode" are all lumped together. One then observes the behavior of this complex system -- and normally the initial results are poor. Modifications must be made; typically such things as changing the particle size of the salt or conducting material and the relative amounts of the two substances are tried. In fact, there are so many variables involved that the proper method of cathode construction is usually the result of the application of an art rather than a science.

Although this conventional procedure for cathode study has been successful in the development of present day cells, it is doubtful whether the expense and time involved to produce rather marginal improvements justifies the procedure. We have, as a result of our work under this program, reached the conclusion that this conventional, emperical approach is woefully inefficient, and that the problem of secondary cell cathodes must be re-studied.

There are three processes which must occur for a secondary cell cathode to be cyclable:

1. On oxidation by anodization, an ionic species must be generated with good efficiency.
2. There must exist, in the environment in which these ionic species are formed, a reservoir of anions such that precipitation may occur.

3. The salt which forms by precipitation, following anodic oxidation must subsequently be available for discharge -- by whatever mechanism the salt discharge occurs.

The discussion of our work will be arranged according to these requirements. It will be realized, however, that this was not the order in which the work was actually done. This is because we did not appreciate, until fairly late in the program, how complex were the chemical and electrochemical problems, and hence how futile was an approach based on conventional procedures of battery development. Thus, much of the data are incomplete, having been collected before a full appreciation of the problem.

Basically, we believe a more detailed knowledge of the fundamental chemical behavior of the various systems is required. For example, solubilization may be induced by various means, thus it is relatively meaningless to speak of the solubility of CuF_2 in propylene carbonate, for example, if, in the actual cell electrolyte, the CuF_2 is solubilized through chemical reaction with the solute. A number of other chemical problems which have critical relevance to cell operation will be discussed.

Secondly, a better knowledge of the basic electrochemistry is required. By this we mean, not the total electrochemistry of a complete charge-discharge cycle, but rather the specific electrochemistry involved in the anodic dissolution of metals and in the cathodic reduction of insoluble salts.

III-B. Anodic Dissolution of Metals in Nonaqueous Solvents.

III-B-1. Introduction. In this section we are concerned only with what happens when a metal is anodically oxidized in various nonaqueous media. It will be shown that copper, silver, cadmium, and lead are oxidized to soluble ions with essentially 100% efficiency. It will be shown that the data on iron, cobalt, and nickel are not as well-behaved, and that anodic dissolution and subsequent cathodic reduction are inefficient. On this basis, copper, because of its higher energy density, will be selected as the element of primary interest.

III-B-2. Anodic-Cathodic Cycling Experiments

Each of the metals -- copper, silver, cadmium, lead, iron, cobalt, and nickel -- have been subjected to anodic-cathodic cycling experiments performed as follows: Electrodes, shown in figure 5, were prepared from discs of each of the metals of interest. In the appropriate electrolyte, each metal was anodically oxidized at various currents, in quiet solution, for 10 sec. Immediately after anodization the current was reversed. Theory predicts that if a soluble species is produced on anodization, and if this species is subsequently capable of undergoing cathodic reduction, there should be observed, for the cathodization which immediately follows the anodization, a transition time exactly equal to one-third the preceding time of anodization. Thus, if one anodizes silver metal to soluble silver ions, and this anodization is continued for 10 sec.; when one reverses the current there should be observed a transition time exactly 3.33 sec. after the current is reversed. Experimental verification of this relationship is a proof that one has obtained efficient anodic generation of the soluble metal ion.

In figure 26 are shown some typical results obtained in BL/0.1 M $LiBF_4$ at 5.6 mA cm^{-2}. Copper and silver behave ideally, and there can be little doubt that in this electrolyte, soluble copper and silver ions have been generated with essentially 100% efficiency on anodization.

However, in Figure 26 one observes that the behavior of iron, cobalt, and nickel is radically different. First we note the difference in potential between the anodization and the subsequent cathodization. This huge difference cannot be iR drop, otherwise comparable differences would have been observed for silver and copper. We must assume that the potential difference reflects the electrokinetic irreversibility of the process. It is even possible to make a rough estimation of the exchange current. To do this, we neglect any effects of concen-

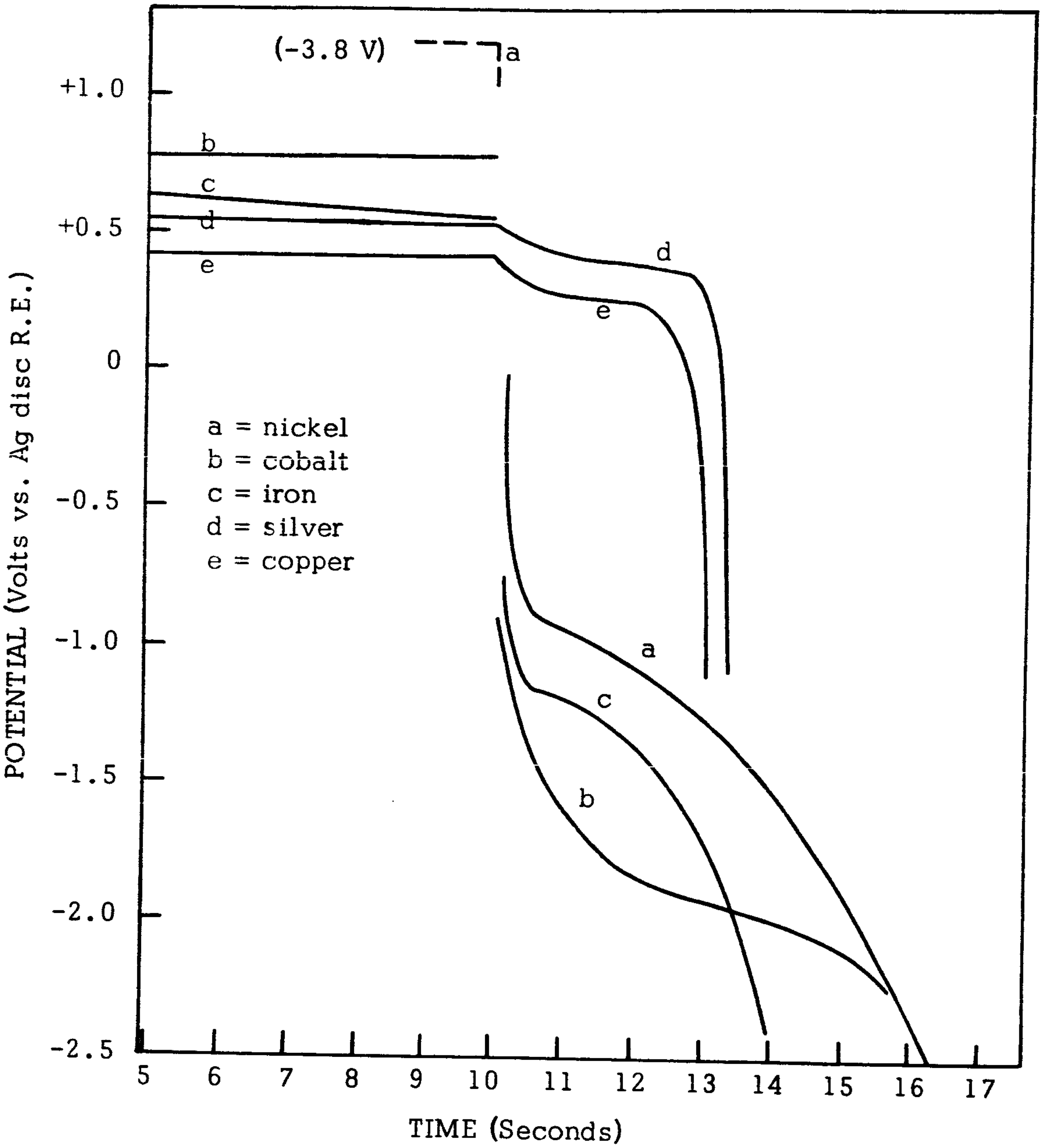


Figure 26: ANODIC-CATHODIC CYCLING IN BUTYROLACTONE

Obtained in BL/0.1 M $LiBF_4$ at 5.6 mA cm^{-2}. Potentials have been corrected for iR drop. The open circuit potential of a lithium electrode in this solution is about -3.0 V vs. the silver disc R.E.

tration polarization and make the approximation $1/2\ (E_{anod.} - E_{Cath.}) = 0.12 \log(i/i_o)$, in which i_o is the exchange current density, and the coefficient is calculated to be 0.12 assuming a stoichiometric number of 1 and a transfer coefficient of about 0.5. Thus, for nickel we would calculate an exchange current of 5.6×10^{-24} mA cm^{-2}, using 4,8 V as the potential difference. For cobalt, using 2.2 V as the potential difference, we calculate an exchange current of 25.8×10^{-11}. Finally, using 1.7 V as the potential difference for iron, one would calculate an exchange current of 2×10^{-8} mA cm^{-2}. These values are given merely to indicate how extremely small is the apparent exchange current. Now, on the high surface area which obtains in porous electrode structures an exchange current of 10^{-3} mA cm^{-2} is probably satisfactory. Exchange currents several orders of magnitude smaller than this would probably spell ultimate trouble.

Such anodic-cathodic cycling experiments were performed in propylene carbonate, dimethylformamide, and butyrolactone, in 0.1 M $LiBF_4$ solutions. At the time these experiments were performed we had not anticipated the use of acetonitrile or dimethylsulfoxide. Later experiments in these two solvents as well as for the first three solvents named were conducted for copper, silver, cadmium, and lead; and, in each case, 100% anodic efficiency was attested by the fact that the subsequent cathodic runs gave the expected transition times. We show below only the results obtained in the butyrolactone solution, since the results obtained in propylene carbonate and dimethylformamide were not significantly different in exposing the marked differences between copper and silver on one hand, and iron, cobalt, and nickel on the other.

Cycling Current	Metal Potential during anodization/Potential during cathodization				
(mA cm^{-2})	Silver	Copper	Iron	Cobalt	Nickel
1.0	+.46/+.42	+.42/+.30	+.50/-.75	+.75/-1.8	+1.8/-1.2
1.8	+.49/+.46	+.41/+.28	+.53/-1.3	+.75/-1.9	+2.0/-1.1
3.2	+.49/+.45	+.44/+.28	+.55/-1.3	+.75/-1.8	+2.2/-0.9
5.6	+.53/+.42	+.44/+.28	+.55/-1.2	+.85/-1.8	+2.2/-0.9
10.0	+.48/+.40	+.44/+.27	+.60/-1.2	+.85/-1.6	+3.0/-0.7
20	+.38/+.24	+.37/+.25	+.60/-1.2	+.8/-1.2	+4.0/-0.7

A problem with iron, cobalt, and nickel is not only that the apparent electrokinetic reversibility is bad, but that one cannot distinguish between electrochemical reactions involving the metal and oxidative decomposition of the electrolyte. Measurements of anodic decomposition of electrolyte have been made by us only in propylene carbonate, and the results are here presented mainly as an illustration of a process that is probably general for all the electrolytes of interest, and one which must be considered before drawing conclusions concerning the processes taking place during the apparently "irreversible" oxidation of metals.

In the experiments on propylene carbonate, platinum disc electrodes as shown in figure 5, were subjected to anodic oxidation, potentiostatically, in stirred PC/0.1 M $LiClO_4$. Satisfactory steady state currents were obtained at currents from 0.005 to 23 mA cm^{-2}. Correction for iR drop was made and the resultant current-potential voltammogram was expressed by the following equation:

$$E(\text{vs. Ag disc R.E.}) = +2.5 \quad + 0.34 \log i\ (\text{mA cm}^{-2})$$

This is significantly more positive than the potentials which were observed in the data shown on the preceding page, and, were a similar relationship to exist in butyrolactone, in which these data were obtained, one would assume that the comparison of the potential for anodization with that for anodic dissolution of solvent did, indeed, suggest that iron, cobalt, and nickel were undergoing anodic dissolution, though very irreversibly.

It was also interesting to note that the PC/0.1 M $LiClO_4$, when subjected to anodic oxidation, produced reaction products which could subsequently be cathodically reduced. Thus prolonged anodization was conducted in quiet solution at 4 mA cm^{-2}; the potential was +2.7 V vs. the Ag disc R.E.. When the current was reversed, reduction was observed at -0.5 V vs. the Ag disc R.E. and polarization did not occur until 30% utilization of the previously formed material was observed. Again, the large differences in anodic and cathodic potentials indicate the existence of extremely irreversible processes.

The apparent electrokinetic irreversibility of iron, cobalt, and nickel and the complications involved in separating the electrochemical behavior of these elements from possible side reactions led to the selection of copper as the element of primary interest.

III-B-3. Anodic Dissolution of Copper Metal

The anodic dissolution of copper was studied by long-term electrolyses, followed by chemical analysis. The cell used for these experiments is shown in Figure 27. The counter electrode compartment is shown on the right. The counter electrode itself was simply a platinum foil or coil, ca. 10 cm^2 in area. The working electrode compartment is shown on the left. The compartments were separated by a glass frit. The working electrode was a copper disc, cut from copper sheet. The diameter of the copper disc was slightly less than the inside diameter of the tube in which the electrode lay horizontally, supported by small indentations pressed into the tube. The area of the working electrode was about 5 cm^2. Electrical contact to the copper disc was provided in three ways. In Figure 27, the cell was provided with a Teflon covered copper wire entering through the side arm. In other cases the Teflon covered copper wire came up through the solution. In still another case, and this was the least satisfactory, electrical contact was provided by a bare platinum wire coming up through the solution. The working electrode was separated from the bulk of the solution in the counter electrode compartment by a glass fiber separator. This was held in place by two Teflon retaining rings, as shown in Figure 27.

After each electrolysis the solutions were analyzed as follows. A one-ml portion of the solution above the separator was diluted to 40 ml. with an aqueous NH_3/NH_4Cl solution and the amount and nature of copper (whether +1, +2, or both) determined polarographically. Then the separator and electrode were removed, the entire counter electrode solution mixed, and a one ml. aliquot again extracted and analyzed polarographically.

The results are shown in Table 25 on the next page. The experiments are numbered for convenience in discussion. In the second column are shown the conditions under which the experiment was performed. The third column gives the total current passed, not the current density. This current was passed for an amount of time required to give the total coulombs shown in the fourth column. The next two columns give the results of the polarographic analyses. The upper figure is the amount of copper found in the solution above the separator; the lower figure is the amount of copper found below the separator. This was calculated from the total amount of copper found after mixing the two solutions.

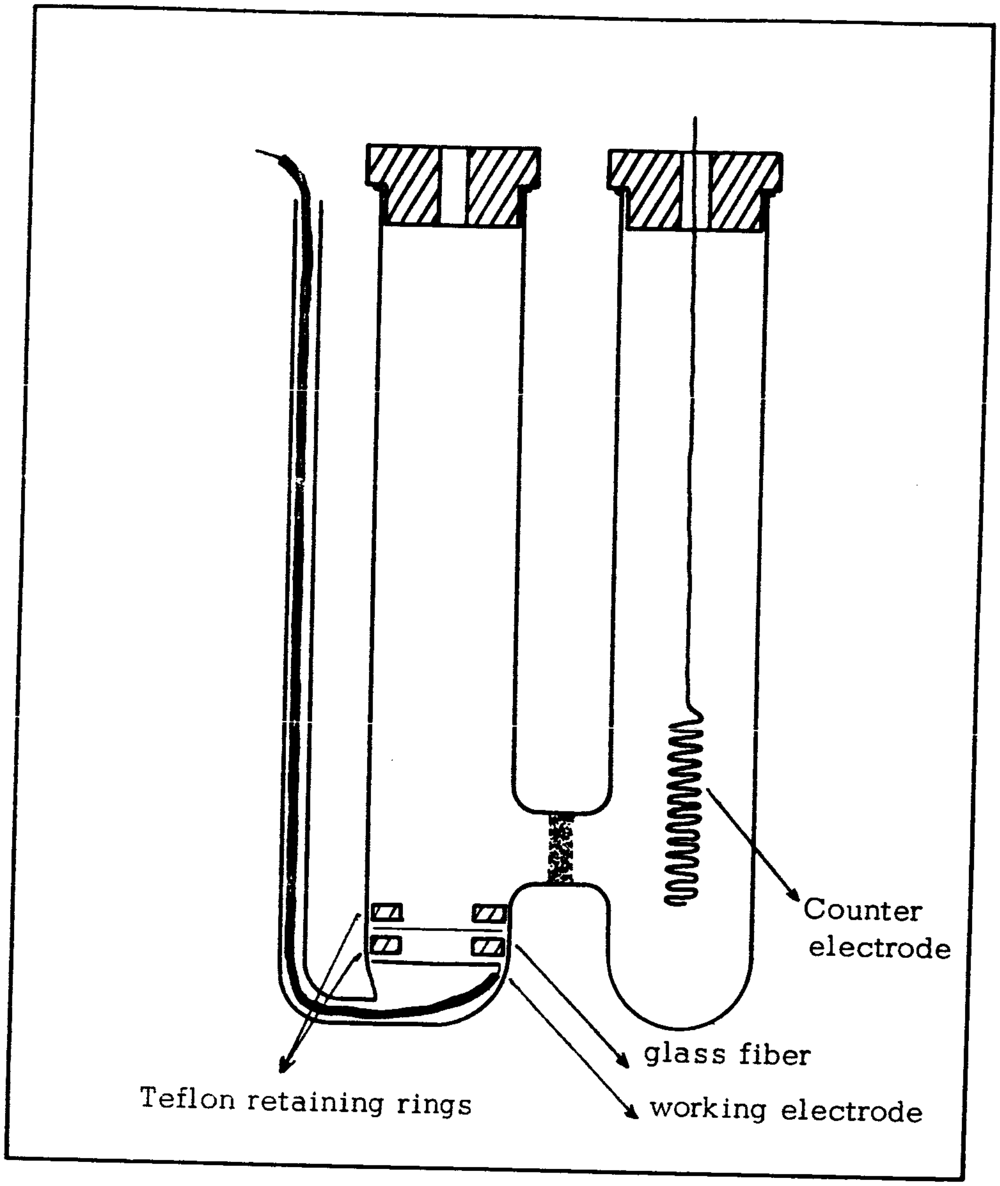


Figure 27: CELL FOR STUDIES OF ANODIC DISSOLUTION OF COPPER

Table 25

Anodic Dissolution of Copper

No.	Conditions	Current	Coulombs Passed	Millimoles of copper Recovered		Coulombs Recovered
				Upper Solution Lower Solution		
				Cu (I)	Cu (II)	
1	PC-1	12	57.5	0.124	0.213	53
2	PC-1	12	115	0.528	0.489	145
3	PC-2	12	87	0.380	0.209	77
4	PC-3	12	129	0.124 0.473	0.192 0.112	116
5	PC-4	12	129	0.154 0.628	0.102 0.219	137
6	PC-4	2.25	129	0.029 0.482	0.193 0.204	126
7	PC-5	2.25	129	0.190 0.166	0.332 0.072	112
8	PC-6	12	131	none 0.383	0.119 0.140	87
9	PC-8	12	129	none --	0.206 --	--
10	BL-3	12	108	0.340 0.253	0.057 0.073	87
11	BL-6	12	129	0.142 0.565	0.018 0.124	97
12	BL-7	12	129	0.407 0.414	0.100 0.168	131
13	BL-7	1	234	0.572 0.107	0.554 0.142	200

Table 25 (Cont'd.)

No.	Conditions	Current	Coulombs Passed	Millimoles of Copper Recovered		Coulombs Recovered
				Upper Solution Lower Solution		
14	BL-4	12	129	0.271 0.759	0.089 0.280	170
15	BL-8	12	129	none --	0.233 --	--
16	AN-4	2.25	129	only copper (I), no analysis because volume of final solution not known.		
17	DMF-4	2.25	129	none none	0.289 0.441	141

Conditions symbols:

All measurement in solvent indicated, 0.1 M in $LiClO_4$. Number following solvent symbol indicates the following:

1 - no separator, no deaeration, Pt wire lead through solution
2 - no separator, continuous deaeration, Pt wire lead through solution
3 - with separator, continuous deaeration, Pt wire lead through solution
4 - with separator, continuous deaeration, Teflon covered Cu wire lead through side arm
5 - Same as 3 above, but lower compartment filled with solid LiF
6 - Same as 3 above, but two layers of separator used, with solid LiF spread between
7 - with separator, continuous deaeration, Teflon covered Cu wire through solution
8 - Same as 4 above, but with salt between two layers of separator. in PC salt was LiF; in BL salt was KF.

and subtracting from the total amount of copper, that previously found by analysis of the solution above the separator. Finally, the last column gives the total number of coulombs recovered. This is calculated from the total amount of each species of copper and the Faraday.

Experiments 1, 2, and 3 were performed without the separator. We have some doubt about experiments 1 and 2 since the solutions were not deaerated, and there may have been significant air oxidation, or the results might reflect some water pick-up. Experiment 3, performed without the separator, is in quite satisfactory agreement with experiments 4 and 5, performed with the separator. All three experiments show about twice as much copper (I) produced as copper (II). Experiment 6 was performed at a lower current and the ratio of the copper species changed. Another difference results from whether or not electrical contact was provided via the side-tube. This is because the Teflon retaining rings could more tightly fit in the tube if the side-tube cell was used; since, otherwise, the retaining rings had to be cut enough to provide for the electrical contact coming up through the solution, and there was probably some leakage. It was particularly interesting to note that apparently the relative amount of copper (I) passing through the separator into the upper solution was significantly less than the relative amount of copper (II).

Before continuing the discussion of the data in Table 25, it is useful to consider the processes by which copper moves from the lower to the upper compartment. We believe this is largely by electrical migration rather than by diffusion, otherwise we would have expected a larger amount of transport. Consider experiments 5 and 6. The upper compartment contains about 22 ml. of solution and the lower compartment, about 3 ml. Thus we calculate the following concentrations:

	Expt. 5	Expt. 6
Copper (I) above separator	0.007 M	0.0013 M
Copper (I) below separator	0.21 M	0.16 M
Copper (II) above separator	0.005 M	0.009 M
Copper (II) below separator	0.073 M	0.068 M

Now experiment 5 lasted 3 hours and experiment 6 lasted 16 hours. Were diffusion the predominant mode of mass transport one would surely have expected the large concentration gradient existing across the separator to have induced a greater amount of transport than that observed. In addition, were diffusion important the longer term experiment 6 should have shown significantly greater transport than the shorter term experiment 5.

We may continue this analysis by recalling that the extent of migration should be proportional to the transport number. This, in turn, will be related to the concentration of the specific ion, the total ionic concentration, and the equivalent conductances of the various ionic species. As electrolysis begins, perchlorate ions should migrate into the lower compartment, and lithium ions should migrate out. The total ionic concentration will increase. When, as a result of continued electrolysis, the copper species comprise a significant fraction of the total ions, they will also participate in the migration of cations out of the compartment. In this context it is particularly interesting to note that apparently the copper (II) migration is significantly larger than the copper (I) migration.

We continue the discussion of the data in Table 25. Experiment 7 was performed, following partially filling the lower compartment with solid LiF. While, the total coulombs recovered is in reasonable agreement with the number of coulombs passed, there is a marked change in the relative amounts of copper species above and below the separator when compared with experiment 6. We believe this is because the actual solution volume in the lower compartment was significantly less than in experiment 6, in which case one would expect more migration to occur earlier.

Experiment 8 was different from experiment 4 in but one respect. Two layers of separators were used, and between the two separators was placed a layer of solid LiF. Comparing the results of the two experiments it would appear that copper (I) had been trapped in the LiF, possibly by the reaction $Cu^+ + LiF = CuF + Li^+$.

Experiment 9 showed similar results. It was different from experiment 8 in that the side-tube cell was used, hence there was tighter separation. However, this did not allow us to conveniently remove the separator and analyze the lower solution, and the results are therefore incomplete.

Experiments 10 - 15, performed in butyrolactone, were not consistent at all. Particularly distressing were the large positive and negative results obtained when the coulombs of recovered were compared with the coulombs passed. Positive results might result through the analytical procedure. If, for example, the solution used for the polarographic measurements were not sufficiently deaerated, some air oxidation of copper (I) might occur, giving positive results. Negative results are more difficult to explain. It is possible that, in experiments 10 and 11, where the platinum wire lead was used, that the resistance across the separator might have been sufficiently large that a significant amount of parasitic oxidation of electrolyte occurred along the platinum wire. Clearly, more experimental work is required before the anodic behavior of copper in butyrolactone can be established.

Experiment 16 was performed in acetonitrile. After the sixteen hours of electrolysis, with continuous deaeration, the volumeof solution was reduced by almost half. The polarograms showed only copper (I) to be present, but since an accurate measure of the remaining volume of solution had not been made, no analyses were performed.

Experiment 17 needs no further comment.

The experiments described above are, of course, merely exploratory. However, they do focus attention on at least two important aspects concerning the copper electrode which have received relatively little attention to date in connection with nonaqueous cells. The first concerns the relative stability of copper (I) and copper (II) in different electrolytes. The second concerns the possible effects of the transport properties. One may speculate that if diffusion is small, and if the species produced on anodic oxidation are mostly unchanged though not necessarily insoluble, that one may be able to use such species as members of a cyclable redox couple.

III-B-4. Anodic Dissolution of Electrodeposited Copper.

The experiments described in the preceding section are rather involved; and more study is required to develop the procedures to the point where one can have sufficient confidence in the results. Short term experiments were thus attempted. These experiments first involved depositing copper metal on polished platinum substrates (the disc electrodes shown in figure 5 were used). After deposition the electrodes were removed from the aqueous $CuSO_4$ solution in which deposition was effected and were thoroughly rinsed first with water, then acetone, and finally dried under a stream of warm air. Deposition was conducted for 100 sec. at 25 mA cm^{-2}. To insure that deposition was efficient, and that the subsequent drying and cleaning did not result in a significant loss of metallic copper, deposited electrodes were put through the same procedure as was later followed before immersion in the nonaqueous electrolytes. Then they were re-immersed in the aqueous solution and the deposited copper anodically stripped. Efficiencies of 95 - 100% were realized.

Such electrodeposited copper electrodes were anodically oxidized in each of the five solvents of interest, PC, BL, DMF, AN, and DMSO. Each solution was 0.5 M in $LiClO_4$. Anodizations were conducted at several currents. The anodic discharge curves were flat (potential vs. time) until the complete dissolution was marked by the reappearance of the shiny platinum substrate, and a sharp change in the potential to more positive values.

The efficiency is obtained by dividing the coulombs of current required to anodically effect complete dissolution of the copper by the number of coulombs which had passed during the preceding deposition in aqueous solution. Since copper was deposited from a solution of copper(II) ($Cu^{++} + 2e^- = Cu^o$), then, if anodic dissolution proceeds with the formation of copper (II) from the metal, 100% stripping efficiency should be realized. On the other hand, if anodic dissolution proceeds with the formation of copper (I), the stripping efficiency should only be 50%. If mixtures of copper (I) and copper (II) are formed, efficiencies will vary between 50 and 100%. The results are shown in table 26, below.

Table 26

ANODIC DISSOLUTION OF ELECTRODEPOSITED COPPER

Current (mA cm^{-2})	Stripping efficiency in PC	BL	DMF	AN	DMSO
0.5	--	--	---	--	50%
1.0	79%	60%	92%	--	52%
2.5	--	61%	98%	45%	--
4.0	--	--	94%	--	--
5	70%	64%	93%	47%	57%

The results indicate that in acetonitrile and dimethylsulfoxide the product of anodic dissolution is essentially all copper (I). In dimethylformamide the product is essentially all copper (II). In butyrolactone mostly copper (I) is produced, with a significant fraction of copper (II). And in propylene carbonate approximately equal amounts of both species are the product of anodic oxidation.

III-B-5. Conclusions. While the data are far from complete, it appears probable that copper is anodically dissolved with 100% efficiency, but that the products of the reaction, copper (I) and copper (II), form in ratios quite different depending on the solvent. While cobalt, nickel, and iron may be anodically oxidized to the soluble ions, they appear to form members of extremely irreversible redox couples with such small exchange currents that their use in secondary cell cathode systems is excluded unless there be some particular environments in which the exchange current is markedly increased.

III-C. Insolubilization of Cathode Salts.

The acquisition of accurate solubility information is a major experimental task. In work which we have done in this area, we have made no attempt to undertake the rigorous purification procedures necessary before reliable data can be obtained, but merely have sought to get some preliminary indication of the solubility of various cathode salts of interest under those conditions under which we expected to study their electrochemical behavior.

We were primarily interested in the copper salts -- CuF_2, CuCl, and $CuCl_2$. While the reagent grade chloride salts were deemed sufficiently pure, and further analysis was not undertaken, there was some question about the purity of the CuF_2. X-ray diffraction was used for this analysis.

A major problem with this material involves the pick-up of water. The extent of this is shown by the data below where 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 to either CuF_2 or $CuF_2 \cdot 2H_2O$. Furthermore, the relative intensities of the lines agree satisfactorily with those values given in the literature. For convenience we compare the intensities of the strongest line for each material; for CuF_2 at 3.219Å and for $CuF_2 . 2H_2O$, at 4.72 Å.

	Relative Maximum Intensity	
	CuF_2	$CuF_2 . 2H_2O$
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 (one sample), pressed at 6000 lb		
after 1 hr	5.8	2.0
after 6 hr	4.5	3.0
after 23 hrs	3.0	4.3
after 47 hrs	2.0	4.8
Powder, placed in desiccator with water overnight	0.0	3.7

These results show that the pickup of water is considerable, and all subsequent data must be considered in this light.

The solubility of CuF_2 in four of the five solvents of interest was examined. Dimethylsulfoxide was not used, since we had not included it in the program at the time this work was done. To a 50 ml. sample of solvent was added enough solid CuF_2 such that, if totally soluble, the solution would be 0.1 M in the salt. The samples were allowed to stand at room temperature, with frequent agitation, in plastic stoppered flasks for one month. After this period of time the specific conductance of the solution was measured. The concentration of dissolved copper was also measured polarographically, by adding a ten ml. aliquot of the solution to 90 ml. of an aqueous NH_3/NH_4Cl, and comparing the polarograms with those of standard copper solutions. The results are shown in Table 27 below:

Table 27

SOLUBILITY OF CuF_2 IN PC, BL, DMF, AND AN

Solvent	Analytically Determined Conc. ($M\ l^{-1}$)	Specific Conductance ($ohm^{-1}\ cm^{-1}$)
Propylene carbonate	0.00016	3.5×10^{-6}
Butyrolactone	0.00022	5.1×10^{-6}
Acetonitrile	0.00075	2.3×10^{-4}
Dimethylformamide	0.00034	1.4×10^{-5}

These low solubilities were somewhat reassuring in view of the fact that the X-ray data, described previously, indicated a substantial amount of $CuF_2.2H_2O$ in the salt. In fact a rough estimate may be made in view of the fact that the sum of the maximum intensities for the single sample which was allowed to sit exposed for a total of 47 hrs are about the same after each of the four times when the X-ray spectrum was run. Thus, we calculate for the powder, directly from the bottle, that about 18% of the total CuF_2 exists as the hydrate. Nevertheless, as can be seen in Table 25, the maximum solubility in any case was less than 1% of the total CuF_2 present in contact with the solvent.

We have not examined the solubility of the other two copper salts, CuCl and $CuCl_2$ in any of the solvents of interest, alone.

The solubilities of the three copper salts were also examined in three solvents, propylene carbonate, dimethylformamide, and butyrolactone, in the presence of each of four lithium salts, LiCl, $LiClO_4$, $LiAlCl_4$, and $LiBF_4$. At the time these measurements were made, we also had some interest in tetrahydrofuran; and measurements were also made with this solvent. In dimethylformamide the solubilities were not measured, unfortunately, since, in most cases it was observed that the color of the solutions was considerably deeper than for the propylene carbonate solutions and we assumed the solubility of the copper salt was larger than in the other two solvents. This is probably true, but it would have been good to have the data.

The data were obtained as follows. To a 50-ml. sample of solvent was added an amount of solid lithium salt such that the concentration, if totally soluble, would be 0.1 M. An amount of copper salt was added such that the concentration, if totally soluble, would be 0.05 M. The solutions were stoppered and allowed to equilibrate, with frequent agitation, for two weeks. The results are shown in Table 28 on the next page. Where we have the data, we also show, at the top of the table, the specific conductance of a solution of the lithium salt alone at a concentration of 0.01 M.

Table 28

Solubility of Copper Salt - Lithium Salt Solutions

NOTE: All conductivities should be multiplied by 10^{-4} to give the conductivity in ohm^{-1} cm^{-1}. Thus a value of 11.5 means a specific conductivity of 11.5 x 10^{-4} ohm^{-1} cm^{-1}.

Salt Combination

Solvent

First line: Conductivity (see above note)
Second line: Concentration of Cu^{++} (M l^{-1})
Third line: Color (RO = red orange, O = orange, YG = yellow green G = green, and LtB = pale blue); XX = no visible solid material.

	PC	BL	DMF	THF
LiCl/---	5.1 (sat'd)	---	---	---
LiCl/CuCl	11.5 Y ---	16.0 Y ---	39.7 Y ---	2.5 Y ---
LiCl/$CuCl_2$	12.4 0.049 XX, O	14.8 0.049 XX, O	32.3 --- XX, O	2.1 --- XX, O
LiCl/CuF_2	7.2 0.029 O	7.9 0.030 RO	14.9 --- XX, O	0.4 --- O
$LiClO_4$/---	17.5	23.5	---	---
$LiClO_4$/CuCl	17.8 --- XX, YG	26.1 --- O	51.9 --- XX, YG	0.7 --- YG
$LiClO_4$/$CuCl_2$	17.7 0.048 XX, YG	25.7 0.008 Y	51.0 --- XX, YG	0.7 --- YG
$LiClO_4$/CuF_2	17.6 0.027 LtB	25.0 0.002 LtB	45.5 --- G	0.5 --- LtG
$LiAlCl_4$/--	20.2	---	---	---
$LiAlCl_4$/$CuCl_2$	20.8 0.023 RO	20.7 0.046 RO	41.1 --- Y	15.3 --- O
$LiAlCl_4$/CuCl	19.3 --- O	33.6 --- XX, RO	50.6 --- Y	13.8 --- O

Table 28 (Cont'd)

Legend: First line: Conductivity
Second line: Measured concentration of Cu^{++}
Third line: Color of solution (see symbols on preceding page)

	PC	BL	DMF	THF
$LiAlCl_4/CuF_2$	17.8 0.013 O	24.0 0.010 O	44.0 --- Y	11.7 --- O
$LiBF_4$/---	16.2	22.5	57.5	---
$LiBF_4/CuCl$	16.7 --- YG	24.9 --- YG	54.6 --- YG	0.4 --- Y
$LiBF_4/CuCl_2$	16.7 0.049 XX, YG	24.4 0.006 Y	41.1 --- XX, YG	0.3 --- O
$LiBF_4/CuF_4$	16.5 0.022 LtB	22.6 none LtB	48.5 --- G	0.2 --- LtB

We draw no conclusions concerning the mixtures containing CuCl. It is improbable that a solution of copper (I) would be colored -- contrary to many examples in Table 28. In the absence of further experimentation it is more reasonable to conclude that significant oxidation of copper (I) to copper (II) may have occurred, probably because of our failure to deaerate the solutions prior to the addition of CuCl.

Some comment concerning the colors is in order. A fairly deep red color is typical of more concentrated chloro-cuprate (II) complex ions. When such solutions are diluted, the red color becomes increasingly less pronounced and finally the solutions are only a faint yellow. On the other hand, a red to yellow color is typical of solutions in which $AlCl_3$ is dissolved, probably through solvent decomposition. Thus, in the $LiAlCl_4$ solutions, one has the possibility that $AlCl_3$ has been formed through donation of a chloride to the copper species, and this has produced the coloration.

The conductivity data are interesting since they show that there is not, in most cases, a change in conductivity proportionate with the increasing solubility of copper species. This suggests more specific interactions, inducing solubilization of the copper salts.

Finally, the question of impurities cannot be overlooked. One would presume the impurities to be largely resident in the solvent rather than in either the lithium or the copper salts. Thus one may compare the $LiClO_4/CuCl_2$ system and the $LiBF_4/CuCl_2$ system in PC and BL. In both systems $CuCl_2$ is less than one-tenth as soluble in BL as in PC, and this should not be true if solubility is primarily a function of the impurities in either of the two copper-lithium salt combinations. It would also appear that the impurity, if this is indeed the source of solubilization, is not water. This can be seen by comparing the results in Table 27 with those in Table 28. Considering the significant amount of water already in the CuF_2 (as $CuF_2.2H_2O$), it is difficult to see why the solubility should show such a marked increase in the $PC/LiClO_4$ and $PC/LiBF_4$ systems, were the presence of water the source of solubilization.

It is clear that the data shown in Table 28 is, like so much of the data accumulated in the field of nonaqueous cell development, not interesting in itself so much as in suggesting the existence of other phenomena which may have relevance to cell operation. In particular, we are concerned with the solubilization of copper salts through more specific interactions with the electrolyte. We consider two simple types of reactions: the solubilization of $CuCl_2$ and CuCl through chloro-complexation, and the solubilization of CuF_2 through displacement by lithium ions.

The complexation of $CuCl_2$ was shown by performing a conductimetric titration. $CuCl_2$ was added to 100 ml. of propylene carbonate in such an amount that, if totally soluble, the concentration would be 0.1 $M\ l^{-1}$. The solution was stirred and the conductivity measured with a dip cell. Conductivity measurements were made until constant values were attained. Then successive portions of solid LiCl were added and stirring continued. The results are shown below:

Concentration of LiCl added if totally soluble ($M\ l^{-1}$)	Specific Conductance ($ohm^{-1}\ cm^{-1}$)
0.000	1.2×10^{-4}
0.049	10.0 "
0.103	18.7 "
0.154	23.4 "
0.21	24.8 "
0.27	24.8 "
0.33	22.4 "

This is, of course, a conventional technique for investigating the stoichiometry of reactions. A plot of the data show two straight lines which meet when one mole of LiCl has been added per mole of $CuCl_2$, from which one would assume the reaction to be: $LiCl + CuCl_2 = Li^+ + CuCl_3^-$.

An identical titration was performed using CuCl rather than $CuCl_2$. When LiCl had been added in sufficient quantity to make the solution 0.1 M if totally soluble, the specific conductance was $21.4 \times 10^{-4}\ ohm^{-1}\ cm^{-1}$. Tripling the concentration of added LiCl increased the conductance to only $22.9 \times 10^{-4}\ ohm^{-1}\ cm^{-1}$, from which one would conclude that CuCl dissolves by: $LiCl + CuCl = Li^+ + CuCl_2^-$.

Finally, CuF_2 was also titrated with solid LiCl. It will be noted in Table 28 that the solubility of CuF_2 is the same in the LiCl/PC and the LiCl/BL systems. However, for the reasons discussed earlier, it was feared that the propylene carbonate was the more impure and butyrolactone was used for the titration. Preliminary experiments indicated that the rate of equilibration was very slow, as attested by steadily increasing specific conductances, and the titration was effected by preparing a set of mixtures. Each datum shown below was obtained from one of this set of eight mixtures, after equilibration for one week:

Concentration of LiCl added, if totally soluble $(M\ l^{-1})$	Analytically Determined Conc. of Cu^{++} $(M\ l^{-1})$	Specific Conductance $(ohm^{-1}\ cm^{-1})$
0.03	0.0125	1.57×10^{-4}
0.05	0.0145	3.04 "
0.10	0.0261	7.65 "
0.13	0.0343	10.9 "
0.16	0.0400	12.3 "
0.25	0.0452	13.5 "
0.35	0.069	17.1 "
0.45	0.079	19.1 "

The results clearly indicate the solubilization of CuF_2 through chloride complexation, but are not sufficiently clear-cut to indicate the stoichiometry of the solubilizing reaction.

A second type of solubilizing reaction is the displacement reaction: $CuF_2 + 2\,Li^+ = 2\,LiF + Cu^{++}$. We write this reaction as the sum of four separate reactions as shown below. Since the potential measurements to be subsequently described were made against a Ag/Ag^+ reference electrode, the data shown below are given versus this couple. The data are for aqueous solution and are obtained from Latimer's monograph.

$$
\begin{array}{ll}
CuF_2 = Cu^o + F_2 & \Delta G_1 = +116 \text{ kcal } M^{-1} \\
Cu^o + 2\,Ag^+ = Cu^{++} + 2\,Ag^o & \Delta G_2 = -21 \quad " \\
2\,Li^o + F_2 = 2\,LiF & \Delta G_3 = -279 \quad " \\
\underline{2\,Li^+ + 2\,Ag^o = 2\,Li^o + 2\,Ag^+} & \underline{\Delta G_4 = +177 \quad "} \\
CuF_2 + 2\,Li^+ = 2\,LiF + Cu^{++} & \Delta G = -7 \text{ kcal } M^{-1}
\end{array}
$$

These data are, of course, for aqueous solutions. The point to be made is that the free energy change is relatively small, corresponding to an equilibrium constant of about $10^5 = (Cu^{++})/(Li^+)^2$. One would expect a change in the value of the free energy in going from aqueous systems to other solvents. This is because the equilibrium depends primarily on the relative solvation energies of the copper (II) ion and the lithium (I) ion.

Theoretically, the equilibrium could be examined by preparing mixtures in various proportions of CuF_2 and an appropriate lithium salt. This is unduly laborious and presents more stringent demands on purification and analysis than yet seems possible.

An alternative procedure is to measure the potentials of the copper (II)/ copper metal and the lithium (I)/lithium metal half reactions in various solvents against some appropriate reference electrode. These will give us the sum of the ΔG_2 and ΔG_4 terms on the preceding page; from which the free energy is then computed, ΔG_1 and ΔG_3 being invariant.

This was the procedure adopted by us and the purpose of the experiments to be described was to obtain some preliminary indication of whether there existed such marked changes in solvation energy as to expect a dramatic shift in the free energy for the displacement reaction.

The procedure used by us for determining the formal reduction potentials of various metals in nonaqueous solvents involved the in situ generation of the metal ions. Specifically the metal of interest was anodically oxidized in quiet solution for a given period of time; the open circuit potential immediately after the current was turned off was the quantity of interest. The means by which this was used to determine the formal reduction potential will be described.

A conventional H-cell as shown in Figure 4 was used. The large compartment contained about 200 ml. of electrolyte and in this compartment sat the lollipop disc electrode assembly shown in Figure 5, constructed for each of the metals of interest. A platinum coil in the same compartment served as the counter electrode. The small amount of total current passed through the counter electrode during the course of a series of runs was not enough to sensibly affect the composition of the solution.

Both compartments were 0.5 M in $LiClO_4$. The purpose of using the fairly concentrated $LiClO_4$ solutions was three-fold: to inhibit the development of density gradients during electrolysis and subsequent convective effects, to maintain the activity coefficient constant, and to prevent ionic migration.

The reference electrode was particularly critical. In the small side chamber of the H-cell (25 ml.), filled with 0.5 M $LiClO_4$ solution, was placed a silver wire. In addition, the solution was made 0.01 M in $AgClO_4$. Thus the reference electrode was a Ag/0.01 M Ag^+ system, and all potentials were measured with respect to this.

The measurements were made as follows. The silver working electrode disc was anodized for 25 sec. at various currents. The potential of the working electrode vs. the reference electrode was continuously recorded from the beginning of anodization to about 10 sec. after the completion of anodization -- 35 sec. The recorder used has a time lag of about 0.5 sec. per full scale deflection, so we arbitrarily chose the open circuit potential, exactly 0.5 sec. after stopping the anodization, as the potential of interest. Now, during anodization, silver ions are being formed and are diffusing away from the electrode. If, however, one arbitrarily selects a constant time for anodization, there will exist at the electrode surface on cessation of anodization, a concentration of silver ions whose concentration should, theoretically, be directly proportional to the current. Since the potential should be related to the concentration by: $E = E_o + \frac{0.059}{n} \log (Ag^+)$, and since $(Ag^+) \propto i$ the plot of potential vs. log i should be linear, providing one measures the potential under the correct conditions. In our procedure, the O.C.V. exactly 0.5 sec. after stopping the anodization was plotted versus the logarithm of the current. The plots were, indeed, linear over two decades of current; the slope was not exactly 0.059/n, but this was ascribed to the arbitrary choice of using the potential 0.5 sec. after anodization, under which conditions the diffusion away from the electrode during the first 0.5 sec. would not be proportionately the same for all currents.

The plots of E vs. log i for the silver electrode crossed the E = 0 axis at a particular current. Since the potential was measured versus a silver electrode in a 0.01 M $AgClO_4$ solution, we assumed that this particular current was the current which generated an amount of silver ions such that, 0.5 sec. after stopping the anodization, the concentration of silver ions at the electrode surface was also 0.01 M, since the potential then was the same as that of the reference electrode. The assumption is perfectly true provided, only, that the exchange current is sufficiently large that the measured potential reflects the equilibrium potential.

We shall call this current, $i_{0.01\ M}$. It is the current which must be passed in a given electrolyte for a given period of time which will generate an amount of silver ions such that the concentration of ions at the electrode surface, 0.5 sec. after stopping the anodization is 0.01 M. Then, the same procedure is followed for copper, lead, and cadmium electrodes. The latter two materials are merely used as further checks on the procedure. In each case a plot of the potential, 0.5 sec. after anodization is halted, is made versus the logarithm of the current. Again, linear plots were obtained over almost two decades of current. We than assume that the diffusion coefficients of the copper, lead, and cadmium species generated are sufficiently similar to that of the silver ion to allow us to assume the continued validity of $i_{0.01\ M}$. This assumption is quite sufficient for our purposes; a difference in the diffusion coefficients of a factor of two would, in fact, ultimately result in an error of only 10 mV for a two-electron oxidation. Now, since lead and cadmium undergo two-electron oxidations it would be incorrect to take the potential at $i_{0.01\ M}$ as that corresponding to a 0.01 M concentration of these species; rather, twice the current is required for the 25 sec. anodization. The potential corresponding to this current, twice the value of $i_{0.01M}$, is taken as the formal reduction potential of the lead or cadmium couple in the electrolyte for a 0.01 M solution. For copper, we must decide whether the oxidation is a one or a two electron oxidation. For simplicity, we have assumed that in all but dimethylformamide, the potential reflects the one-electron oxidation to copper (I), and therefore we take the potential off the potential vs. log i plot at $i = i_{0.01\ M}$.

These measurements were made in each of the five solvents of interest and also in aqueous solution, 0.5 M in $LiClO_4$. The results are shown in

Table 29 below. In addition, lithium was electrodeposited on the center silver disc electrode of the structure shown in Figure 5 and the open circuit potential of the electrodeposited lithium electrode measured versus the silver/silver ion reference electrode. In Table 29 we also show the calculated potentials for aqueous solution, using the simple Nernst equation and the standard reduction potentials, without further corrections.

Table 29

Formal Reduction Potentials in Nonaqueous Solvents

Measured potential of metal/metal ion (0.01 M) couple versus silver/silver ion (0.01 M) couple in solvent indicated, made 0.5 M in $LiClO_4$. The lithium potential is for the lithium/lithium ion (0.5 M) couple.

			Couple		
	Cu^+/Cu	Cu^{++}/Cu	Pb^{++}/Pb	Cd^{++}/Cd	Li^+/Li
PC	-0.15	--	-0.83	-0.94	-3.67
BL	-0.21	--	-0.82	-0.96	-3.60
AN	-0.58	--	-0.42	-0.66	-3.20
DMF	--	-0.41	-0.80	-1.09	-3.80
DMSO	-0.35	--	-0.82	-1.02	-3.59
H_2O (Expt.)	--	-0.37	-0.85	-1.09	--
H_2O (Calc.)	-0.28	-0.40	-0.87	-1.12	-3.74

The only major difference is observed in acetonitrile. This is not surprising. It is, in fact, well known that a shift in the E.M.F. series as shown in Table 29 occurs in this solvent because the solvation energies of copper (I) and silver (I) are unusually large in acetonitrile compared to the other ions, and this results in a shift in the entire series to more positive values.(27)

It may be argued that the data reflect the presence of water. While we estimate the concentration of water in this work to be about 0.01 M, as will be discussed in the later section on purification, the argument is still cogent.

(27) I. M. Kolthoff, *J. Polarographic Soc.*, *10*, 22 (1965).

The obvious picture, often advanced, that small amounts of water effect strong thermodynamic changes should not, however, be too readily accepted. We may consider a propylene carbonate solution, 0.5 M in $LiClO_4$, 0.1 M in water, and 0.01 M in some ion such as cadmium, for example. The solution will be approximately 14 M in propylene carbonate also, based on the molecular weight and the density. To assume that in this milieu, cadmium (II) is going to "see" water to the exclusion of the other materials in solution is to neglect the very strong interactions between the lithium ion and water, the probable interaction between the solvent itself and water, and most important of all, the interaction between the <u>unsolvated</u> perchlorate ion and water. We claim for the data in Table 29 only the virtue that it reflects the real situation which exists in the fairly concentrated electrolyte solutions in which the discharge behavior of CuF_2 was studied.

Finally, we considered the estimated potential for the Cu^{++}/Cu couple, since this is the quantity to be used in determining whether the displacement of Cu^{++} from CuF_2 by the lithium ion should occur. If it is true, in a given solvent, that Cu(I) is the stable copper species, this means nothing more than that the free energy for the following reaction is negative:

$$Cu^{++} + Cu^{o} = 2\ Cu^{+}$$

For this to be true, the reduction potential for the Cu^{++}/Cu system must be more positive than for the Cu^{+}/Cu system.

Now we go back to page 153 , where the displacement reaction was broken down into its individual components. We note that the sum of ΔG_2 and ΔG_4 is nothing more than twice the difference in the reduction potentials. It is easily shown that for $\Delta G = 0$, the difference in reduction potentials must be greater than 3.55 V. Using the values for the reduction potential of the lithium couple in Table 29 we calculate what the reduction potential for the Cu^{++}/Cu^{o} couple must be for the displacement reaction to have a positive free energy:

PC	more positive than -0.12 V	DMF	more positive than -0.25 V
BL	more positive than -0.05 V	DMSO	more positive than -0.04 V
AN	more positive than +0.35 V		

The crystal field stabilization of copper (II) in aqueous solution is about 20 kcal M^{-1}. In other words, the free energy change for the reaction, $2\ Li^+ + Cu^o = Cu^{++} + 2\ Li^o$, is about 20 kcal M^{-1} (0.5 V) more negative than would be the case were there no crystal field stabilization. It is then easily seen that the free energy for the displacement reaction, shown at the bottom of p. 153, should be +13 kcal M^{-1} (-7 + 20), and the equilibrium should lie far to the left, which is the desired situation.

If the displacement reaction equilibrium lies to the left, then one has a possible procedure for the cycling of copper fluoride electrodes. If copper (II) is produced on anodization, and in the electrode is contained a supply of insoluble LiF, then precipitation should occur by:

$$Cu^{++} + 2\ LiF = CuF_2 + 2\ Li^+,$$

which is, of course, the reverse of the displacement reaction.

Such a reservoir of fluoride ions is not only desirable but, indeed, necessary, in order to conserve cell weight and keep the energy density within reasonable bounds. It is, furthermore, likely to be the only possible kind of reservoir of fluoride ions, because of the extreme unlikelihood of being able to get a soluble fluoride reservoir -- that is, an electrolyte in which a fluoride salt is sufficiently soluble. The reasons for this will be briefly discussed below.

Let us consider the four halides of lithium and the free energy of solution. This is calculated from the the difference between the free energy of formation of the salt and of the hypothetical mean molal solution, as given by Latimer.

$LiI = Li^+ + I^-$ $\Delta G = -18.6$ kcal M^{-1} (in aqueous solution)
$LiBr = Li^+ + Br^-$ $\Delta G = -13.6$ " "
$LiCl = Li^+ + Cl^-$ $\Delta G = -9.9$ " "
$LiF = Li^+ + F^-$ $\Delta G = +3.3$ " "

We may also obtain an estimate for the free energies of the first three reactions in propylene carbonate. For 0.1 M LiI and LiBr solutions in PC, we have measured the potential for the reaction:

$$\mathrm{Li + AgX = Ag + Li^+ + X^-},$$

by anodizing a silver electrode in the solution to the insoluble salt (Note: both AgI and AgBr appear to be sufficiently insoluble in PC). Then lithium is cathodically deposited on another electrode in the same solution. The measured potentials for the above reaction are +2.45 V in the LiI solution and +2.55 V in the LiBr solution. This is converted to the free energy for the above reaction in a hypothetical mean molal solution by the relationship:

$$E = -(\Delta G - RT \ln a^2)/23$$

(The number, 23, is for the conversion from kcal M^{-1} to volts.) The free energy so calculated by assuming the activities to be equal to the concentration are given below, and combined with the literature values for the free energies of formation of the salts to give the free energy of solution of a hypothetical mean molal solution in propylene carbonate:

$$\begin{array}{ll}
\mathrm{Li + AgI = Ag + Li^+ + I^-} & \Delta G = -53.6 \text{ kcal } M^{-1} \\
\mathrm{LiI = Li + 1/2\, I_2} & \Delta G = +64 \quad '' \\
\mathrm{Ag + 1/2\, I_2 = AgI} & \Delta G = -15.9 \quad '' \\
\hline
\mathrm{LiI = Li^+ + I^-} \text{ (in PC)} & \Delta G = -5.5 \quad ''
\end{array}$$

and

$$\begin{array}{ll}
\mathrm{Li + AgBr = Ag + Li^+ + Br^-} & \Delta G = -55.9 \quad '' \\
\mathrm{LiBr = Li + 1/2\, Br_2} & \Delta G = +81 \quad '' \\
\mathrm{Ag + 1/2\, AgBr = AgBr} & \Delta G = -22.9 \quad '' \\
\hline
\mathrm{LiBr = Li^+ + Br^-} \text{ (in PC)} & \Delta G = +2.2 \quad ''
\end{array}$$

The free energy of solution of LiCl is calculated from the measured solubility in PC, 0.055 M. Since $\Delta G = -RT \ln a^2$, we find, on the assumption that activities are equal to concentrations,

$$\mathrm{LiCl = Li^+ + Cl^-} \text{ (in PC)} \qquad \Delta G = +3.5 \quad ''$$

The actual free energies of solution of hypothetical mean molal solutions should probably be even more positive than those values calculated, since ionic dissociation is not complete, as is indicated by the measured equivalent conductances: 0.1 M LiI, $\underline{\Lambda = 18.8}$; 0.1 M LiBr, $\underline{\Lambda = 12.4}$; 0.055 M LiCl, $\underline{\Lambda = 3.9}$.

Were the trends in the free energy of solution observed in propylene carbonate to continue through the fluoride, it is clear that the solubility of LiF would be negligible. The reason why the free energies of solution are so much less negative in PC than in water is primarily because the anion is largely unsolvated. This is most simply explained by noting that the positive end of the solvent dipole, which is that center at which anion - solvent specific interactions arise, is sterically "hidden" in the sense that negative ions may not approach the positive end of the dipole as well as positive ions may approach the negative end of the dipole. Thus the coulombic interaction between the dipole and the anions is negligible and solvation is small, resulting in a more positive free energy of solution. Were a solvent to have a sufficiently exposed positive center, this would also be a center more subject to nucleophilic attack; such a solvent would be expected to be unstable with respect to active metals -- as the case with water.

As has long been known, for a salt of a given anion, the free energy of solution tends, in many cases, to become more negative with increasing size of the cation -- that is, the solubility increases the larger the cation. This is primarily a result of the fact that, in many solvents, the lattice energy of the salt decreases more rapidly than the solvation energy of the cation. Doubtless, there may exist solvents in which the fluorides of large cations, such as tetralkylammonium salts, or complex cations of sulfur, phosphorous, and arsenic, may be satisfactorily soluble. While it is clear such materials could not be used in nonaqueous cells because of weight considerations, it would indeed be interesting to observe the behavior with respect to cycling of fluoride electrodes in such media.

We conclude this discussion of solubility of cathode salts by noting that the whole question of solubility is quite complex. Specific interactions including complexation and displacement, which solubilize cathode salts, have been briefly examined. A lot more data is needed, and must be collected with attention to the possible existence of these and other specific interactions. While solvation theory will not, itself, suggest the "best" systems, it is a useful framework on which to hang the facts, and to spotlight unexpected phenomena.

III-D. Discharge Behavior of Cathode Salts

III-D-1. Introduction

In these sections we shall describe the results obtained in a large number of experiments on the electrochemical discharge of AgCl and CuF_2 in both aqueous and nonaqueous media. It will be observed that there are marked changes in the efficiency of discharge depending on the electrolyte. For AgCl electrodes these will be largely ascribed to passivation type phenomena, which is typical of other aqueous cathodes. For CuF_2 such simple explanations are not possible. It seems clear that rather specific chemical effects are involved in the discharge of CuF_2, and it may be noted at this point that much of the previously described work was done as a result of the work on the discharge of CuF_2 and the difficulty in interpreting the results.

III-D-2. Discharge of AgCl

At the time the work began in our laboratory on the discharge of cathode salts, little work had been done by other workers in the field of nonaqueous primary cells on the discharge of low capacity electrodes at high rates. Since we felt such a cathode would be the most desirable for a secondary cell, it was necessary to investigate the performance under such conditions in nonaqueous electrolytes. We began with AgCl as a test case, since it is known that the salt is inherently reducible, electrochemically, whereas this point had not been established for CuF_2.

We were initially concerned with three problems relating to the discharge of cathodes in poorly conducting nonaqueous media:

a. The basic validity of the measurements. Does the electrode itself contribute a significant fraction of the iR drop; that is, is the resistance of the electrode alone a major source of the total cell resistance?

b. Structural problems. Is the inherent structure of the electrode sufficiently sound that one may be reasonably confident that low efficiencies are not simply due to structural collapse with concomitant loss of electrical contact and discharge efficiency?

c. Parasitic reductions. To what degree is it likely that, at low current densities, apparently high efficiencies reflect concurrent parasitic reduction of impurities in the electrolyte and impurities imbedded in the electrode?

AgCl electrodes were prepared by evenly distributing over a platinum substrate in the recess of the electrode shown in Figure 7 (this electrode will hereafter be called the "recessed electrode") a mix of silver powder and silver chloride. It was somewhat difficult to work with the material directly from the bottle but it was found that mixing the two materials together in a mortar and pouring over them a little liquid nitrogen produced a sufficiently workable mix. The mix was pressed into the recessed electrode at 1500 lb. pressure.

The electrodes were first discharged in aqueous HCl (1 M). This was done to insure that the structural integrity of the electrodes was maintained throughout discharge. The fact that essentially 100% efficiency was obtained even at extremely high currents (61 mA cm^{-2}) is, to us, proof that the basic electrode is "sound". These results are shown in Table 30.

Next the electrodes, prepared in identical fashion, were discharged in a dilute aqueous LiCl solution. The specific conductance of this solution was about 290 ohm^{-1} cm^{-1}, which is typical of values found for nonaqueous electrolytes. The rationale for the discharge studies in this solution was, if the source of inefficiency for discharge in nonaqueous media is primarily the result of low conductivity, this effect should as easily be seen in aqueous media of the same conductivity. These results are also shown in Table 30 and; as will be noted, the efficiencies again were essentially 100% at currents less than about 20 mA cm^{-2}.

Finally, the electrodes, prepared again in the same fashion as in the preceding two paragraphs, were discharged in PC/1 M LiBF$_4$. Efficiencies were negligible, only a few percent. It was necessary to decrease the capacity and the current; these results are also shown in Table 30.

Table 30

DISCHARGE OF AgCl ELECTRODES

Symbols:
Cap. = Capacity in mA-hr cm^{-2}
Cur. = Discharge current in mA cm^{-2}
Eff. = Efficiency, obtained by dividing the number of mA-hr reduced on discharge by the number of mA-hr pressed into the recessed electrode.
Mix = Mix ratio by weight Ag : AgCl

H_2O/HCl				$H_2O/0.04$ M LiCl				PC/1 M $LiBF_4$			
Mix	Cap.	Cur.	Eff.	Mix	Cap.	Cur.	Eff.	Mix	Cap.	Cur.	Eff.
				1:10	34	34	75%				
				1:10	34	17	95%				
				1:10	34	8.5	97%				
1:1	17	61	102%								
1:9	17	61	96%								
1:20	17	61	98%								
1:50	17	61	98%								
				1:10	17	34	67%				
1:20	17	17	102%	1:10	17	17	93%	1:20	17	17	3%
				1:10	17	8.5	97%	1:20	17	17(1)	3%
								1:20	17	17(2)	5%
								1:10	17	17	2%
								1:10	17	17	2%
								1:1	17	17	2%
								1:1	17	17	2%
				1:10	8.5	34	80%				
				1:10	8.5	17	88%				
				1:10	8.5	8.5	97%	1:20	8.5	8.5	10%
								1:10	8.5	8.5	10%
								1:10	8.5	4.2	27%
								1:10	8.5	2.1	25%
								1:10	8.5	1.4	44%
								1:10	8.5	1.0	48%
								1:10	8.5	.53	64%

other pressures

(1) 400 lb

(2) 250 lb

The discharge curves were quite flat in all but the discharges performed in the aqueous LiCl solution at 34 mA cm^{-2}; and the determination of reduction efficiency was unambiguously determined from the point at which very sharp polarization occurred. It appeared that the 1:10 mix, with a capacity of 8.5 mA-hr cm^{-2} was sufficiently well-behaved to allow examination of other electrolytes.

First, examination of the discharge behavior was made in various propylene carbonate solutions, 0.5 M $LiAlCl_4$, 0.25 M Morpholinium PF_6, and 0.5 M KPF_6. The results are shown in Table 31 on the next page. In some cases there was added some $LiClO_4$ to the mix. This was done, following the subsequently described work on CuF_2, where it was assumed that the addition of the soluble $LiClO_4$ would produce greater electrode porosity. For convenience we also include in Table 31 certain of the data from Table 30. These data are asterisked.

The increased efficiency at lower currents is what is normally expected of battery electrodes. Two relationships between current and time of completion of the reaction are often used in discussing passivation:

$$(i - i_t)\, t = k$$

$$i\, t^n = k'$$

in which k and k' are constants, and i_t is also a constant. Both equations essentially say that there are two processes which occur on electrolysis; one is the actual discharge of material, the other is a type of "coverage" process. In the case of the discharge of AgCl in lithium salt solutions we may consider that this "coverage" process is the growth of a resistive film of LiCl on the surface, or an accumulation of LiCl in the pores of the electrode. Now, since lithium chloride is, to some degree, soluble in propylene carbonate, we must also consider the rate at which LiCl may dissolve and move back out into the bulk of electrolyte. Thus, we consider the following two reactions:

$$AgCl + e^- + Li^+ = Ag^o + LiCl \text{ (precipitate)}$$

$$LiCl \text{ (precipitate)} = LiCl \text{ (dissolved)}$$

If i, the rate of discharge, is equal to, or less than, i_t, the rate of dissolution, then 100% efficiency should be realized. At higher currents, the efficiency will be less, and will be determined by the degree to which the discharge current is larger than the rate of dissolution. It will be noted that the second equation above,

Table 31

DISCHARGE OF AgCl IN PROPYLENE CARBONATE

Sumbols: Cap. = Capacity in mA-hr cm^{-2}; all electrodes in this table had capacities, based on the initial weight of AgCl, of about 8.5 mA-hr cm^{-2}.

Cur. Discharge current in mA cm^{-2}

Eff. = Efficiency, obtained by dividing the number of mA-hr realized on discharge by the number of mA-hr pressed into the recessed electrode

Mix = Mix ratio by weight Ag : AgCl : LiClO$_4$

Mix	Cur.	Eff.	Mix	Cur.	Eff.	Mix	Cur.	Eff.	Mix	Cur.	Eff.
1:20*	8.5	10%									
1:10*	8.5	10%									
1:10:1	8.5	20%	1:10:1	8.5	13%						
1:10*	4.2	27%				1:10	4.2	10%	1:10	4.2	none
1:10:1	4.2	35%	1:10:1	4.2	24%						
1:10*	2.1	25%				1:10	2.1	45%			
1:10*	1.4	44%									
1:20	1.4	80%									
1:10*	1.0	48%									
1:10*	0.53	64%				1:10	0.53	93%			
1:10:1	0.53	87%	1:10:1	0.53	52%						
1:10*	0.18	91%									
									1:10	0.10	38%

when applied to batteries, is the familiar Peukert equation, originally applied to the discharge behavior of lead acid cells. We note that the asterisked data in Table 31 give reasonable agreement with both equations given on the preceding page. This immediately suggests some type of passivation or blocking phenomena. We note, further, that the discharges in the KPF_6 solution are particularly poor. This is not surprising when we compare the solubilities of LiCl and KCl in propylene carbonate. We have found that the solubility of LiCl is about 0.055 M; while the solubility of KCl is only 0.00058 M.

Considering the variability of the data we do not draw any conclusions regarding the $LiAlCl_4$ and $MoPF_6$ solutions, except to note that the efficiencies are about the same or slightly better than in the $LiBF_4$ solution.

The addition of $LiClO_4$ to the mix appears to effect some improvement; this suggests inhibition of discharge efficiency by some blocking effect. The possibility of this will be further examined later in connection with the discharge of $AgNO_3$ electrodes.

Discharges were also conducted in butyrolactone, dimethylformamide, and acetonitrile. No experiments with AgCl have been performed by us in dimethylsulfoxide. The results obtained are shown in Table 32. Again data from Table 30 is repeated for clarity, and this data is asterisked.

The data in the lithium salt solutions is concordant with the solubilities of the lithium and potassium chlorides, which we have found and show below for the four solvents:

in	PC	DMF	BL	AN
Solubility of LiCl ($M\ l^{-1}$)	0.055	>0.1	>0.1	0.027
Solubility of KCl ($M\ l^{-1}$)	0.00058	0.0018	0.00063	0.000124

It is assumed that the greater efficiency in BL and DMF when compared with the other two solvents is a result of the greater solubility of LiCl in these two solvents. The inefficiencies in the KPF_6 solutions is also ascribed to the low solubility of KCl in all of these four solvents.

The effect of decreasing the electrolyte concentration was studied in propylene carbonate and butyrolactone. $LiClO_4$ was used as the supporting electrolyte, it being assumed that there is no major difference expected between results with this solute and $LiBF_4$ (At the time the experiments were performed we had no $LiBF_4$ available).

Table 32

Discharge of AgCl in PC, BL, DMF, and AN

Symbols: Cap. = Capacity; all electrodes shown in this table had capacities of 8.5 mA-hr cm^{-2}.

Cur. = Discharge current, in mA cm^{-2}

Eff. = Efficiency, obtained by dividing the number of mA-hr realized on discharge by the number of mA-hr pressed into the recessed electrode.

Mix = All mixes were 1:10 by weight, Ag:AgCl

	PC	DMF	BL	AN	BL	AN	BL	AN
	$LiBF_4$	$LiBF_4$	$LiBF_4$	$LiClO_4$	$MoPF_6$	$MoPF_6$	KPF_6	KPF_6
Cur.	Eff.	Eff.	Eff.	Eff.	Eff.	Eff.	Eff.	Eff.
17	--	58%	60%	--	--	--	--	--
8.5	10%	58%	63%	23%	--	11%	--	--
4.3	27%	56%	60%	56%	13%	63%	0	--
2.1	25%	--	--	36%	52%	--	--	--
0.53	64%	--	95%	--	88%	--	--	8%
0.2	--	--	--	--	--	--	14%	--

The $LiBF_4$, $LiClO_4$, and KPF_6 solutions were 1 M. The $MoPF_6$ solution was 0.25 M.

The propylene carbonate solution was made 0.2 M in $LiClO_4$ (specific resistance = 333 ohm-cm). The butyrolactone solution was made 0.1 M in $LiClO_4$ (specific resistance = 370 ohm-cm). All electrodes had theoretical capacities of 8.5 mA-hr cm^{-2}, and contained 1:10 parts by weight of Ag:AgCl. As indicated, several electrodes were prepared with an additional amount of solid $LiClO_4$, the weight percent of which is given below:

Current (mA cm^{-2})	PC (no $LiClO_4$ in mix)	BL (No $LiClO_4$ in mix)	BL	% $LiClO_4$ by weight in mix
17	--	--	67%	25%
8.5	8%	--	65%	12%
8.5	--	--	68%	25%
4.3	8%	67%	75%	25%
2.1	8%	60%	--	--
1.1	--	--	67%	25%
0.5	--	78%	--	--

It is not clear to us why there should be such a difference for the PC solution when compared with the data in table 32, but apparently very little change for the BL solution.

It seems apparent that, in considering all the data collected on the discharge of AgCI electrodes, that significant differences exist and it seems unlikely that these are simply due to small variations in electrode construction. We therefore assume that the sources of these differences arise from particular chemical interactions. In the porous type structures we have been considering, one must consider not only what happens to the chloride ion on discharge, but also mass transport phenomena. It would, for example, make quite a difference if, in one solvent the transport number of the chloride ion were sufficiently large that most of the chloride escaped from the electrode by electrical migration, before precipitating the chloride salt, whereas, in another solvent, the migration of chloride might be much less than that of the cation <u>into</u> the electrode, and more rapid blocking or surface coverage would occur.

III-D-3. Discharge of CuF_2.

The initial work was done merely to try to establish a reasonable electrode mix composition. The results are shown in tables 33 and 34. Various

Table 33

DISCHARGE OF CuF_2 IN H_2O, ESTABLISHMENT OF MIX COMPOSITION

All discharges performed in aqueous, 1 M $LiClO_4$. The solution was saturated with CuF_2 and the concentration of copper (II) was determined polarographically, and was about 0.01

Efficiencies are calculated from the weight of CuF_2 in the mix, and assume a two electron reduction to copper metal on discharge. The discharge curves were normally flat, and the completion of discharge was quite unambiguously determined from the time at which the potential sharply changed to more negative values. The potential along the plateau is given for those discharges where the curve was flat during discharge. This potential appears in parenthesis

Cap. (mA-hr cm^{-2})	17	8.5	8.5	8.5	6.4	4.3
Cur. (mA cm^{-2})	17	8.4	4.3	2.1	6.4	4.3
Mix Ratio Cu: CuF_2						
0:1	13%					
1:1	9%					
3:1		30%				
6:1		37%(-.06)				
9:1		52%(-0.17) 56%(-0.14) Figure 28-- ----50%(-0.12) 61%(-0.09) 61%(-0.10) 47%(-0.06) 43%(-0.06)	40%(-0.01) 33%(0.00)	24%(+0.1)		
14:1		44%(-0.09)				
19:1					48%(-0.06)	31%(-.03) 32%(-.02)

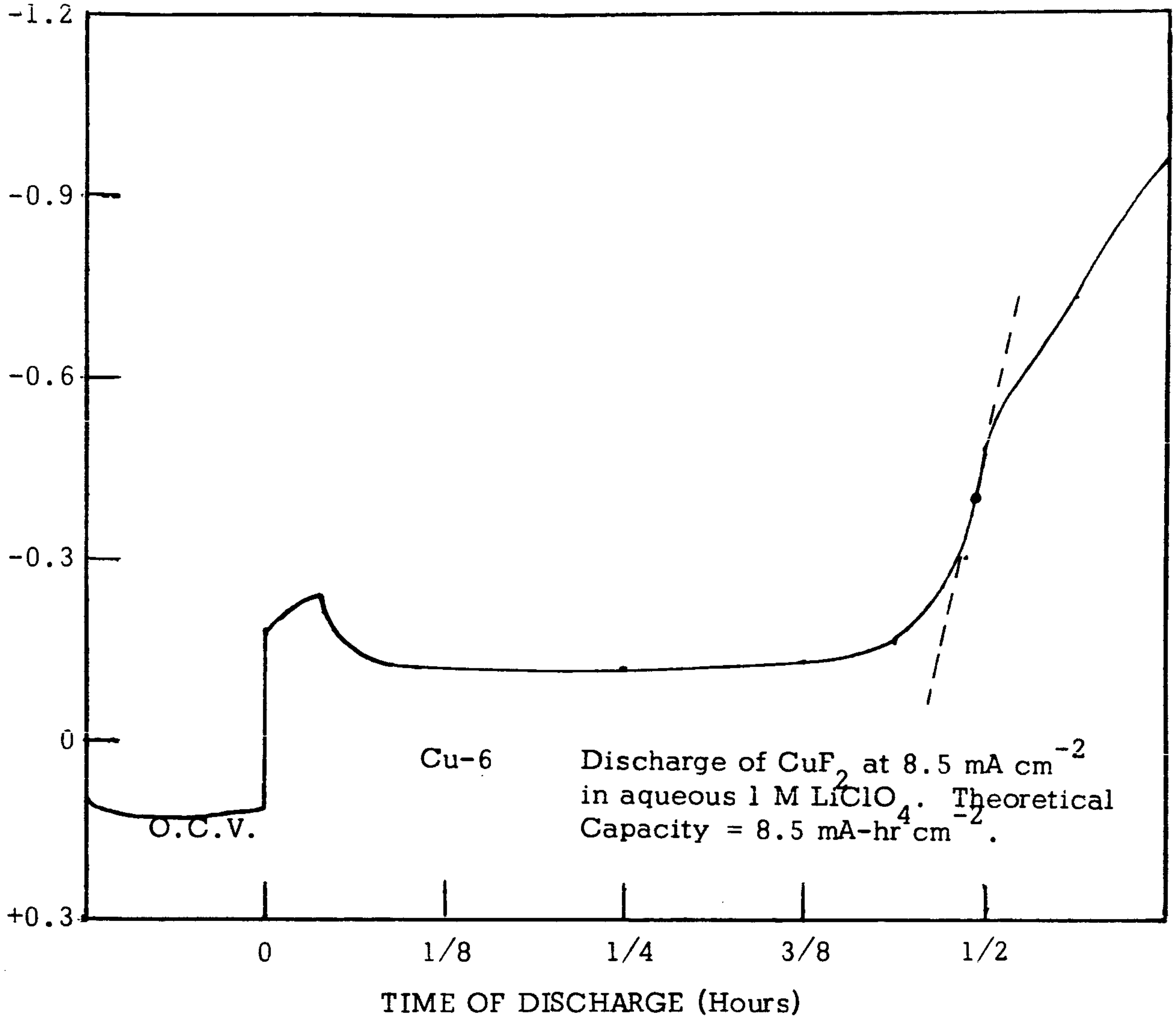


Figure 28: DISCHARGE OF CuF_2 IN AQUEOUS SOLUTION

Table 34

DISCHARGE OF CuF_2 IN PC, ESTABLISHMENT OF MIX COMPOSITION

Efficiencies calculated as described at the top of table 32.

Cap. (mA-hr cm^{-2})	8.5	8.5	4.3	4.3	4.3	4.3
Cur. (mA cm^{-2})	4.3	0.53	8.5	4.3	2.1	0.35
Mix Ratio: Cu:CuF_2:$LiClO_4$: Teflon molding powder (all be weight)						
9: 1:0:0	13% 13%	no break	23%			
9:1: :0 Fig.29---	50%(-.33) 51% 21%(with 1 d. water)		47%	53%(-.42) 51%(-.45) 32%(soaked in PC 1 hr)		17%
9:1:3:0	6% (most of fix fell off)					
9:1:1:.5	51% 50% 28% (soaked in PC 1 hr)	22% 37%		42%** 43%**	40%**	
9:1:1:1				43%		

- -

Mix

9:1:1 (naphthalene) heated in vacuum oven, after pressing, at 150° C for time indicated:

Pressure z (lb)	Time of heating (hr)	Cap. (as above)	Cur.	Eff.
7000	1/2 (at 750°C)	8.5	4.3	0
7000	none	8.5	4.3	0
7000	1 (at 60° C)	8.5	4.3	4%
3000	1/2	8.5	4.3	4%
7000	1/2	8.5	4.2	3%
3000	1 1/2	8.5	4.3	15%
3000	1 1/2	8.5	0.56	22%
7000	1 1/2	8.5	4.2	23%
3000	16	8.5	4.3	51%

mix compositions were used, and it was found that a large excess of conducting material was required. This, of course, is completely unsatisfactory for an operating battery electrode because of the weight loss, but it is satisfactory for an electrode, the use of which is to investigate the effects observed in different electrolytes. Most discharge curves had an appearance similar to that shown in figure 28. The initial potential jump we assumed to reflect the time required to effect uniform electrical contact throughout the electrode.

Discharges of the 9:1 mix seemed to give satisfactorily reproducible behavior in the aqueous solution, and this composition was used to study the discharge in propylene carbonate. A PC/1 M $LiBF_4$ solution was used.

In this work we were particularly interested in seeing if we could not get better that 50% efficiency. Contrary to what would conventionally be expected, it appeared that the lower the current the less the efficiency. This was credited to dissolution of the CuF_2, and, as discussed earlier in connection with the displacement reaction, this was a reasonable expectation.

The consistency with which efficiencies close to 50% were realized was disconcerting. At the time the experiments were performed it was feared that the copper metal used as the conducting material might have something to do with this, though exactly how was not clear. The high proportion of copper was also unsatisfactory, but it was difficult to work with a mix of lower copper content with the $LiClO_4$ incorporated in the mix, because of insufficient mechanical integrity.

The undesirability of copper in the mix led to the use of silver powder as the conducting material. It was not anticipated that there sould be any chemical reaction of CuF_2 with the silver metal, though this possibility must not be ruled out. The results obtained by incorporating the silver powder in the mix are shown in table 35, on the next page.

The 20:10:3.3 mix gave sufficiently good reproducibility to allow its use in the study of electrolytes and the results of these experiments are shown in table 36. It will there be observed that the discharges in acetonitrile were the best, and this solvent was used for a further examination of the electrode mix ratios. These results are also shown in table 36.

Table 35

DISCHARGE OF CuF_2 IN PC, ESTABLISHMENT OF MIX COMPOSITION

Cap. (mA-hr cm^{-2})	34	17	17	8.5	8.5	8.5	8.58	8.5	4.3	4.3
Cur. (mA cm^{-2})	8.5	8.5	4.3	8.4	4.3	2.1	1.1	0.53	4.3	0.53
Mix Ratio Ag: CuF_2 : $LiClO_4$										
80 : 10 : 10										
5 : 10 : 10					22%					
5 : 10 : 1.7			21%(-.5)							
20 : 10 : 3.3		10%	22%	22%	31%** 29%** 26% 29%	26% 31%	39%** 37%** 24%	29%**		
3 : 10 : 1.4	11%	10%	22% 23%							
1.2 : 10 : 1.2			4% 7% 13% (with Cu screen imbedded in mix)							

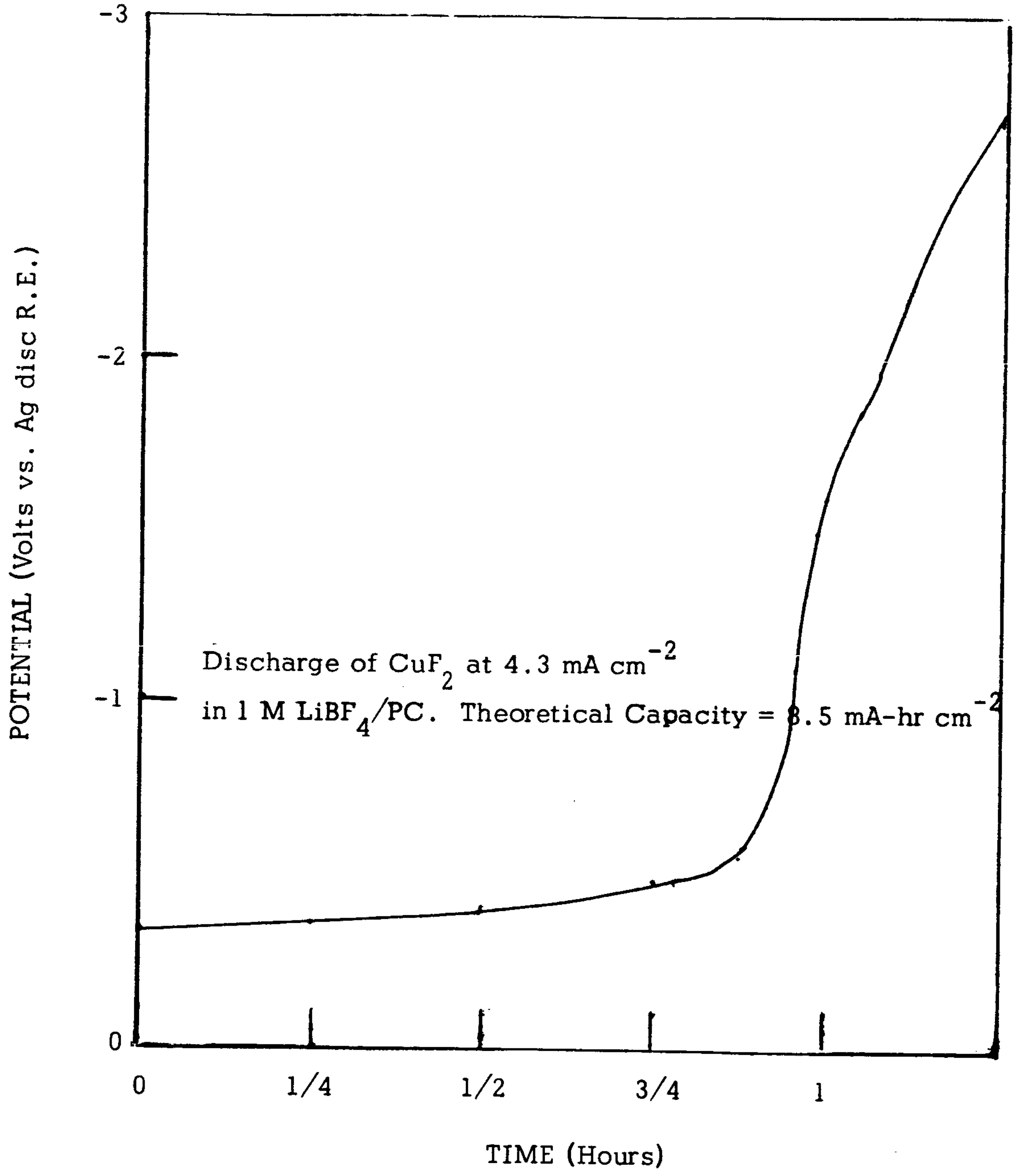
(** = with platinum screen imbedded in mix)

Table 36

DISCHARGE OF CuF_2 IN PC, BL, AND AN

Cap. (mA-hr cm^{-2})	17	17	8.5	8.5	8.5	8.5	8.5	8.5
Cur. (mA cm^{-2})	4.3	1.1	17	8.3	4.3	2.1	1.1	0.53
Solution Mix ratio ($Ag:CuF_2: LiClO_4$)								
PC/1 M $LiBF_4$ 20 : 10 : 3.3	22%			22%	29%		24%	
BL/1M $LiBF_4$			22%	23%	26%			
BL/0.5 M $LiClO_4$ 20 : 10 : 3.3					13%			
BL/1 M $LiBF_4$ 0.5 (graphite) :3:1					24%			
BL/ 1 M $LiBF_4$ 0.5 (acetylene black) :3:1	49%	39%			45%			
BL/0.1 M $Mg(ClO_4)_2$					8%	8%	13%	
BL/0.5 M "					12%	11%	12%	
AN/0.5 M $LiClO_4$ 20 : 10: 3.3			45%	46% 48%	45%	49%		
PC/1 M KPF_6		5%						
AN/1 M KPF_6 20 : 10 : 3.3					0			0
PC/0.25 M $MoPF_6$					24%	32%		
AN/0.25 M $MoPF_6$ 20 : 10 : 3.3				8%	11%			
AN/0.5 M $LiClO_4$ (Different mix ratios)								
3 : 10 : 1.4					48%			
5 : 10 : 1.7	(electrode fell off)							
10: 10: :0		(no potential) break after 17 hrs.)			50%			
20: 10 : 0					(electrode fell off)			
20: 10: 0 (repeat)					42%			

80 : 10 : 10 Cap. = 4.3; Cur.= 4.3; Eff. = 39%
160: 10 : 20 Cap. = 2.1; Cur.= 4.3; Eff. = 30%
320: 10: 40 Cap. = 1.1; Cur. = 4.3; Eff. =13%



Discharge of CuF_2 at 4.3 mA cm^{-2} in 1 M $LiBF_4$/PC. Theoretical Capacity = 3.5 mA-hr cm^{-2}

Figure 29: DISCHARGE OF CuF_2 IN PROPYLENE CARBONATE

We conclude this discussion of the discharge behavior of the CuF_2 electrode by noting that, as with the AgCl electrode, the discharge behavior is more markedly a property of the electrolyte than of the mode of construction. Again, one must look for specific interactions which alter the performance. In particular, one must anticipate solubilization of CuF_2 through displacement by the solute from its fluoride, and one step reductions such as: $CuF_2 + e^- + 2\,Li^+ = Cu^+ + 2\,LiF$, and perhaps the self-complexation on discharge through a reaction such as:

$2\,CuF_2 + 2e^- + Li^+ = Cu^o + CuF_3^- + LiF$.

III- D. Discharge Behavior of Other Salts.

Several other salts were discharged in PC/1 M $LiClO_4$. The electrodes were prepared in 20 : 10 : 3.3 weight ratio mixes (Ag: Salt:$LiClO_4$). All had capacities of 8.5 mA-hr cm^{-2} and all were discharged at 4.3 mA cm^{-2}. The results are shown in Figure 30.

It was particularly interesting to note that CuCl gave only 50% efficiency and further discharges of this material were done as indicated below:

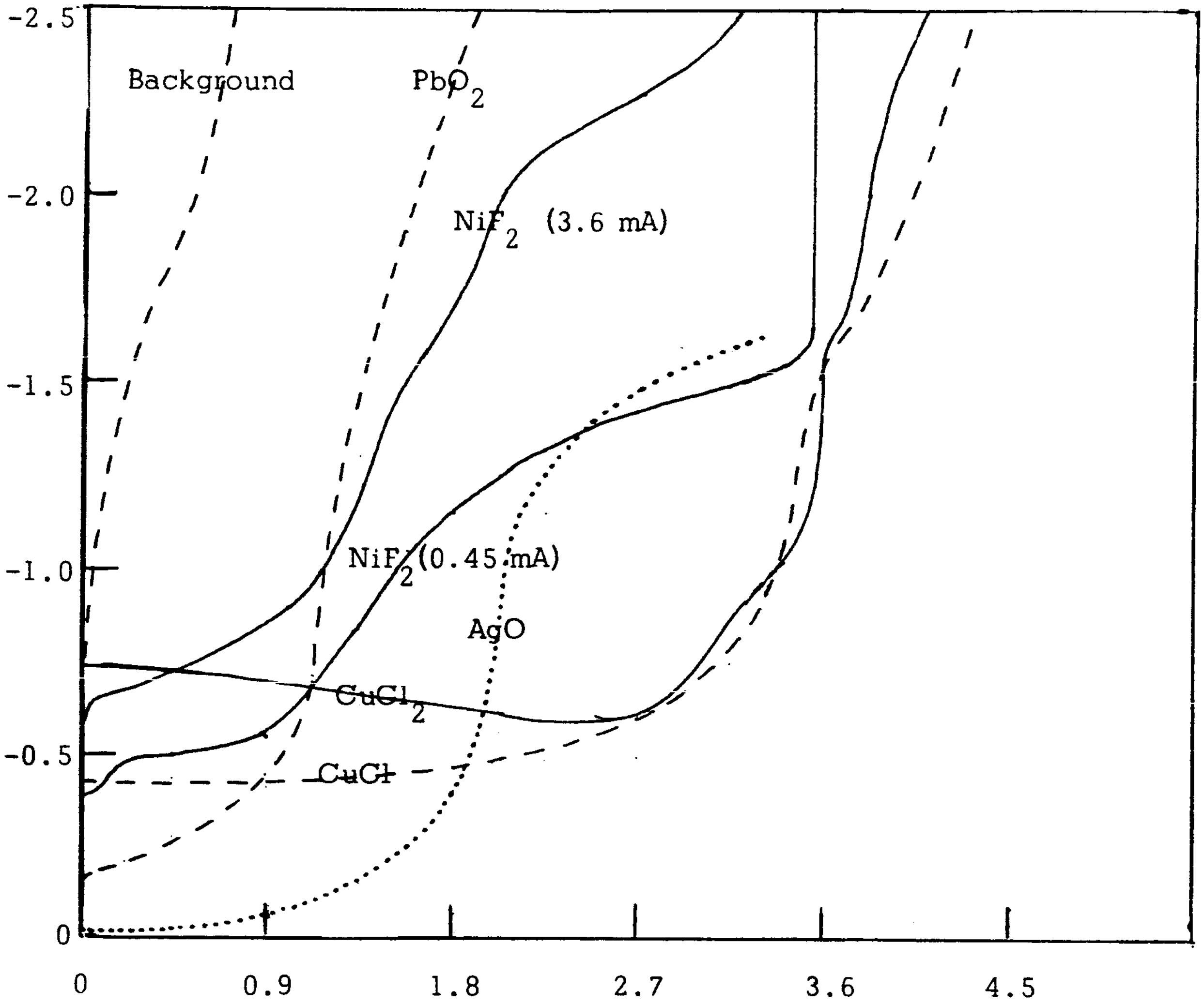
Mix Ratio Ag: CuCl : $LiClO_4$	Cap. (mA-hr cm^{-2})	Cur. (mA cm^{-2})	Eff.
20: 10: 3.3	8.5	4.3	48%
2.4: 10 : 0	17	1.0	56%
"	17	8.5	47%
2.5: 10 : 1.2	17	8.5	50%
"	8.5	4.3	47%

The 50% efficiency seems inherent in the system and we conclude that this results from self-complexation during discharge by the reaction:

$2\,CuCl + e^- = Cu^o + CuCl_2^-$.

The discharge of $AgNO_3$ was also studied, because this is one of the few salts where, on discharge, the volume of the products is not significantly larger than the volume of reactants, for a reaction of the type $\underline{MX} + Li^{\pm} = \underline{M} + \underline{LiX}$ and we use only the volume of the underlined materials. The results were as follows:

Mix Ratio: Ag : Ag NO_3	Cap.	Cur.	Eff.
1 : 20	8.5	8.5	90%
1 : 20	17	4.3	89%
1 : 20	17	1.0	86%



AMOUNT OF DISCHARGE (mA-hr)

Figure 30: CATHODIC DISCHARGE OF VARIOUS MATERIALS IN PROPYLENE CARBONATE 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.

III-E. Cycling of Cathodes

III-E -1. 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 a one-electron change. This is in considerable excess of the amount of current passed during one 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:

III-E-1-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 31 is shown the charge and discharge for the 25th cycle. Cathodic 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		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 cathodic recovery is given below versus the amount of anodic charge.

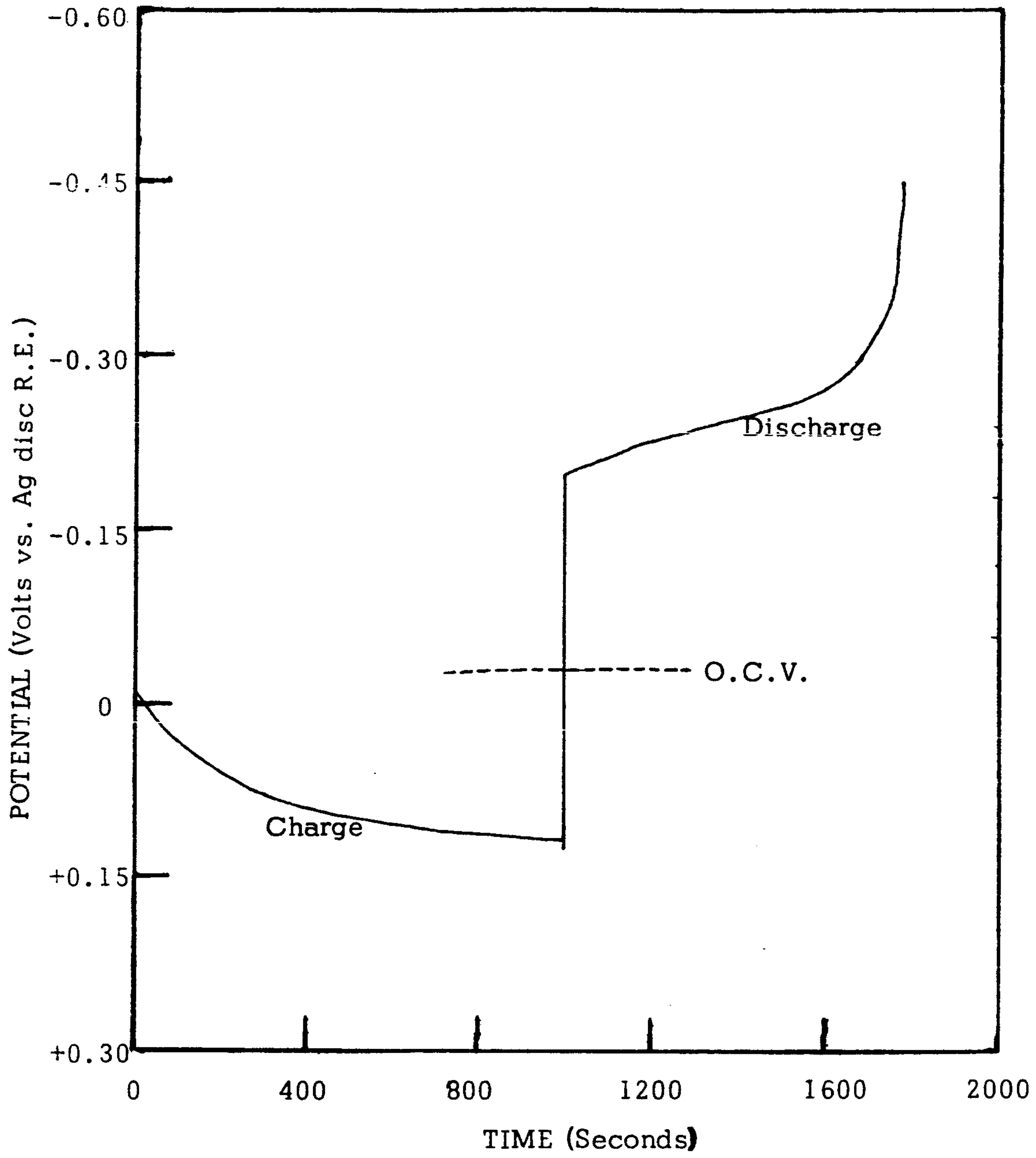


Figure 31: CYCLING OF COPPER ELECTRODE IN PROPYLENE CARBONATE

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 polarization.

Anodic Charge (Coulombs)	Cathodic Recovery
1	95%
2	90%
5	82%
10	74%
25	66%
40	63%

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.

III-E-1-b. Butyrolactone, 0.5 M in LiCl

The results on the cycling of copper in this solution were totally unsatisfactory. As on the initial cycles in propylene carbonate, described in the preceding section, anodization was performed at 10 mA for 1000 sec. On subsequent current reversal, only about 20% cathodic recovery could be realized before the electrode polarized. In other words, the cycling behavior was similar in kind to the cycles shown in Figure 31, except on discharge the electrode polarized much earlier, and instead of 70-76% recovery, only 20% or less was realized. This behavior persisted through ten cycles, and no further work was done in butyrolactone.

III-E-1-c. Dimethylformamide, 0.5 M in LiCl

Again, cycling was attempted under the same conditions as in propylene carbonate and butyrolactone. As with butyrolactone solutions, the cathodic recoveries were negligible -- only about 10 to 20%. The cycling was continued for 38 cycles, and though the character of the curves changed there was no improvement in cathodic recovery, and no further work was done in dimethylformamide.

III-E-1-d. Conclusions. The results are not surprising in view of what has previously been said concerning the solubility of copper species in chloride media. Beyond the simple statement that apparently copper will not cycle in the butyrolactone and dimethylformamide electrolytes, there is little more than can be done by way of interpreting the data. We do not believe such experiments constitute a valid screening procedure, since other effects may be operative which produce "apparent" cycling. For example, it may be conjectured that in the propylene carbonate, the product of anodization is a neutral species, only a small amount of which leaves the electrode by diffusion, whereas in butyrolactone or dimethylformamide, the product of anodization may be a negatively charged ion which rapidly leaves the electrode by electrical migration. In such cases, the apparent cycling would not provide a reliable criterion for the evaluation of the three systems with respect to their performance in a secondary cell type of environment.

III-E-2. Cycling of Silver Chloride Systems

A few experiments were performed to see whether the silver electrode could be cycled in the presence of an insoluble chloride reservoir. A mix, comprising equimolar amounts of silver (0.0290 g.) and lithium chloride (0.0114 g.) was pressed into the recessed electrode at 1500 lb. 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 anodic polarization occurred after 23 min., gave 100% recovery on discharge. The electrode remained compact and firmly adherent to the platinum substrate.

For comparison a second electrode was prepared in the identical way. This was anodized at a lower current, 4.2 mA cm^{-2} for 1/2 hr. Subsequent current reversal at the same current gave 100% efficiency.

Finally, a third electrode was prepared, using $LiClO_4$ instead of LiCl in the mix. As with the first electrode, this electrode was anodized at 8.5 mA cm^{-2} for 1/4 hr. On current reversal the efficiency was only 7%, compared with the 93% realized when LiCl was incorporated in the mix.

The results clearly indicate that true cycling was occurring via the presence of the LiCl. It is, of course, obvious that, since the LiCl is somewhat soluble in propylene carbonate (0.055 M), the behavior might largely be the result of this limited solubility; and the principle of using a salt displacement reaction for charge is not fully demonstrated.

III-E-3. Salt Displacement Cycling of Copper Electrodes

Electrodes were prepared of copper powder and either LiF or LiCl. The objective was to see whether there was evidence that, on charge, the insoluble copper salt could be formed.

The electrodes were prepared by sintering together equal parts by weight of the copper powder and the lithium salt in argon atmospheres at 650-700°C for one half hour. The electrochemical behavior was then studied in PC/1 M $Mg(ClO_4)_2$, since it was desirable to have present an electrolyte which is not electrochemically reduced at potentials positive to that of the lithium open circuit potential, and previous experiments had demonstrated that this was the case for the PC/$Mg(ClO_4)_2$ solutions.

With the Cu-LiF electrode anodization was performed at various currents and for various periods of time, the current was then reversed and, but negligible recovery could be obtained on cathodization. Identical results were obtained when copper powder was sintered under the same conditions but without the incorporation of LiF. The results in this latter case were identical to those in the former. Thus, there was no evidence that the presence of LiF has resulted in the production of an insoluble CuF_2 deposit which could be subsequently discharged.

The Cu-LiCl and Cu-LiF electrodes, prepared by sintering, were also subjected to cathodization in the PC/$Mg(ClO_4)_2$ electrolyte. There was no evidence for lithium deposition in the Cu-LiF system, whereas, for the Cu-LiCl electrode, lithium could be deposited. More detailed electrochemical studies were not performed.

A number of other attempts have been made to dry to induce the salt displacement formation of CuF_2. These have all involved trying to anodize mixtures of copper metal and LiF. Two types of electrodes have been used. One consists of simply placing the mixture in the bottom of a glass tube, 3/8 in. in diameter, the end of which is closed by a glass frit. A platinum foil disc is placed on top of the mixture to serve as the current collector. In order to hold the platinum current collector firmly against the mixture in the bottom of the tube, a glass rod, about 1/8 in diameter, fitting snugly inside the glass tube, is inserted, so the bottom of the rod presses against the platinum foil. Slight pressure is maintained by holding the glass rod in place with rubber bands fastened to the outside of the tube in which the mix is placed.

The second electrode is even simpler, and consists of a small stainless steel cup, about 1/4 in deep and about 1 cm^2 in area. The mixture is simply placed in the cup, which is then suspended in the solution.

In both cases a PC/0.5 M $LiClO_4$ solution was used, and the potentials were measured against a reference electrode consisting of a silver wire in a 0.5 M $LiClO_4$ - 0.01 M $AgClO_4$ solution in the side compartment of the cell.

The results are typified by those shown below, which were obtained in the stainless steel cup, suspended in the solution. It will be recalled that the potential of a Cu/0.01 M Cu^+ electrode is about -0.15 V vs. this reference electrode and that of the Cu/0.01 M Cu^{++} electrode is about the same in view of the fact that both copper species are produced in approximately equal amounts of anodization of metallic copper in propylene carbonate.

			E (vs. Ag/0.01 M Ag^+)
Run 1:	A mixture of copper powder and CuF_2 was pressed into the cup at about 1500 lb. the potential was measured.		-0.49 V
Run 2:	Copper powder was pressed in the bottom of the cup and anodized at 1 mA for 20 min. The open circuit potential decay was measured with time.	t = 0	-0.07 V
		t = 2 hrs	-0.10 V
		t = 4 hrs	-0.12 V
		t = 6 hrs	-0.14 V
		t = 8 hrs	-0.16 V
		t = 10 hrs	-0.18 V
		t = 12 hrs	-0.22 V
		t = 14 hrs	-0.26 V

Run 3: Copper powder and LiF were placed in the bottom of the cup. Potentiostatic anodization was conducted with these results.

Potential of anodization	Subsequent O.C.V.
-0.2 V (4.5 min)	initially, -.24 V, steady drift to -0.32 V after 6 min.
-0.1 V (14 min.)	-0.14 V for 6 min.
O V (11 min.)	-0.095 V for 5 min.
±0.1 V (6 min.)	-0.7 to -0.8 V for 8 min.
+0.2 V (4 min.)	-0.065 V for 6 min.
+0.3 V (4 min.)	-0.055 V for 6 min.
+0.4 V (4 min.)	

Run 4: Copper powder (12 millimoles) and LiF (4.5 millimoles) pressed into bottom of cup. Cycling was conducted as indicated: (Potentials are corrected for iR drop)

Anodize 1 mA, 20 min	-0.10 V to -0.06 V (apprx. linear)
then reduce at 1 mA	-0.06 V to -0.38 V after 20 min. gradually, then abruptly changed to -0.8 V in the next minutes. Efficiency = 100%
Anodize at 2 mA 20 min.	-0.12 V to -0.06 V (gradual change)
then reduced at 2 mA	-0.06 V to -0.42 V after 35 min. gradually, then abruptly changed to -1.0 V in next min. Efficiency = 75%
Anodize 1 mA 20 min., reduce potentiostatically at -0.5 V	Integrated recovery current = 15 mA-min; Efficiency = 75%
Anodize 1 mA 50 min., reduce potentiostatically at -0.5 V	Integrated recovery current = 42 mA-min; Efficiency = 84%
Anodize 1 mA 100 min., reduce potentiostatically at -0.5 V	Integrated recovery current = 90 mA-min; Efficiency = 90%

We do not believe that the above data reflect the anodic formation of CuF_2, since the potentials are close to those one would expect for a system containing significant concentrations of soluble copper species. The apparent efficiencies probably reflect nothing more than that the soluble copper species could not migrate away from the electrode sufficiently rapidly to prevent their subsequent recovery on cathodization.

III-F. CONCLUSIONS, CYCLABLE CATHODES.

The data suggest that iron, cobalt, and nickel are not useful elements for incorporation in secondary cell cathodes, as they are too irreversible, electrokinetically. Further experiments are needed, however, to determine whether, in fact, it is possible to anodically oxidize these metals with satisfactory efficiency in organic electrolytes.

Most of our work has been concerned with the copper system. The problems are chemical rather than electrochemical. While it is possible to anodically oxidize copper to copper (I) and copper (II) with 100% efficiency, it has not yet been possible to find those conditions under which the product of oxidation can be made to precipitate in the electrode and be available for subsequent cathodic discharge.

In chloride media, there is a strong tendency for copper (I) and copper (II) to form chloro-complexes. Thus, on anodization, soluble species normally form which migrate away from the electrode. On cathodization, inefficiency results through the reaction, $2CuCl + e^- = Cu^o + CuCl_2^-$, and the latter species leaves the electrode before it can be reduced.

In fluoride media there are two problems. The first concerns the displacement of copper (II) from the fluoride by lithium ions, through the reaction: $CuF_2 + 2\,Li^+ = Cu^{++} + 2\,LiF$, which results in a loss of efficiency through dissolution and migration away from the electrode of copper (II). The second problem concerns the difficulty in finding a satisfactory reservoir for fluoride ions, to allow the precipitation of CuF_2 on anodic charging. We have proposed the use of a reservoir of the insoluble alkali metal halide, and have found this proposition to work in the case of the silver chloride electrode. Efforts to use the same principle in attempting to cycle the copper fluoride electrode have not been successful.

A problem in both fluoride and chloride media concerns the relative stability of copper (I). In both media, the product of reduction of copper (II) appears to be a soluble copper (I) species. Thus, the cathodization of copper (II) fluoride is probably described by: $CuF_2 + e^- + 2\,Li^+ = Cu^+ + 2LiF$, and, since most of the copper (I) leaves the electrode before it can be reduced, maximum efficiencies of about 50% are realized.

Although one would expect that the unfavorable chemical situation which exists with respect to cathodes would limit cell performance, this must be tested in experimental cells. If it is found that there is a correlation between experimental cell performance and these chemical problems, then it is obvious that further work must be concentrated on finding a solution to the chemical problems. This involves careful measurement of the equilibria which prevail and attempts to alter the equilibrium in such a way as to improve performance.

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. Vapor phase chromatography is performed as follows: Two conditions of operation are used:

a. Isothermal runs

Injector temperature:	220°C
Detector temperature:	200°C
Column temperature:	constant at 200°C
Water retention time:	ca. 25 sec.

b. Temperature programmed runs

Injector temperature:	220°C
Detector temperature:	200°C
Column temperature:	constant at 100°C for

first 100 sec. following sample injection, then increased at 48° per min. up to 200°C at 175 sec. Held constant at 200°C until sample has been entirely eluted. A typical chromatogram of a temperature programmed run is shown in Figure 32.

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

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

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

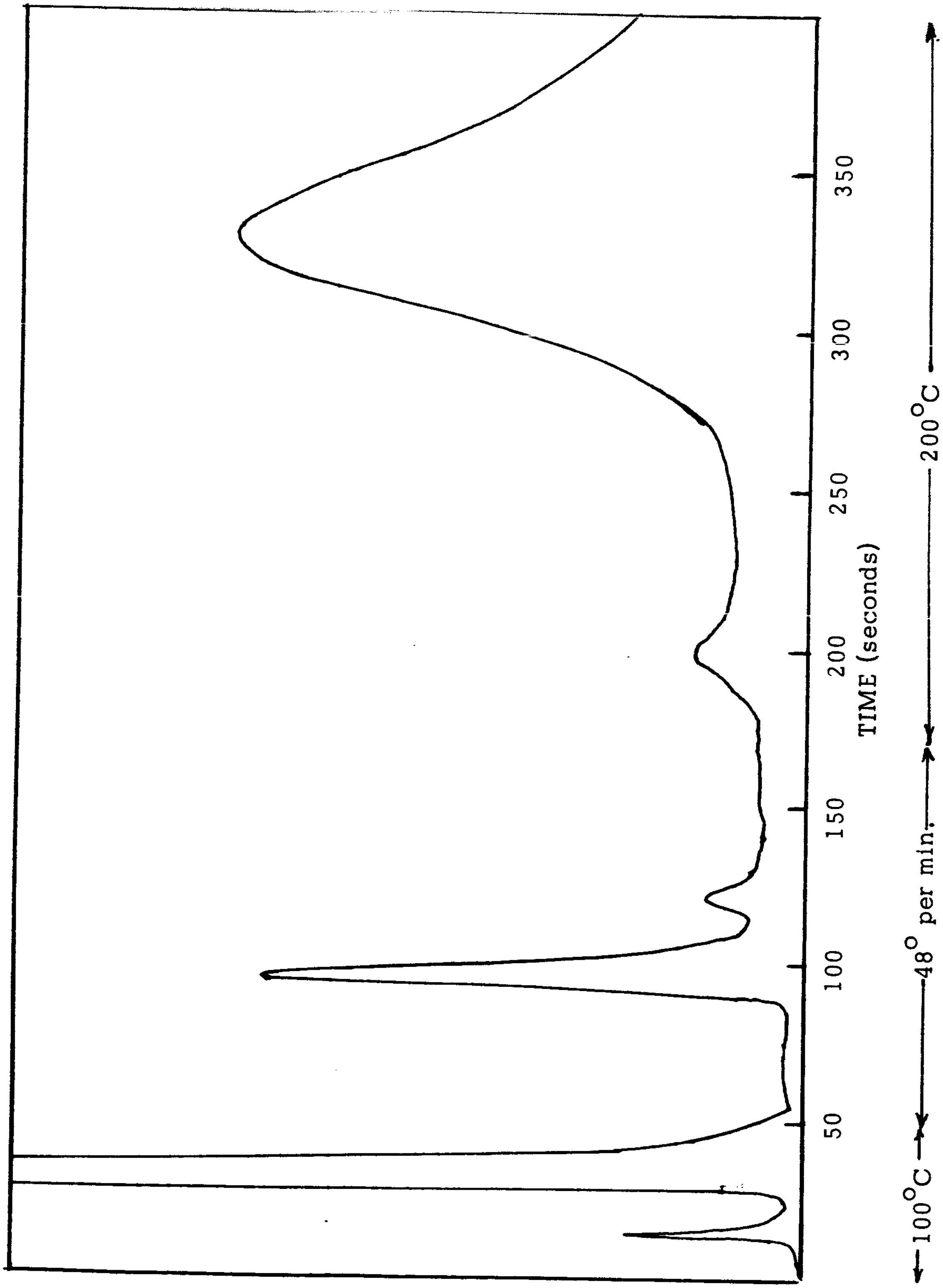


Figure 32: VAPOR PHASE CHROMATOGRAPH OF PROPYLENE CARBONATE

Vacuum distillation of two 3-kg quantities of propylene carbonate was performed for the purification tests. 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 37, 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 37

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%	---	---	---
2 - 24	5 mm.	74-80	9:1	---	0.04	78	---
3 - 38	5 mm.	80-96	9:1	---	0.06	11	---
4 - 60	5 mm.	96	9:1	--	0.03	0.12	---
5 - 1000	5 mm.	96	9:1	---	0.01	0. 02	---
6 - 1000	5 mm.	96	9:1	---	0.002	0.006	---

The determination of the components was made by adding to successive portions of the propylene carbonate, small amounts of a variety of materials whose presence was deemed likely. Those materials which gave totally new peaks were not considered present in the initial sample. Those materials which enhanced peaks were considered to be the components initially present. The following materials were investigated for their presence as impurities in the propylene carbonate: isopropyl alcohol, propionaldehyde, propiolactone, propionic acid, propionic anhydride, allyl alcohol, propylene oxide, and propylene glycol. Only the latter two were initially present in measurable amount.

Several facts are evident. (1) 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 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 above described second distillation were combined and re-distilled 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 in table 38 on the next page.

Table 38

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			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 39

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	$56-60^{\circ}$	9:1	0.08%
2 - 150	3-4	62°	9:1	0.65%
3 - 600	3	$60-62^{\circ}$	9:1	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 $40-50^{\circ}$C. A liter of this material, which had stood over molecular sieves for two months, contained about 0.0036% water.

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-received material was about 0.098% by weight.

IV-A-6. Acetonitrile

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. Determination of Water in P.C.-Salt Solutions

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 33 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 34. The

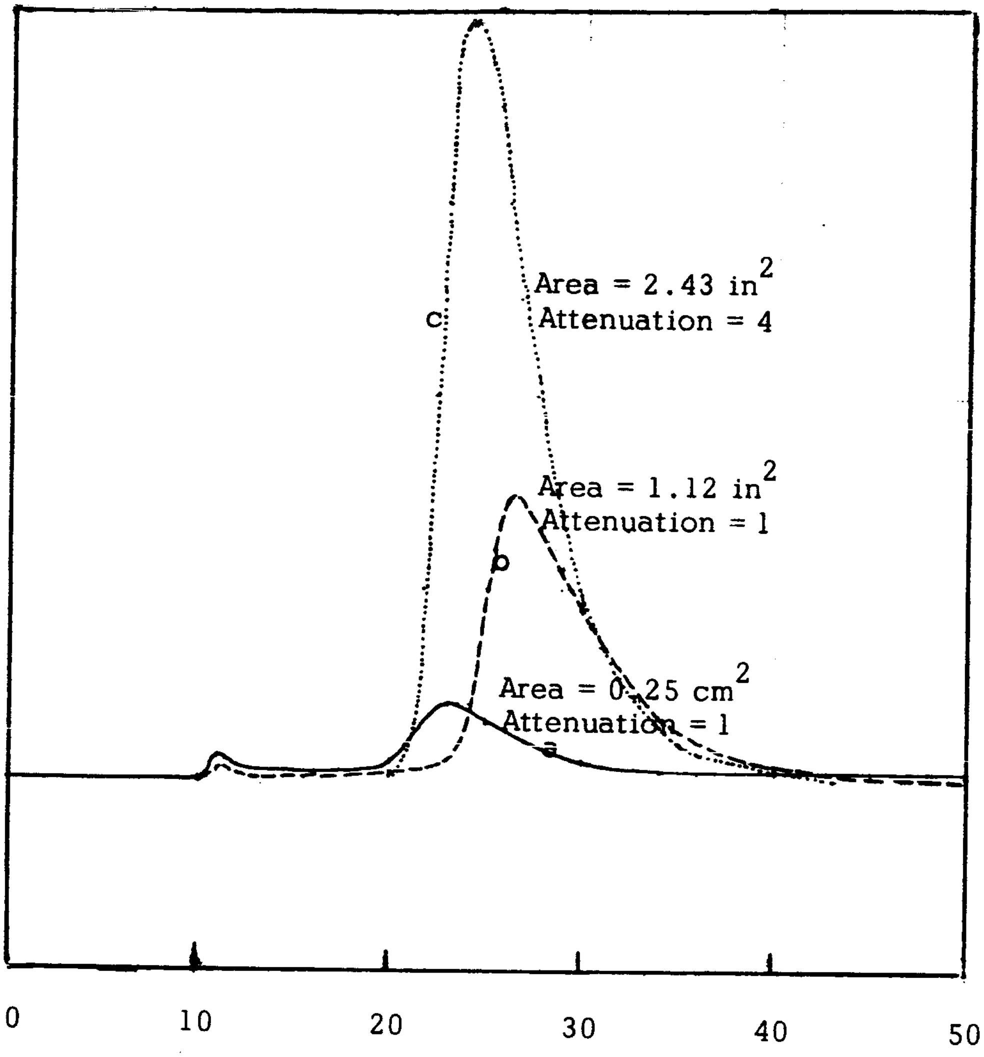


Figure 33 : VAPOR PHASE CHROMATOGRAM OF WATER IN PROPYLENE CARBONATE Performed with 0.8 microliter samples. Column temperature = 200° C.

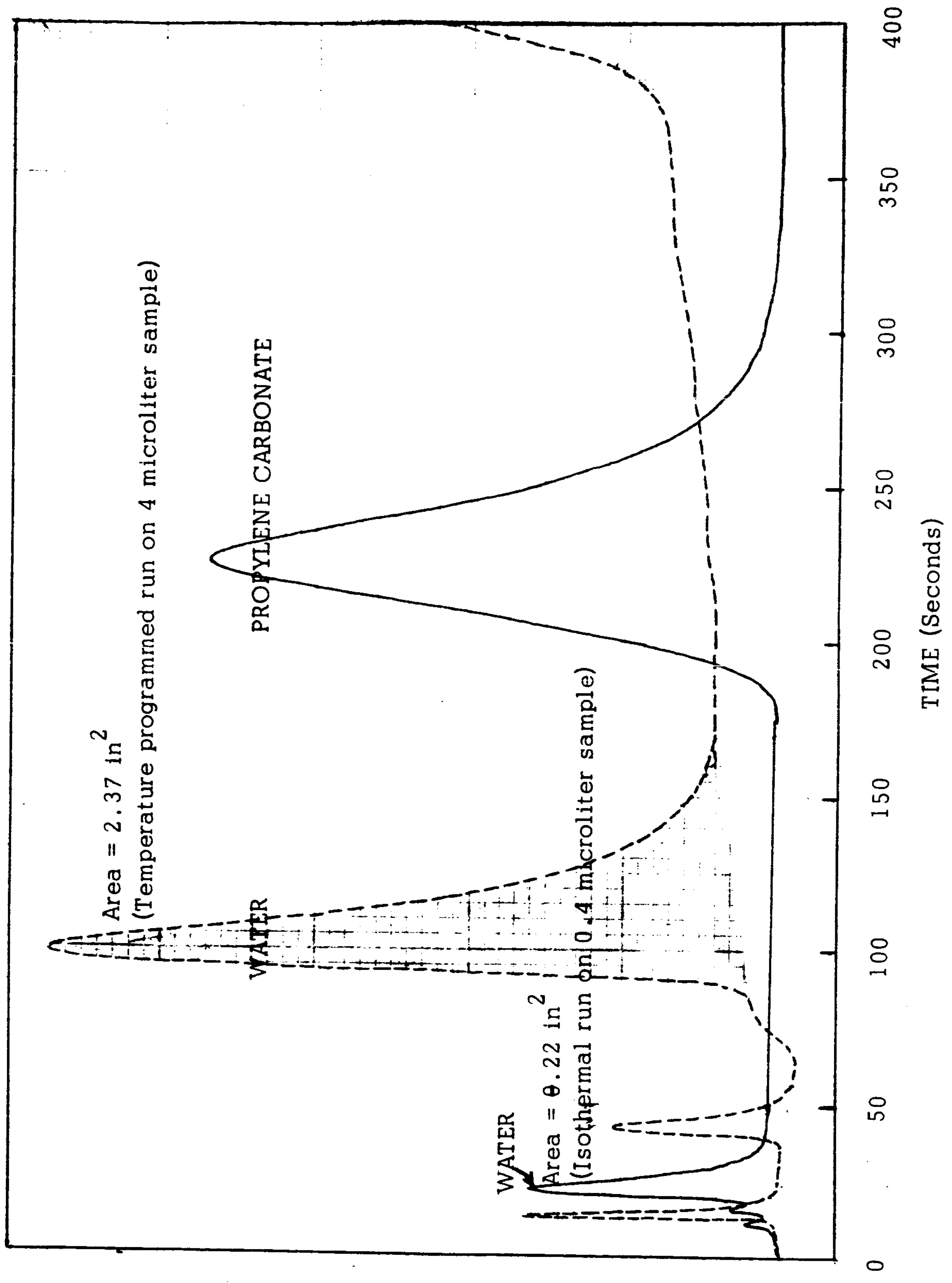


Figure 34: VAPOR PHASE CHROMATOGRAMS IN PROPYLENE CARBONATE

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

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 34 is 2.37 in^2. In a constant temperature run it will be observed that no peaks are apparent between the water and the propylene carbonate. The first peak in Figure 34 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.

Another question concerns the lower limits at which water may be detected. In Figure 35 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.

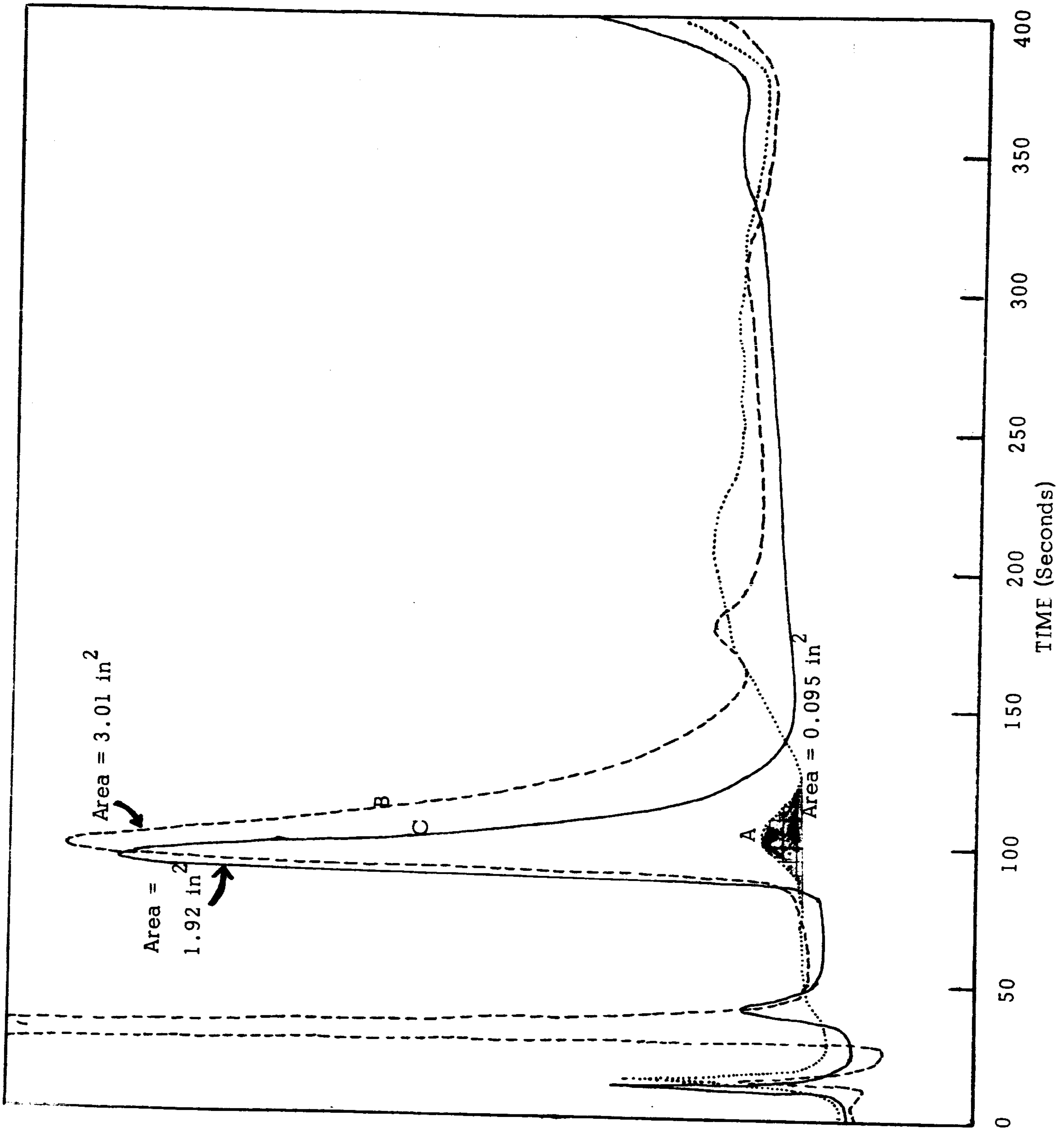


Figure 35: VAPOR PHASE CHROMATOGRAMS OF PROPYLENE CARBONATE
Performed with 4 microliter samples with temperature programming (see text) all runs done at attenuation = 1.

APPENDIX I. Abbreviations

In this report concentrations are expressed in moles per liter ($M\ l^{-1}$). The current is always in milliamperes (mA). The extent of electrochemical reaction is normally in millicoulombs per square centimeter ($mC\ cm^{-2}$). Potentials are in volts and, unless otherwise indicated, are given with respect to a silver wire immersed in the same solution.

Table 40

Abbreviations

C = Concentration, in $M\ l^{-1}$

C^o = Bulk concentration

D = Diffusion coefficient, in $cm^2\ sec^{-1}$

d_D = Thickness of the Nernst diffusion layer

d_L = Distance between the tip of the Luggin capillary and the electrode surface.

E = Potential, in Volts

G = Gibbs free energy

mC = Millicoulombs

n = Number of electrons involved in an electrochemical reaction

i = Current density, in $mA\ cm^{-2}$

i_L = Limiting current density

i_o = Exchange current density

$iT^{1/2}$ = the product of the current density and the square root of the transition time. in $mA\ cm^{-2}\ sec^{1/2}$

t = time, normally in seconds.

t_+, t_- = transference number of the indicated ion

T = the chronopotentiometric transition time, or the temperature

z = the absolute value of the ionic charge

ρ = the specific resistance in ohm-cm

λ = the ionic equivalent conductance, in $ohm^{-1}\ cm^2$ equivalent^{-1}

Λ = the equivalent conductance of a salt, in $ohm^{-1}\ cm^2$ equivalent^{-1}

APPENDIX II. Preparation of $LiAlCl_4$ and $LiBF_4$.

Since these two materials are salts of the strong Lewis acids, $AlCl_3$ and BF_3, which catalyze decomposition of propylene carbonate, and, probably most of the other solvents, some care must be used in the preparation so the uncombined Lewis acids do not come in contact with solvent.

Three methods have been used for the preparation of $LiAlCl_4$ solutions. The first, and least satisfactory, involves the dirrect addition of stoichiometric amounts of LiCl and $AlCl_3$ to the solvent. By this procedure, the solvent undergoes extensive decomposition, attended by deep discoloration.

A second procedure involves refluxing $AlCl_3$ and LiCl together in ether. The ether is distilled off, and the requisite amount of solvent added to the precipitated salt. The resultant solutions are colorless or very light yellow. After several days the discoloration becomes more pronounced.

The third, and simplest procedure, which has been used in the work reported in this paper, consists of mixing together equal moles of LiCl and $AlCl_3$ and heating the mix in a closed container until fusion is observed. The cooled material, when dissolved in solvent, results in solutions which are essentially colorless.

The commercial $LiBF_4$ we have found to be contaminated with electroactive impurities. The procedure we have followed in synthesizing the salt consists first in purifying an ethereal BF_3 solution by distillation. To the colorless solution is added an equivalent amount of LiF and the mixture is refluxed. The ether is distilled off and the colorless salts when dissolved in propylene carbonate or butyrolactone give clear solutions which, by vapor phase chromatography, do not give evidence of significant decomposition.