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FINAL REPORT

July 1963 - September 1964

RESEARCH & DEVELOPMENT OF A HIGH CAPACITY NONAQUEOUS SECONDARY BATTERY

by

K.R. Hill and R.G. Selim

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

August 15, 1965

Contract No. NAS 3-2780

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

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RESEARCH AND DEVELOPMENT OF A HIGH CAPACITY, NONAQUEOUS SECONDARY BATTERY

by K. R. Hill and R. G. Selim

SUMMARY

The promise of propylene carbonate as a solvent for supporting certain secondary battery electrodes is confirmed. Lithium may be deposited from a variety of solutions incorporating this solvent; the electrodeposits appear to be stable with respect to self-discharge by the solvent but are sensitive to the presence of impurities, both water and other, unknown impurities. Electrodeposits of lithium evidently may be oxidized with 100% efficiency, however efficiencies of deposition of better than 80% have not yet been observed. The deposition of lithium and subsequent anodic dissolution appear to proceed without serious electrokinetic irreversibility.

Silver may be anodized to insoluble silver chloride. When the current is reversed following anodization, essentially 100% recovery of the current passed on the previous anodization is obtained. There does not appear to be evidence of significant electrokinetic irreversibility. Copper is less satisfactory. When copper is anodically oxidized in chloride media and the current reversed, recoveries in the range of 50-80% are realized. The evidence indicates that this is because of the slow solubility of the copper salts formed on anodization. Iron, cobalt and nickel are probably unsatisfactory. Severe activation overvoltage is evident on both anodization and on subsequent cathodization. It is, in fact, possible that these three metals are not oxidized to the soluble ions at all, but that oxidation may be of solvent, and subsequent cathodic reduction may be of the by-products formed during the previous anodization. Couples employing the three metals, iron, cobalt and nickel, are not of further interest at present.

The role of impurities, including water, is more ambiguous than had been

anticipated. Solvent purification has been routinely effected by vacuum distillation. Pre-electrolysis of $LiAlCl_4$ solutions effects some improvement insofar as the cycling efficiency of the lithium electrode is concerned. The method of preparation of the $LiAlCl_4$ solutions is important. The direct addition of LiCl and $AlCl_3$ to propylene carbonate is less satisfactory than is an indirect synthesis involving first the chlorination of aluminum in ethyl ether, then the addition of the requisite volume of propylene carbonate followed by the vacuum evaporation of the ether. This gives a nearly colorless solution of $AlCl_3$, which, on the addition of LiCl yields the $LiAlCl_4$ solution. The manner in which water is detrimental is not clear. Although the presence of water is deleterious, it is not as serious as might be expected. Direct electrochemical evidence for the presence of water cannot be obtained. That is, limiting currents for water reduction at potentials positive to the lithium electrode cannot be observed.

A major consideration in this work has been an assessment of the degree to which various basic electrochemical techniques, particularly chronopotentiometry and solid electrode polarography, may yield useful data. These techniques have been extensively used in this work, and their utility is well-demonstrated. However, complete interpretation of the data is not yet possible, since the conditions under which the techniques have been employed are not those leading to well-defined theoretical description.

It had been reported in the literature that mixtures of dialkyl beryllium compounds and alkali metal salts sometimes produce complex compounds which are liquid at room temperature and have conductivities similar to those of fused salts. We have tried to prepare eighteen such complexes. In only five cases were liquid mixtures produced and the maximum conductivity was only 4×10^{-4} ohm^{-1} cm^{-1}. This was realized with a mixture of one mole of cesium fluoride to two moles of diethyl beryllium. The organoberyllium complex salts have not demonstrated promise as battery electrolytes.

I. Introduction

As stated in the contract, the objective of our work has been "an investigation of the basic nature of the most promising couples and nonaqueous electrolytes in order that a thorough understanding of the underlying principles associated with a high capacity, non-aqueous, secondary battery be obtained."

Neglecting considerations of high energy density, relatively few materials exist with the unique combination of properties such that these materials can be incorporated into aqueous primary or secondary cells operating at reasonable rates. A large number of systems exist with high theoretical energy density -- these systems primarily incorporate light active metal anodes (lithium, magnesium, aluminum, etc.) and oxides, fluorides, and chlorides of the first row transition elements (copper, nickel, cobalt, etc.). However, these systems with high theoretical energy density are insufficiently stable in aqueous solution to allow the fabrication of useful cells. Very limited information exists regarding the electrochemical behavior of these systems in other electrolytes.

Recent interest in the use of these systems with high theoretical energy density was engendered by the work of Harris[1], who demonstrated the ability of a variety of cyclic esters to support active metal electrodeposition. These solvents -- ethylene carbonate, propylene carbonate, γ-butyrolactone, γ-valerolactone, ethylene trithiocarbonate, and cyclopropanone -- were of particular interest because of their high dielectric constants. This suggested the possibility of obtaining electrolytes with these solvents of sufficiently high conductivity to allow incorporation in primary and secondary batteries.

Work in the application of these solvents to the development of high energy density cells was initiated by Lockheed[2], who later concentrated on the development of lithium-silver chloride cells operating in propylene carbonate electrolytes.

In spite of the large amount of work reported, relatively little quantitative

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(1) Harris, W. S., Electrochemical Studies in Cyclic Esters," AEC Report, UCRL 8381, 1958.

(2) H. F. Bauman, J. E. Chilton, G. M. Cook, "New Cathode-Anode Couples Using Nonaqueous Electrolyte". ASTIA AD 4105577, July 1963.

information on the basic electrode processes and the influence of electrolyte on these processes existed. It was our objective to investigate these processes by techniques analogous to those commonly employed in the investigation of electrochemical phenomena in aqueous media. It was first necessary to determine whether these conventional electrochemical techniques could be employed to obtain useful information by which the relative ability of various systems to sustain operation allowing ultimate incorporation in secondary cells could be assessed. It was found that such information could be obtained, but it quickly became apparent that the electrode processes were considerably more complex than had been anticipated. Therefore, subsequent work was focused on a more exhaustive examination of but a few specific systems. The table of contents will indicate the variety of phenomena examined. All of these phenomena would be expected to influence the development and performance of secondary cells. However, the degree to which these specific phenomena are important can, indeed, only be a matter of conjecture until cells have been developed which exhibit sufficiently good operating performance to allow the resolution of effects ascribable to the various phenomena.

The history of the development of aqueous cells suggests, we believe, the reasonability of anticipating that the upgrading of non-aqueous cells to give performance comparable to that of present aqueous cells will demand the acquisition of a good deal of background information about the chemical and electrochemical characteristics of the various systems proposed. This report is intended to supply some of this information as well as to indicate areas in which more detailed work is required.

II. Metal Salt Cathodes

A. Introduction

Three inter-related and equally important objectives have guided our work with possible cathode materials:

1. To investigate the general applicability of standard electrochemical techniques to measurements performed in propylene carbonate and similar solvents. Though such techniques as polarography and chronopotentiometry are employed in the investigation of electrochemical phenomena occurring in aqueous media incorporating an excess of supporting electrolyte, it is not yet clear the degree to which such techniques may yield equivalent information in non-aqueous solvents in the absence of excess supporting electrolyte.

2. To investigate the nature of the species present in solution. The behavior exhibited by an electrode is intimately related to the composition of the solution in which the electrode operates and it is desirable that some information about the solution species potentially available for participation in electrode reactions be obtained.

3. To investigate the utility of various systems with respect to their charge-discharge efficiency. High energy density demands efficient cycling performance, at least under ideal conditions, and we have been concerned with the degree to which various systems display inherent cycling efficiency.

B. Experimental

1. Electrode Fabrication

In a research effort in which the objective is the gathering of data representing fundamental electrochemical phenomena and in which the maximum control must be exercised over all variables, the most important experimental tool is the working electrode itself. For this reason the utmost care and consideration went into the design and use of the working electrodes employed in this program.

In Figure 1 is shown, at the left, a completed electrode of the type used in most of our work. It consists of six metal discs surrounding a central silver disc, the whole imbedded in epoxy. The mold in which the electrodes are prepared is shown at the right in Figure 1. The metal discs were sliced from 5 mm rods of high purity metals (99.99% or better), and had an area of about 0.2 cm^2. Each disc had a separate lead, and a bundle of leads were drawn out through a glass tube sealed on the glass mold, as shown in Figure 1 at the right. After the epoxy had hardened overnight the entire electrode surface was mechanically ground and polished.

Normally the six circumferential metal discs served as the working electrodes. Thus six runs could be made before the electrode need be removed and repolished. Electrochemical measurements gave identical results on all six working electrodes.

The center silver disc served as the reference electrode, thus eliminating the necessity for a more complicated structure employing a Luggin capillary. Initially it had not been anticipated that such a simple procedure could be used. However, it was observed that the silver disc assumes a constant and reproducible potential in all of the solutions examined, thus allowing it to be used as a reference electrode. The potential of the silver disc was about +3.0 V versus a lithium electrode in a solution of lithium ions.

2. Cells

A variety of electrolysis cells were employed, all of relatively simple, modified H-cell design. The most frequently used style of cell is shown in Figure 2. It consisted of a cylindrical main compartment having a volume of about 250 ml. This was separated by a glass frit tube from a smaller side compartment for the counter electrode, fitted with a Teflon stopcock for drainage. The main compartment was covered with a Teflon stopper having appropriate holes or slots for inserting a "lollipop" assembly and a fritted glass gas bubbler. The latter had a

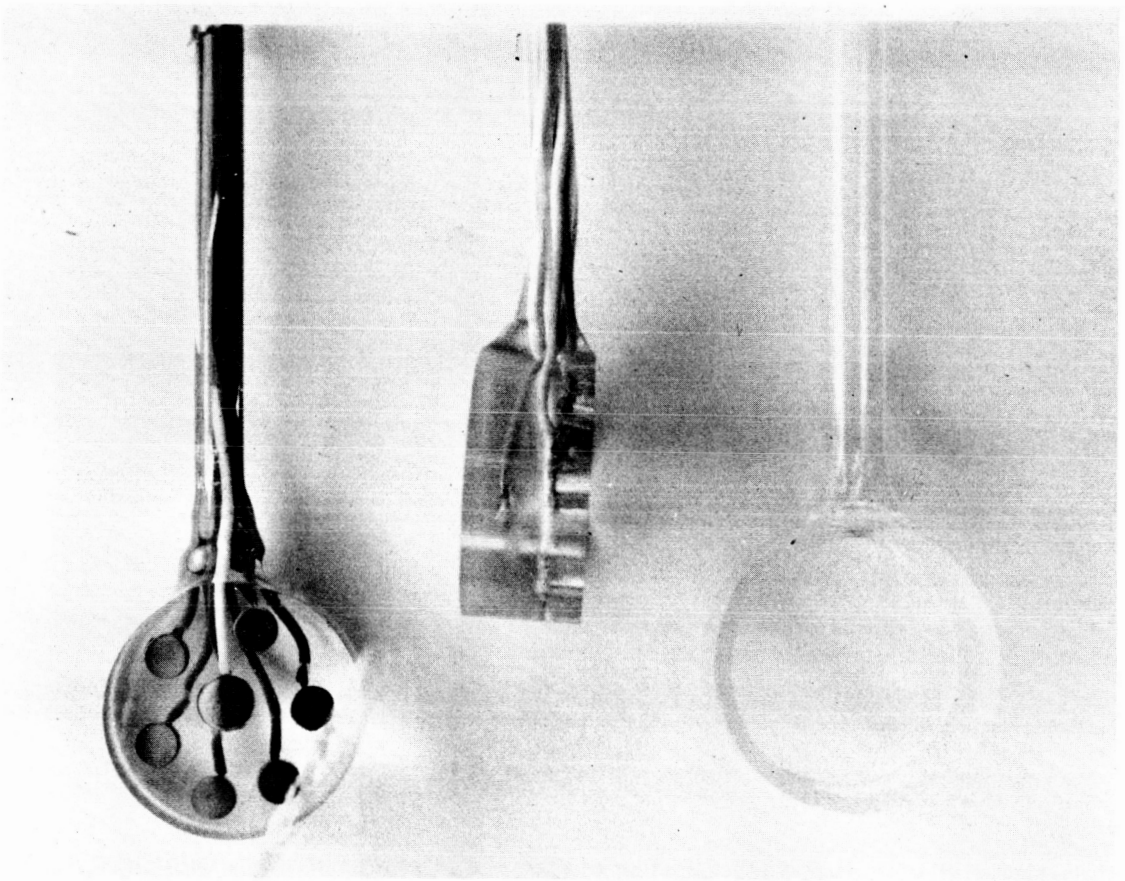

Figure 1 ELECTRODE STRUCTURE

Electrode shown actual size. On the right is shown the glass mold in which the electrode is prepared. Metal discs sliced from high purity metal rod are soldered to individual, insulated copper wires. The discs are sealed in epoxy resin and the surface is polished. Front and side views of the completed electrode are shown in the left and center. Normally, the circumferential discs serve as individual working electrodes, and the center disc (silver) serves as the reference electrode without further treatment.

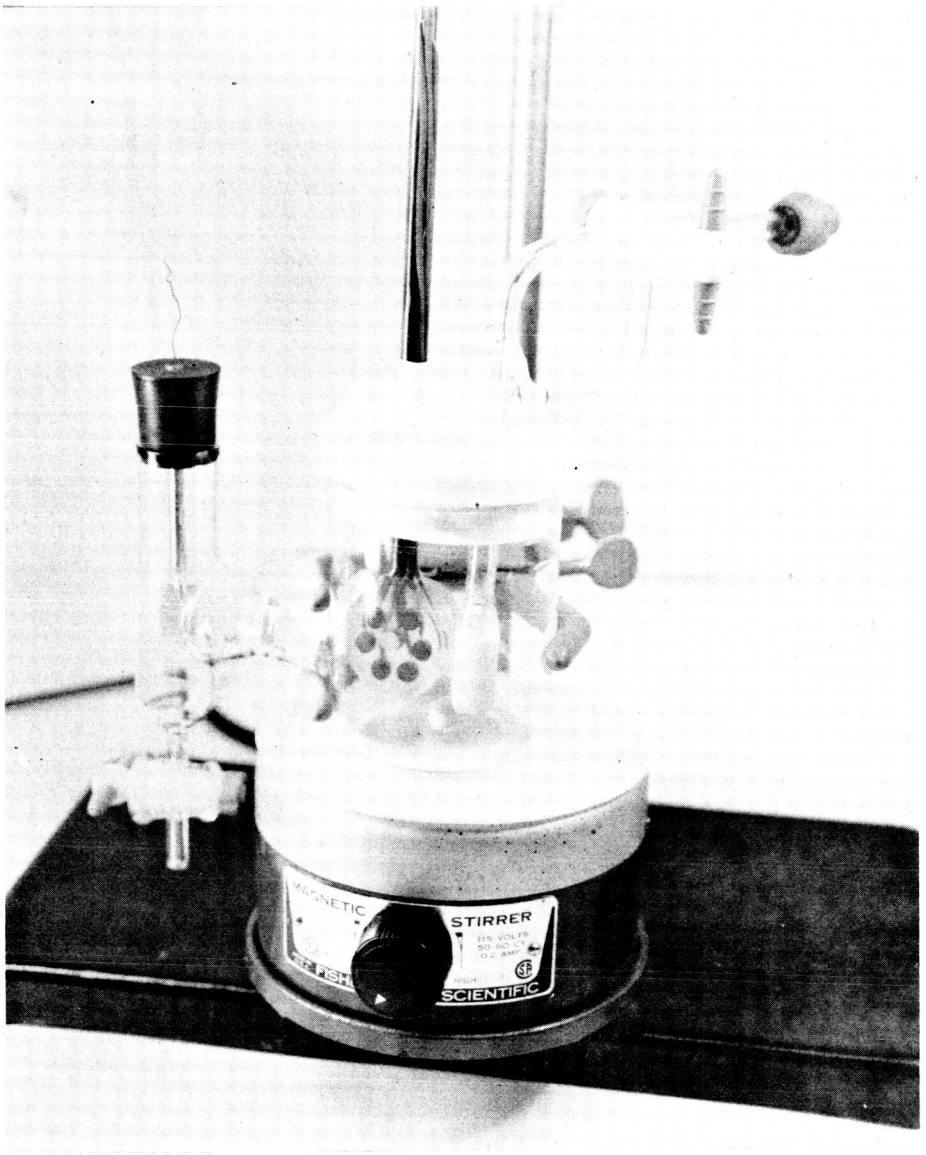

Figure 2 ELECTROLYSIS CELL

Electrolysis cell for the performance of electrochemical experiments, showing counter electrode chamber on the left and working electrode chamber on the right. In the working electrode chamber are immersed the electrode (shown in figure II-1) and the deaeration apparatus.

3-way Teflon stopcock to allow nitrogen or argon either to be bubbled through the solution or directed over its surface. Provision was made for stirring the main compartment with a Teflon covered magnetic stirring bar. Some cells were fitted with glass water jackets for use where temperature control was desired.

3. Electrical Circuitry

All chronopotentiometric measurements were made using the system shown schematically in Figure 3 and assembled for use in Figure 4 or using completely equivalent systems in which the design was simplified by grounding the working electrode, eliminating the voltage reference source, and continuously measuring the potential of the reference electrode versus the grounded working electrode directly via the electrometer; thus the instrumentation used is conventional. An adjustable constant current was supplied by an Electronics Measurement Model 630-C or C-631 constant current supply. An electronically regulated constant current supply is essential in work performed in poorly conducting solutions. This is because the resistance between the counter electrode and the working electrode (particularly the resistance through the glass frit) is so high that the total iR drop of the cell may be as large as 100 V. (Note: This is not the iR drop included in the measured potential between the working and reference electrodes.) Furthermore the iR drop through the cell varies with time, especially at high currents, probably through Joulean heating in the glass frit. As will be seen, the potentials of both working and counter electrode may vary by as much as ten or more volts during the course of electrolysis. Thus, to prevent undesirable fluctuations in the cell current this current must be regulated electronically or be provided by an inconveniently large bank of batteries.

For precision work the magnitude of the current was determined by measuring the voltage drop across a precision resistor with a Rubicon potentiometer. Normally such accuracy was not necessary, and a milliammeter was used to measure the current.

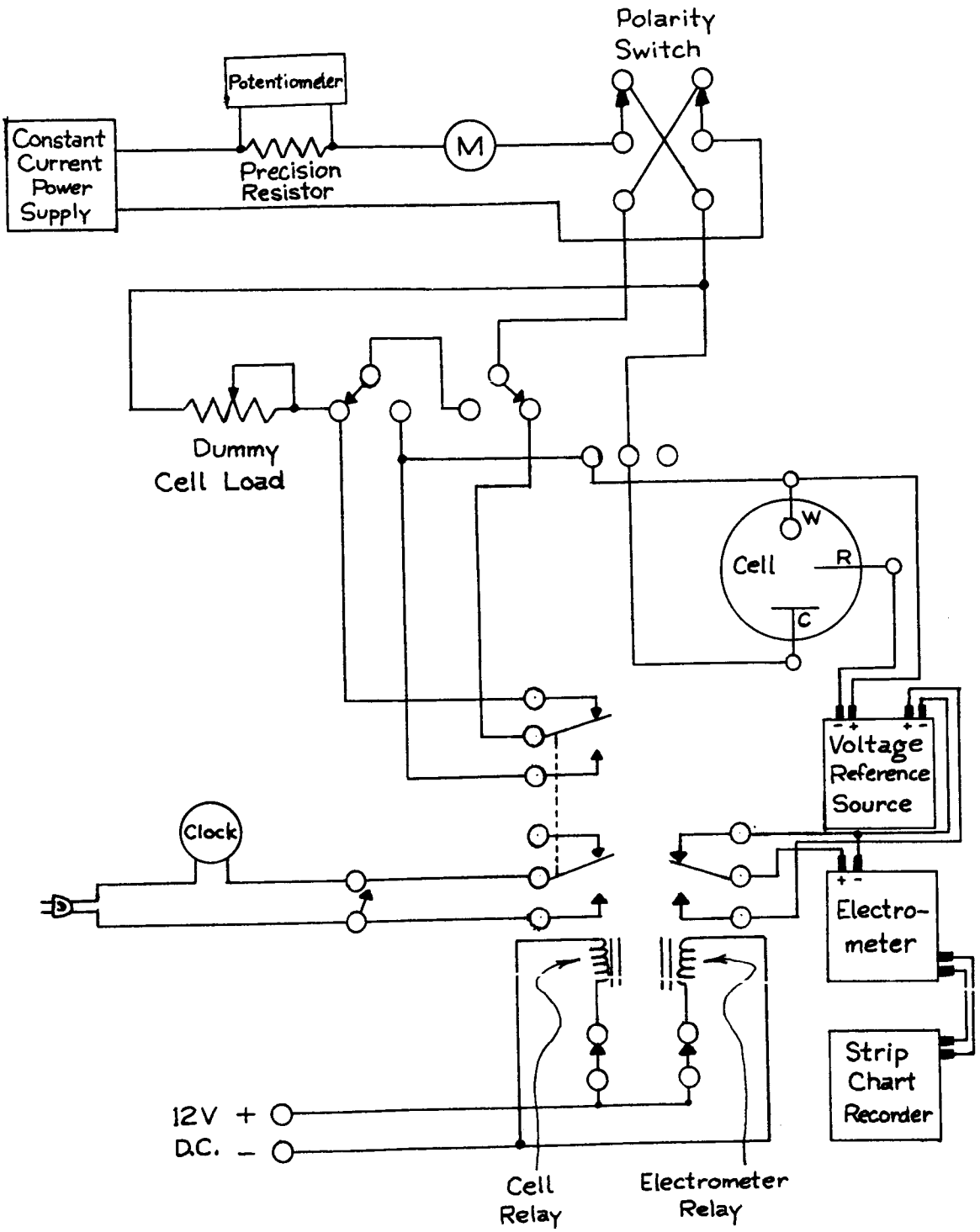

Figure 3 SCHEMATIC DIAGRAM OF CHRONOPOTENIOMETRIC CIRCUITRY.

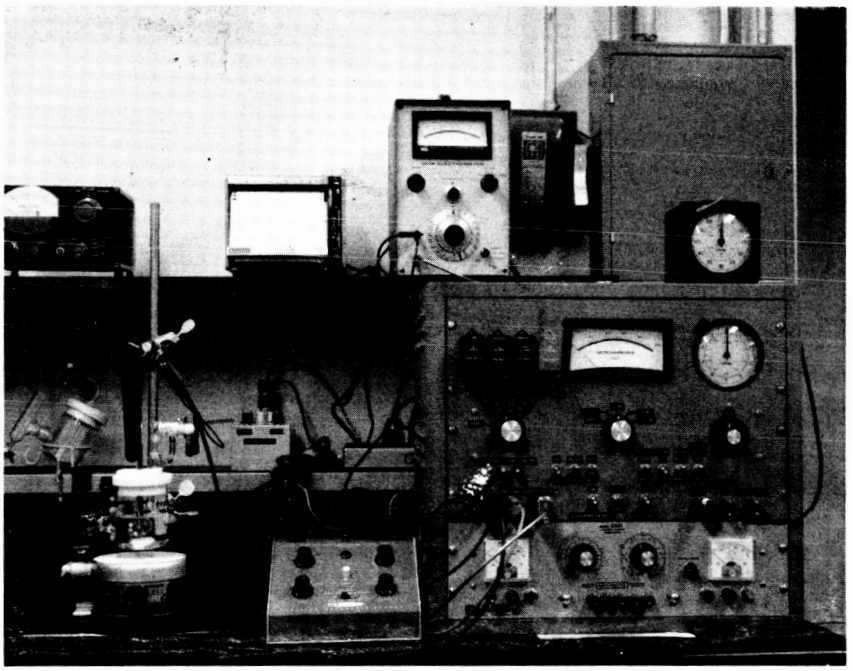

Figure 4 APPARATUS FOR CHRONOPOTENTIOMETRIC MEASUREMENTS.

Mercury relay switches were used to switch the current from the dummy load resistor to the cell, thus eliminating the contact jitter present with mechanical switching. The mercury relay also switched on a resettable electric clock for accurate transition time measurements.

The potential between the working and reference electrodes was measured by either a Keithley 610-A electrometer or an E-H Research Laboratories Model 230 electrometer. The electrometer output was fed either to a Varian Model G-14 or a Moseley Model 680 strip chart recorder. For transition times of less than 3 seconds a Tektronix oscilloscope was used and the transition times read directly off the screen. None of the three recording instruments was equipped with satisfactory zero offset and when such offset was desired a Heath Voltage Reference Source was incorporated in the apparatus as shown in Figure 3.

Potentiostatic measurements were carried out using a Wenking Electronic Potentiostat. This instrument essentially employs an electrometer and a variable constant current supply. The instrument senses the potential between the reference and working electrodes and varies the current between the counter and working electrodes such that this potential remains constant at the preset value. The resultant current was normally recorded with the Varian Model G-14 strip chart recorder.

4. Purification and Preparation of Solutions

All of the propylene carbonate, butyrolactone, and acetonitrile used in making up solutions for this work were vacuum distilled from Practical Grade material, except for a few experiments in which impure material was deliberately used. Vacuum distillations were carried out in a 90 cm jacketed, electrically heated column packed with Berl saddles and fitted with a water jacketed receiver. This apparatus is shown in Figure 5, which also shows the method of rack mounting the column and the placement of a plastic shield to guard it. The first 200 ml. of distillate were discarded after each fresh addition to the 2 liter stillpot. Distillate was then collected at 2 mm Hg at a reflux ratio of 1:1. Considerable care was required to prevent flooding of the column when working with

the high boiling solvents. Karl Fisher titrations of the distillates so obtained consistently gave residual water concentrations of around 0.02% which is about the lower limit for the titration apparatus.

Further purification of the salts from which the electrolytes were prepared was not attempted by us. The solutions were prepared by weighing the requisite amount of salt in an argon filled dry box and adding the salt in small amounts to the required amount of purified solvent.

During the preparation of aluminum chloride-propylene carbonate solutions it was found that even with slow addition of very small increments of aluminum chloride to the vigorously stirred solvent considerable heat was generated and the resulting solutions were yellow to dark reddish-brown. The effects of this are discussed later in more detail; however, it was found necessary to develop an alternative method for preparing aluminum chloride solutions. This consisted of dissolving a weighed amount of high purity aluminum wire in dry ethyl ether continuously saturated with dry hydrogen chloride gas. Dry nitrogen was then bubbled through the solution to remove excess hydrogen chloride and half of the required volume of distilled propylene carbonate was then added. The ether was removed by vacuum distillation at 40^{o}C and the residual clear, colorless solution diluted to the required volume with more propylene carbonate. Although solutions prepared in this way were nearly colorless, decomposition occurred slowly with time as evidenced by the gradual discoloration.

5. Experimental Procedure

Solutions prepared as described above were removed from the dry box in stoppered containers. The H-cell was prepared to receive the solutions by rinsing with acetone and drying in an oven. After removal from the oven, the cell was assembled with the Teflon stopper and argon or nitrogen continuously passed through the cell. When the cell had cooled, the solution was poured into it in the open atmosphere. Argon effectively blankets the solutions and protects it from atmospheric contamination as evidenced by the fact those phenomena most probably

Figure 5 APPARATUS FOR VACUUM DISTILLATION

influenced by the presence of water or oxygen picked up from the atmosphere did not seem to vary significantly even over a period of several days when the cell was allowed to remain in the open atmosphere with a continual flow of argon played across the surface of the solution. This will be discussed in more detail later. Nitrogen was used in those rare instances when argon was not available. Solutions were deaerated about twenty minutes prior to performing the experiments. Meanwhile the electrodes were polished on a wheel with one-micron alumina, rinsed first with water, then acetone, and dried under a stream of warm air. Finally they were wiped with tissue and immersed in the cell. Appropriate leads were attached and the experiments begun. It will be recognized that with the use of a single electrode for each experiment a large number of manipulations would be involved before the total number of experiments performed in a given solution could be completed. For this reason we have found the use of the six-electrode lollipop described above particularly advantageous in reducing the number of manipulations and the chances for inadvertant contamination during the removal, cleaning, and replacement of the electrode.

C. Results

1. Anodic-Cathodic Cycling Experiments in Screening Secondary Battery Cathodes

Since the cathode of a battery is much heavier than feasible anodes because of the high equivalent weight of most practicable cathode materials, it is particularly important that efficient electrochemical utilization of active cathode materials obtain on charge and discharge. In brief, it is necessary that, on charge, it be possible to form large amounts of insoluble, non-passivating films per unit area. It is further necessary that these films be capable of undergoing discharge with good efficiency. These are requirements which, in fact, are met by very few electrochemical systems.

Since, in the operation of an actual battery, the various effects ultimately limiting energy density may be mutually obscured, it is desirable that

relatively simple experiments be performed in which may be observed the degree to which the basic behavior of the various systems meets the conditions described in the preceding paragraph. It is further desirable that these experiments be of such a nature that the utility of modifications in a given system can be readily assessed. Much of our work in studying possible cathodic materials has been concerned with the evaluation of a number of possible systems using relatively unsophisticated anodic-cathodic cycling experiments.

The general procedure followed involves first oxidizing an electrode anodically in quiet solution at varying currents and for varying amounts of time. The current is then reversed and the electrode cathodized. The current may be reversed immediately after anodization or a period of time may be allowed to elapse before commencing cathodization. Properly performed and interpreted such experiments indicate whether a material can be oxidized to an insoluble, non-passivating film, the degree to which the film is chemically and physically stable, and the degree to which the film can be electrolytically reduced.

a. The Silver Electrode. In solutions of $LiClO_4$ and KPF_6 the silver ions formed on anodization are soluble. This is indicated by the results shown in Figures 6 and 7. The following facts are important:

(1) A plot of anodic potential versus current is linear, indicating that the observed polarization results from iR drop.

(2) The transition time observed on cathodization is about one-third the time of previous anodization. Theory predicts[1] that if a soluble, cathodically reducible species is produced on anodization, then cathodization immediately imposed following anodization will be attended by polarization after a period of time one-third that of the previous anodization. The solubility of the silver ion produced on anodization is further attested by the fact that brief stirring following anodization completely removes these ions from the region of the electrode and subsequent cathodization evidences no reduction of silver ions.

(1) P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers, Inc., New York, 1954, p. 195.

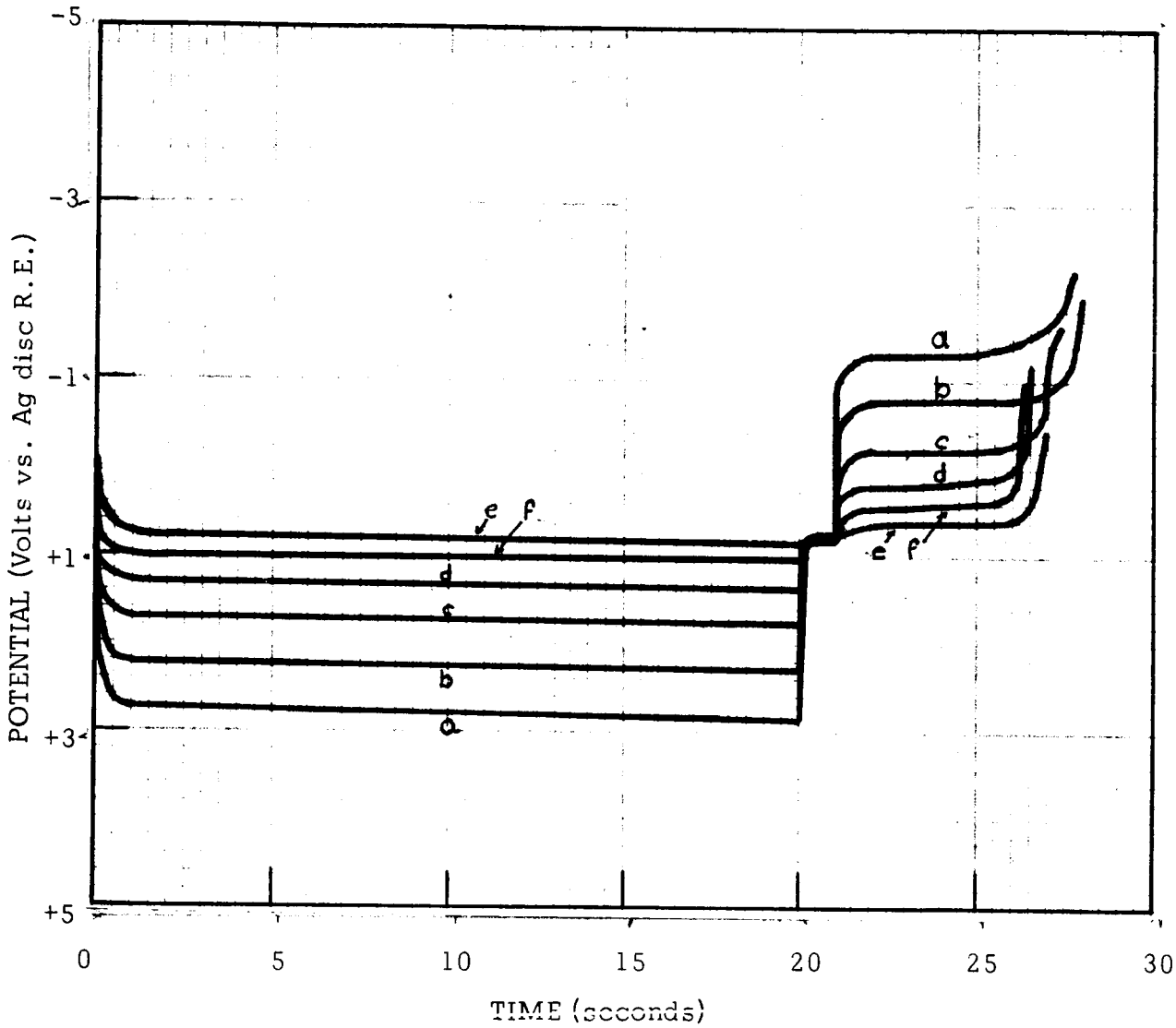

Figure 6 ANODIC-CATHODIC CYCLING ON SILVER.

In propylene carbonate, 1.0 M in $LiClO_4$. Polished silver electrode anodized at current indicated for 20 sec., followed by a 1 sec. pause, followed by cathodization at the same current as the previous anodization.

Curve a: 58.8 mA cm^{-2}

Curve b: 44.2 mA cm^{-2}

Curve c: 29.4 mA cm^{-2}

Curve d: 17.6 mA cm^{-2}

Curve e: 8.8 mA cm^{-2}

Curve f: 2.9 mA cm^{-2}

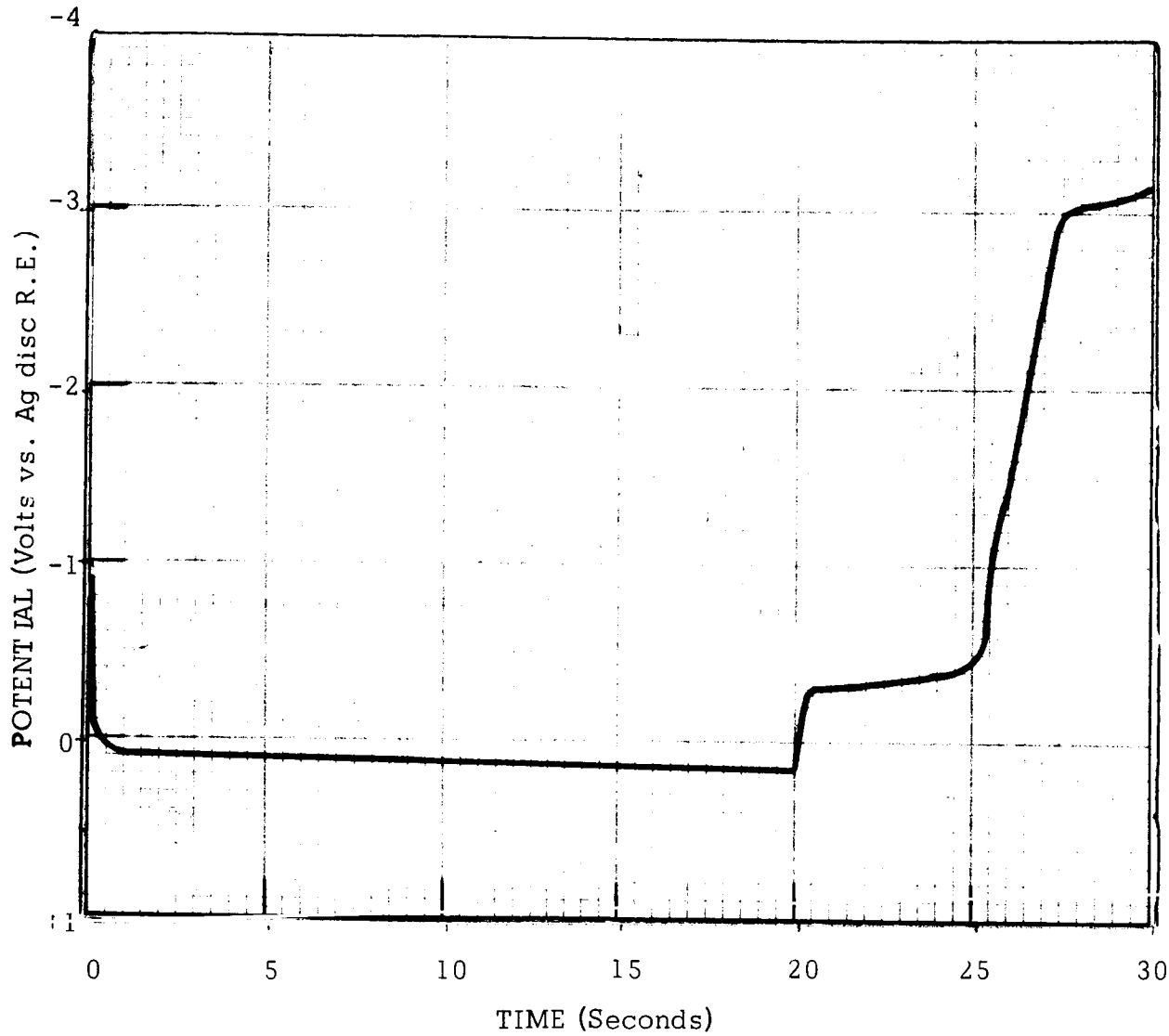

Figure 7 ANODIC-CATHODIC CYCLING ON SILVER

In propylene carbonate, 0.2 M in KPF_6. Polished silver electrode anodized at 2.5 mA cm^{-2} for 20 sec. followed by immediate current reversal.

(3) Etching of the silver metal occurs on prolonged anodization. On anodic-cathodic cycling such as that shown in Figure 6 the silver electrode becomes blackened through the deposition of finely divided silver metal.

In chloride containing solutions deposits of insoluble silver chloride form on anodization. Typical results are shown in Figure 8. If the current is sufficiently high and/or anodization is prolonged, concentration polarization due to inadequate supply of chloride species may occur. Since chloride donating species can no longer reach the electrode at a rate sufficiently rapid to supply all the imposed current, two reactions will occur -- one the formation of silver chloride and the other the formation of other soluble or insoluble silver ions. Behavior shown in Figure 9 demonstrates this.

On anodization in quiet, chloride-containing solutions well-defined transition times are obtained. Typical results are shown in Figure 10. Initially the relationship between $iT^{1/2}$ and the concentration of $AlCl_3$ was rather irreproducible. We have since discovered that this is because of the slow loss of $AlCl_3$ from solution, and this is considered in more detail in section D, wherein is also discussed the conclusion that all three chlorides are available for the reaction: $3\ Ag^{o} + AlCl_3 = 3\ AgCl + Al^{+3} + 3e^{-}$.

Reduction of AgCl films at low currents is complicated by the fact that the reduction of background impurities (Species A) discussed in Section III is augmented following the reduction of AgCl. This phenomenon is shown in Figure 11. Curve a. shows the reduction obtained on polished silver. Curve b. shows the reduction obtained when the silver is previously anodized to AgCl. The initial potential plateau at about -0.3 V corresponds to the reduction of the previously formed AgCl. A second potential plateau at about -1.5 V corresponds to background reduction. It will be observed that the length of this potential plateau is several times larger than that observed on the polished silver. The cause of this augmented background reduction is as yet unclear but is most likely due to the more active surface area presented by the electrode following discharge of AgCl.

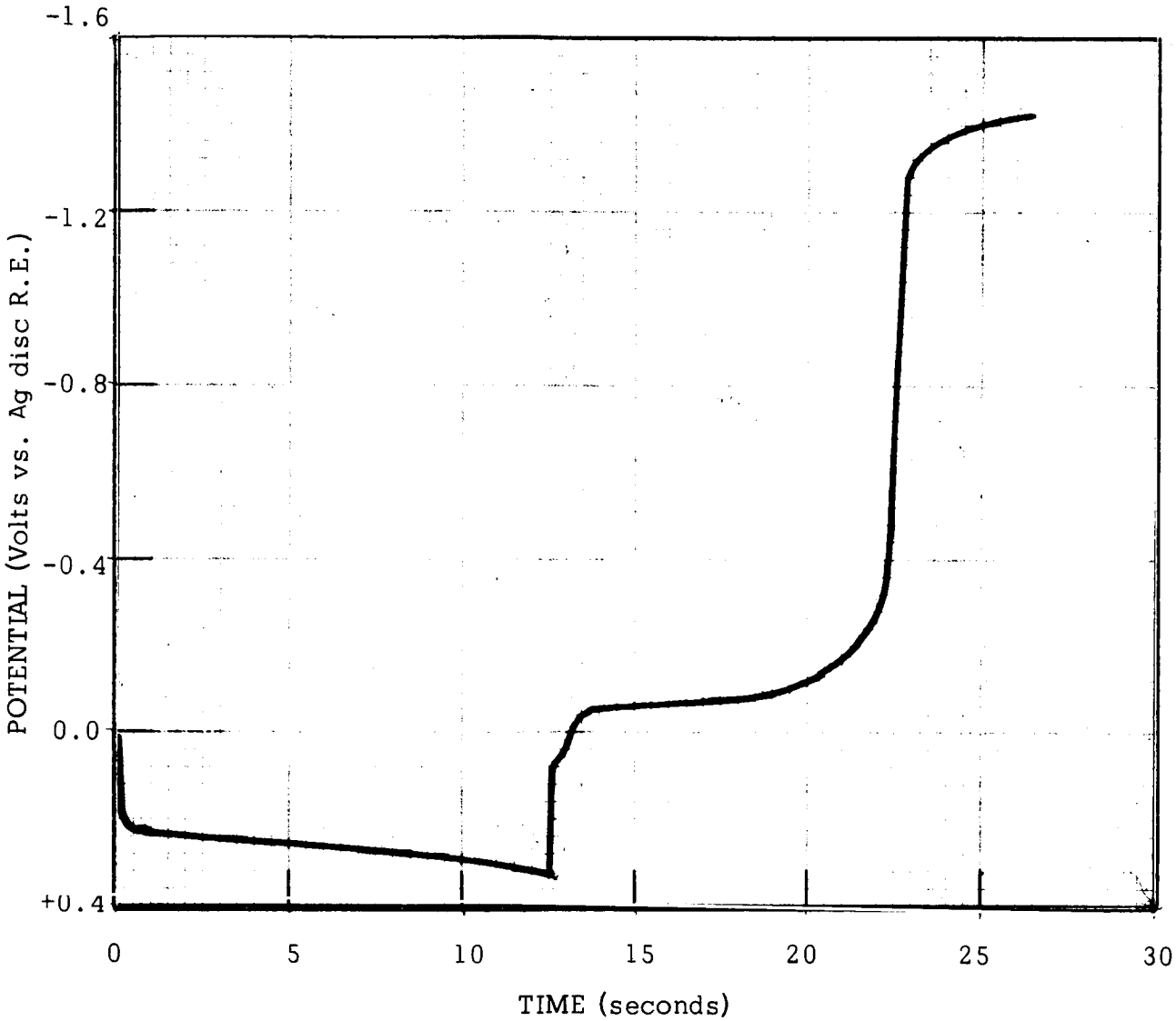

Figure 8 ANODIC CATHODIC CYCLING ON SILVER

In propylene carbonate, 0.2 M in $LiClO_4$ and saturated with LiCl. Polished silver electrode anodized at 1.2 mA cm^{-2} for 20 sec. followed by immediate current reversal.

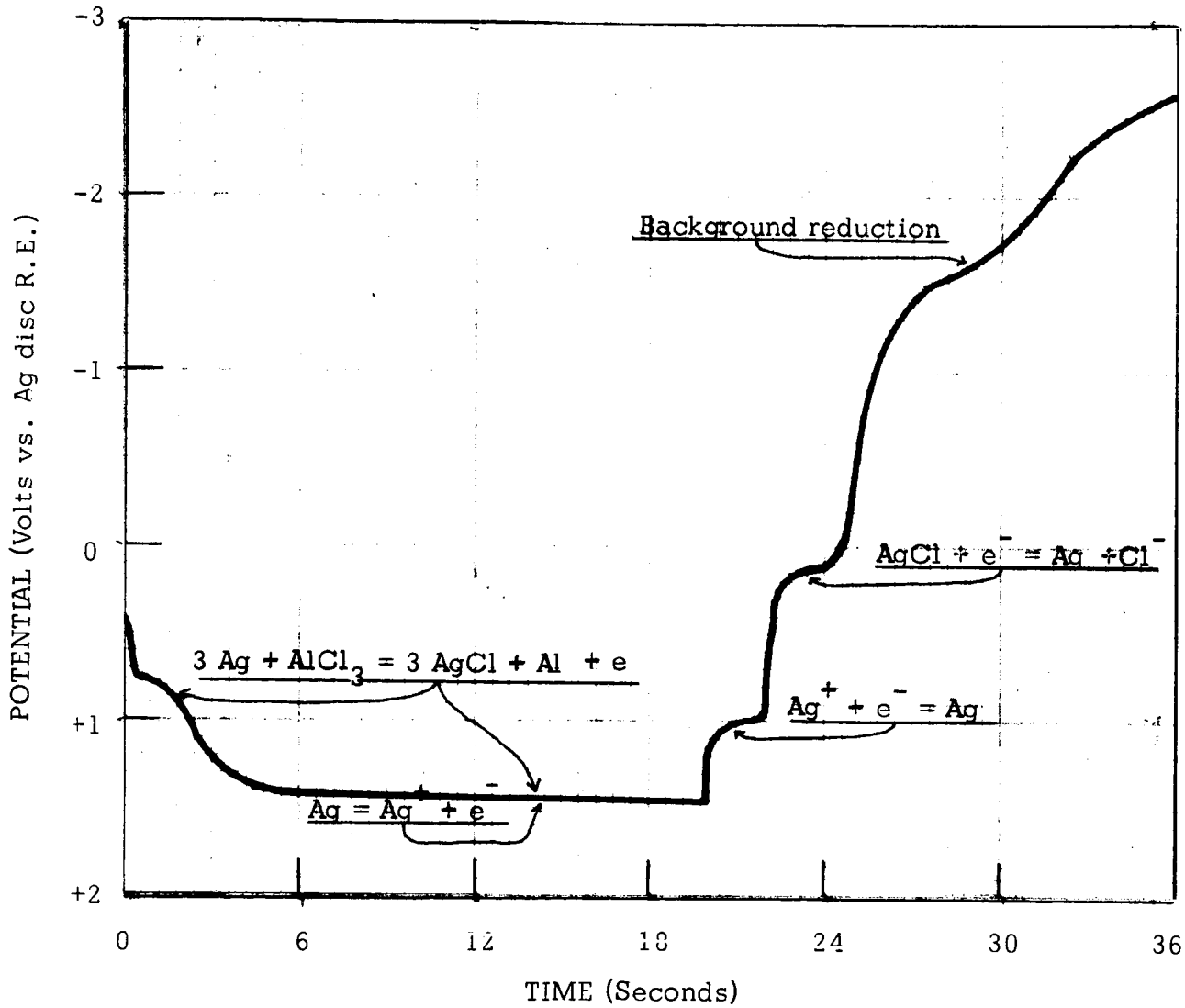

Figure 9 ANODIC-CATHODIC CYCLING ON SILVER

In propylene carbonate, 1 M in $LiClO_4$ and 0.05 M in $AlCl_3$. Polished silver electrode anodized at 5.9 mA cm^{-2} for 20 sec. followed by immediate current reversal.

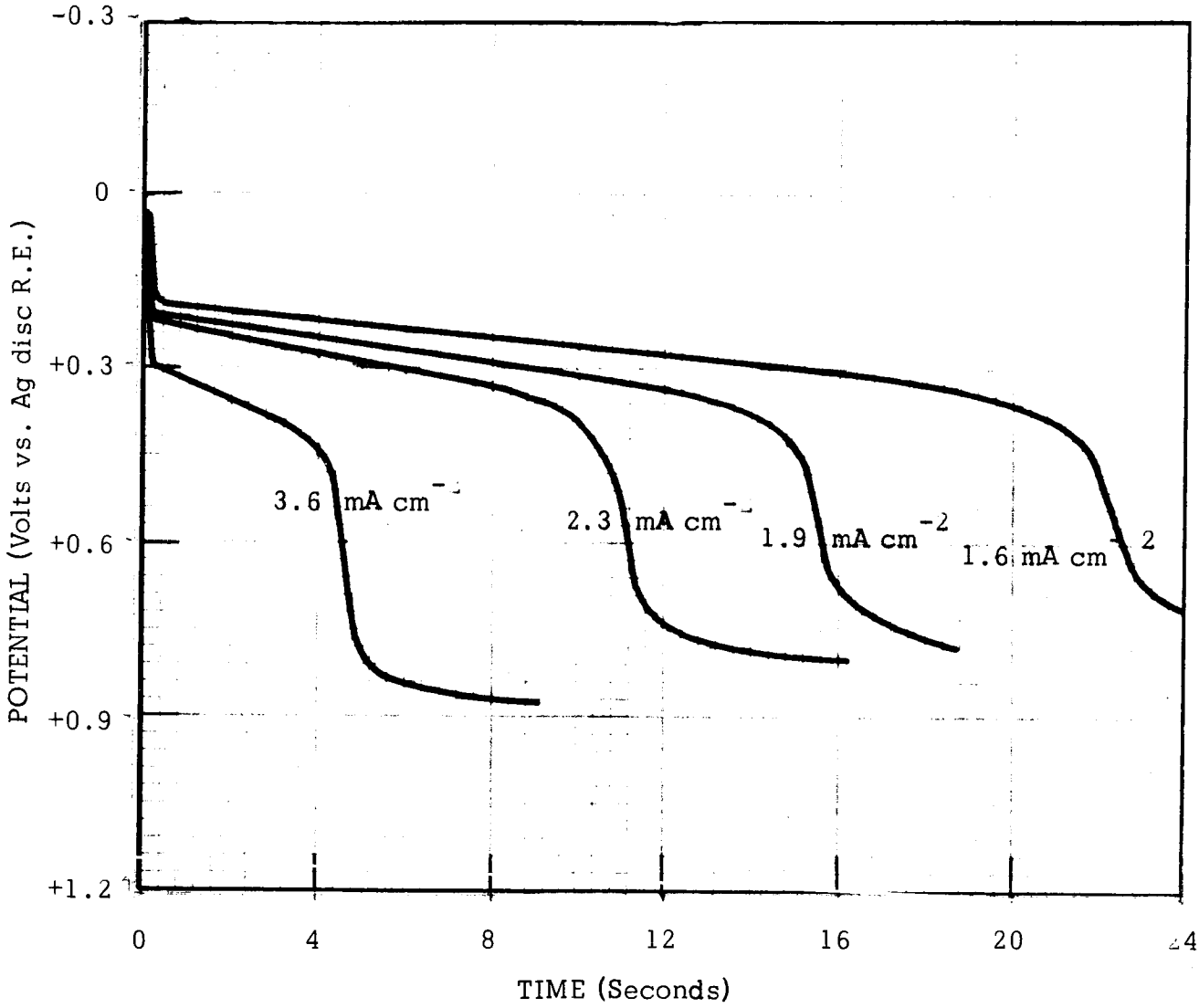

Figure 10 ANODIC CHRONOPOTENTIOMETRY ON SILVER IN CHLORIDE MEDIA

In propylene carbonate, 0.4 M in $LiClO_4$ and 0.02 M in $AlCl_3$. Polished silver electrodes anodized atcurrent indicated.

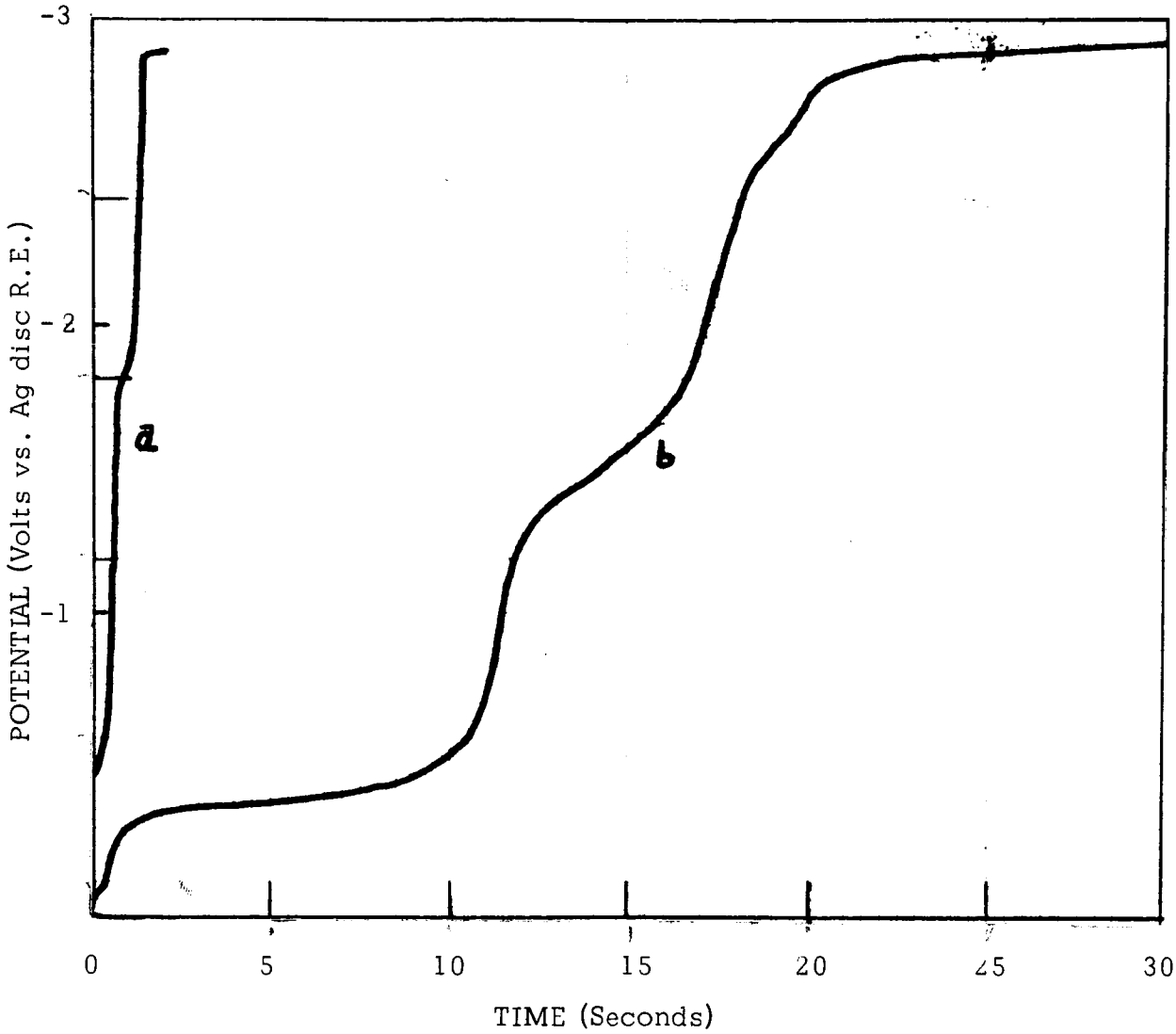

Figure 11 CATHODIC REDUCTION OF AgCl

In propylene carbonate, 1.0 M in $LiClO_4$ and 0.1 M in $AlCl_3$.

Curve a: Reduction on polished silver at 3 mA cm without prior formation of AgCl.

Curve b: Reduction of AgCl formed by anodic oxidation of polished silver at 2.4 mA cm^{-2} for a total of 35 mC cm^{-2}. Reduction shown in curve b performed at 3 mA cm^{-2}.

No evidence has yet been obtained by us for the passivation of silver on anodization in non-aqueous chloride media. As much as 1000 mC cm^{-2} of AgCl can be formed anodically without polarization through passivation. Furthermore these deposits can be subsequently reduced cathodically with excellent efficiency. Further evidence for the failure of silver to passivate can be obtained from potentiostatic measurements. On potentiostatic anodic oxidation the current remains essentially constant for long periods of time and the magnitude of the steady state current is (in mA cm^{-2}) in stirred solution of the same order of magnitude as is the anodic $iT^{1/2}$ (in mA cm^{-2} $sec^{1/2}$).

Though the anodization of silver to AgCl does proceed with equal ease in both $LiClO_4$ and KPF_6 electrolytes containing $AlCl_3$, the cathodic reduction of the silver chloride so formed is not the same. There is clear indication that, in KPF_6, a passivating film of KCl forms on discharge of AgCl. The phenomena of passivation inhibiting discharge is not often encountered in aqueous batteries and was investigated in more detail in propylene carbonate solutions by forming various anodic films in aqueous solution and then observing their subsequent discharge behavior in non-aqueous electrolytes.

Deposits of AgCl may be formed by anodization of polished silver electrodes in a variety of aqueous chloride media. The electrodeposits are normally adherent and stable and the electrodes so formed may be washed and dried without any loss of active material. All of the depositions here reported were rather arbitrarily performed in stirred aqueous solution, 1 M in $HClO_4$ and 0.05 M in HCl, at current densities of 2.5 to 5 mA cm^{-2}. The stability of the deposits was determined by removing the electrodes from solution following forming, rinsing thoroughly with first water then acetone, and drying under a stream of warm air. The electrodes were re-immersed in the aqueous solution and cathodically discharged. The amount of current required for complete reduction was within a few percent of that which had passed during the previous anodization.

Films containing 100, 400, and 800 mC cm^{-2} of AgCl, formed and dried

as described above, were prepared and the electrodes were then discharged in propylene carbonate solutions containing various concentrations of $LiClO_4$ -- from 0.05 M to 0.6 M. The current density of discharge varied from 2.5 to 40 mA cm^{-2}, and discharges were conducted in both stirred and quiet solution.

Typical discharge curves are shown in Figure 12. Discharges in dilute solution were characterized by the slow and continuous increase in potential as shown in Curve A. The potential largely reflects the iR drop resulting from the low conductivity of these dilute solutions. With increasing concentration of $LiClO_4$ the iR drop decreases and the discharge curves become better defined, and a sharper potential break is obtained at the completion of discharge, as shown in Curve C. For discharges at high currents and/or low electrolyte concentration the poor definition of the discharge curves made it impossible to select a given time as truly corresponding to complete discharge. When well-defined discharge curves were obtained, efficiencies of better than 95% were normally found. Discharge efficiency did not sensibly vary as a function of initial film thickness or whether electrolysis was conducted in stirred or quiet solution. Neither was discharge efficiency particularly sensitive to the current as long as the resultant iR drop was not excessive. These results are not surprising and indicate that passivation does not occur during the discharge of AgCl in $LiClO_4$. There was some evidence of passivation at currents of 40 mA cm^{-2} but these results were not satisfactorily reproducible. Best results were obtained in solutions 0.4 and 0.5 M in $LiClO_4$ at currents of 10 mA cm^{-2} or less.

During discharge LiCl does precipitate at the electrode surface to some degree by the reaction: $AgCl + Li^+ + e^- = Ag^o + LiCl$. This can be seen by the fact that if AgCl is discharged in a $LiClO_4$ solution containing no chloride and if, following discharge, the current is reversed and the electrode anodized, as much as 60% of the chloride discharged can be recovered, resulting in the formation of AgCl on anodization. This indicates that the chloride ions formed on discharge have not simply disappeared into the comparatively vast bulk of solution but remain on the surface in some form, doubtless as LiCl. However, any LiCl remaining

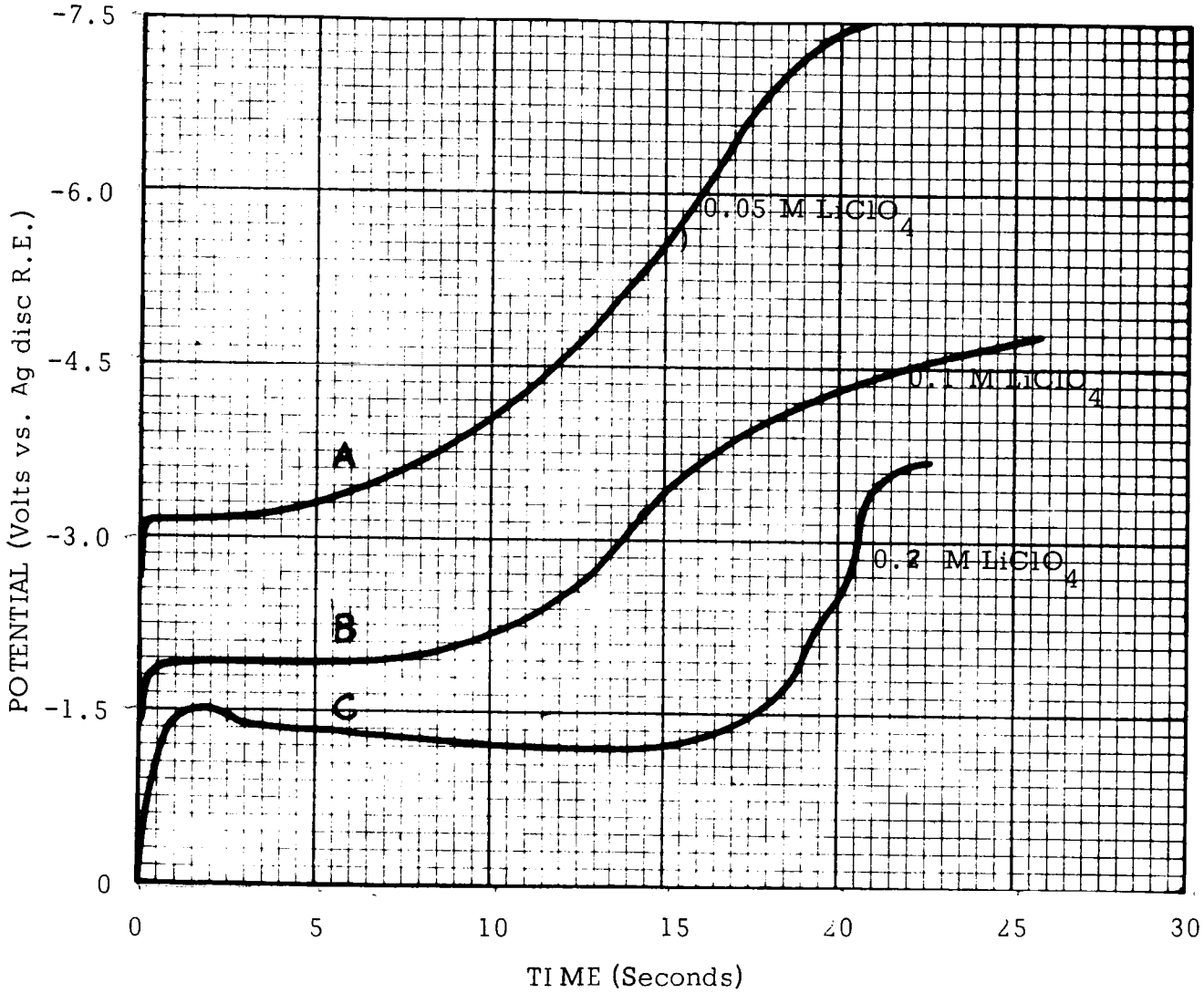

Figure 12 CATHODIC REDUCTION OF AgCl

In propylene carbonate solutions of $LiClO_4$ of concentration indicated. Cathodization performed at 25 mA cm^{-2}.

AgCl formed by anodization of polished silver electrodes in aqueous solution, 1 M in $HClO_4$ and 0.05 M in HCl. Anodization performed at 5 mA cm^{-2} to give a total of 500 mC cm^{-2}. Films dried with acetone and immersed in propylene carbonate and discharge performed as described above.

on the electrode is slowly lost from the surface through slow dissolution.

Films of AgCl were grown on polished silver for various lengths of time in aqueous chloride media and were then discharged in propylene carbonate, 0.5 M in KPF_6. The initial potential during discharge was about -0.15 V versus the silver disc reference electrode but after a short period of time the potential rose sharply to -2 V, and this occurred long before all of the silver chloride had been discharged. The electrodes were then removed from solution, washed, re-immersed in the aqueous $HClO_4$-HCl solution and any AgCl remaining on the electrodes cathodically discharged. The results are shown in Table 1 on page 25.

The 0.5 M KPF_6 solution was then made 0.03 M in $AlCl_3$ to see whether this might allow more satisfactory discharge of the AgCl. A 500 mC cm^{-2} film of AgCl prepared as described above was subjected to cathodization in this solution at 0.5 mA cm^{-2}; however, apparently passivation still occurred after only 7.5 mC cm^{-2} of AgCl had been reduced.

The presence of a passivating film of KCl was further suggested by the fact that if the electrodes, previously filmed with AgCl, were discharged in KPF_6 solutions until the potential break signalling passivation, and if the current were then immediately reversed a potential break of several hundred millivolts ensues after an amount of anodic current has passed approximately equal to the cathodic current passed until passivation. This corresponds to the successive cathodic and anodic reactions:

$$AgCl + K^+ + e^- = Ag^o + KCl \text{ (on electrode surface)}$$
$$Ag^o + KCl \text{ (on electrode surface)} = AgCl + K^+ \text{ (in solution)} + e^-.$$

The equality of the total anodic current to the previous cathodic current suggests that all of the KCl formed on discharge of AgCl does remain on the electrode surface.

A study of the formation of silver oxide films and their subsequent discharge in propylene carbonate was performed. When silver metal is anodically oxidized in aqueous alkali only about 50 mC cm^{-2} of Ag_2O can be formed before

Table 1

Discharge Behavior of Silver Chloride Films in Potassium Hexafluorophosphate Solution

Amount of AgCl Deposited, mC/cm^2	Discharge Current in KPF_6, mA/cm^2	AgCl reduced before passivation, mC/cm^2	AgCl recovered after passivation, mC/cm^2
50	0.5 mA cm^{-2}	15(1)	23
100	0.5	12(1)	82
150	0.25	19(1)	150
100	0.25	20(1)	93
500	1.0	5(2)	(3)
500	0.75	6(2)	(3)
500	0.60	6(2)	(3)
500	0.50	10(2)	(3)
500	0.40	14(2)	(3)

(1) in stirred solution

(2) in quiet solution

(3) recoveries not determined

Slightly better discharge efficiency attends lower current densities and increased agitation but it can be seen that the improvement is negligible. Experiments were also conducted in which 100 millicoulombs/cm^2 of AgCl were reduced in KPF_6, and reduction continued beyond the passivation time until a total of 60 millicoulombs/cm^2 has been passed. However, subsequent recovery of AgCl was no different from that observed when excess cathodization had not been performed beyond the passivation time. One concludes that, following passivation, further reduction of AgCl does not occur in KPF_6. It will be noted that the sum of the cathodic recoveries does not equal the total amount of AgCl deposited. This is not too surprising in view of the small amounts of deposits formed and the several operations performed; and, in view of the unsatisfactorily low discharge efficiency due to passivation we have not been further concerned with the discrepancy.

passivation. However, larger amounts of Ag_2O can be formed if a deposit of active silver metal is first formed on the polished silver substrate as follows: Polished silver is anodically oxidized to AgCl in aqueous chloride media and the deposit is then cathodically reduced in the same solution. A fine gray to black deposit of silver metal thus results. When such electrodes are anodically oxidized as described below, the amount of oxide which can be formed per apparent surface area is much greater than on the polished silver surface alone.

"Active" silver electrodes as they will hereafter be denoted, prepared as described in the preceding paragraph, were oxidized to Ag_2O by placing in aqueous solution, 1 M in $NaNO_3$ and 0.05 M in KOH, and oxidized at +0.1 to +0.2 V, potentiostatically, versus a Ag/Ag_2O electrode in the same solution. The resultant anodic current was fairly constant at between 5 and 10 mA cm^{-2} for a period of time and then rapidly decayed to negligible values signalling the completion of anodization. The amount of oxide which could be so formed was dependent on the amount of active silver initially present. The oxide formed was adherent, could be washed and dried without loss, and could be cathodically discharged in aqueous solution with good current efficiency. Typical results relating the amount of oxide formed to the amount of active silver initially deposited are shown in Table 2.

Table 2

Silver Oxide Formation on Active Silver Electrodes

Active silver initially deposited (mC cm^{-2})	Ag_2O Formed (mC cm^{-2})
500	420
1000	780
1500	1170
2000	1560

Reproducibility was excellent and this procedure provides a good means for developing active surfaces in a controlled way. Other methods of preparing active silver surfaces were attempted involving the electrodeposition of silver from $AgNO_3$ solution under various conditions and electrolytic etching. All activation procedures described in Table 3 below involved the passage of 1000 mC cm^{-2} of electricity. The amount of Ag_2O which could be formed was determined by cathodic reduction in aqueous media and the results are shown below:

Table 3

Active Silver Electrode Preparations

Activation Procedure	Amount of Ag_2O Formed (mC cm^{-2})
Deposition of Ag from aqueous $AgNO_3$ at 5 mA cm^{-2} for 200 sec.	85
Deposition of Ag from aqueous $AgNO_3$ at 25 mA cm^{-2} for 40 sec.	200

Table 3 (Cont'd)

Active Silver Electrode Preparations

Activation Procedure	Amount of Ag_2O Formed ($mC\ cm^{-2}$)
Deposition of Ag from aqueous $Ag\ NO_3$ at -0.1 V; resultant limiting current for reduction = 40 $mA\ cm^{-2}$. Electrolysis continued for 25 sec.	200
Etched at 25 $mA\ cm^{-2}$ for 40 sec.	48
Anodically oxidized to AgCl in HCl at 5 $mA\ cm^{-2}$ for 200 sec. followed by reduction to Ag^0 at 5 $mA\ cm^{-2}$ in same solution	780

Considerable time was spent in studying the properties of such active silver electrodes since we felt such electrodes might in the future be useful tools in investigating electrokinetic problems which had been anticipated, but the initial purpose of the work was simply to obtain large deposits of Ag_2O. It was observed, however, that deposits of Ag_2O cannot be satisfactorily discharged in propylene carbonate solutions of $LiClO_4$. In a typical case films containing 330 $mC\ cm^{-2}$ of Ag_2O were discharged in 0.1 M $LiClO_4$ at currents of from 0.5 to 7.5 $mA\ cm^{-2}$ in stirred solution. (Note: The limiting current in such a solution is about 20 $mA\ cm^{-2}$.) After an initial potential plateau at about +2.4 V versus a lithium electrode in the same solution lasting for about 100 $mC\ cm^{-2}$, regardless of the current, the potential suddenly became more negative by about 0.6 V. Identical films were discharged potentiostatically in the same 0.1 M $LiClO_4$ solutions at +2.1 V versus a lithium electrode in the same solution. The resultant current continuously decreased from initial values of about 4 $mA\ cm^{-2}$ to less than 0.15 $mA\ cm^{-2}$. The total current passed during

during potentiostatic reduction was again only about 100 mC cm^{-2}, or during potentiostatic reduction was again only about 100 mC cm^{-2}, or 30% of the film initially present.

Films initially containing about half the amount of Ag_2O, 150 mC cm^{-2}, were discharged in 0.1 M $LiClO_4$ in propylene carbonate. Again discharge utilization was inefficient, being about 20 to 25%. Some increase in efficiency of discharge was obtained when 100 mC cm^{-2} of Ag_2O were formed on a surface containing a total of 1000 mC cm^{-2} of active silver. Discharge of such a surface, whereon most of the active silver remained un-oxidized, was about 50% efficient. If, as appears likely from the information given above, that low discharge efficiency of Ag_2O results from the formation of passivating films of Li_2O by the reaction: $Ag_2O + 2\,Li^+ + 2e^- = 2\,Ag^o + Li_2O$, then it is unlikely that satisfactorily large deposits of any other metal oxide can be completely discharged in propylene carbonate solutions of $LiClO_4$.

b. The Copper Electrode. The behavior of the copper electrode is considerably more complicated than is the behavior of the silver electrode. This is unfortunate, since its lower equivalent weight makes it a more desirable cathode constituent than is silver.

The general nature of the electrochemical behavior of polished copper electrodes in propylene carbonate is seen in Figures 13 and 14. Figure 13 shows the anodic-cathodic cycling observed in $LiClO_4$ and KPF_6. In both solutions the behavior is identical to that obtained with silver -- the copper anodically dissolving to ionic species soluble in the electrolyte rather than to insoluble films. This is determined from the fact that cathodic transition times are about one-third the time of previous anodization, and that stirring quickly removes such ionic species from the vicinity of the electrode and subsequent cathodization after stirring does not result in the reduction of any copper species.

Figure 14 shows the type of complex behavior observed in chloride

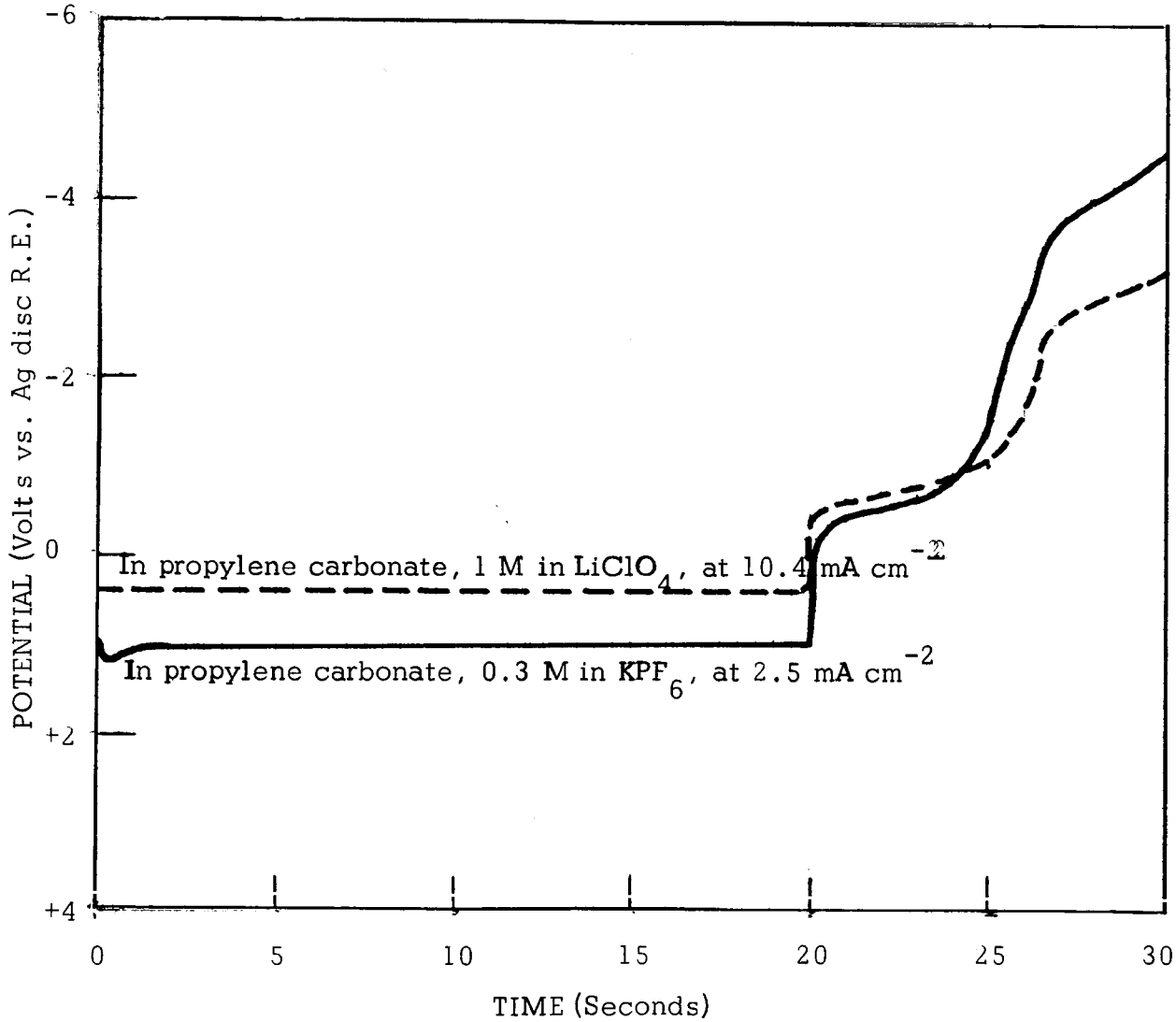

Figure 13 ANODIC-CATHODIC CYCLING ON COPPER

Measurements performed on polished copper under conditions indicated

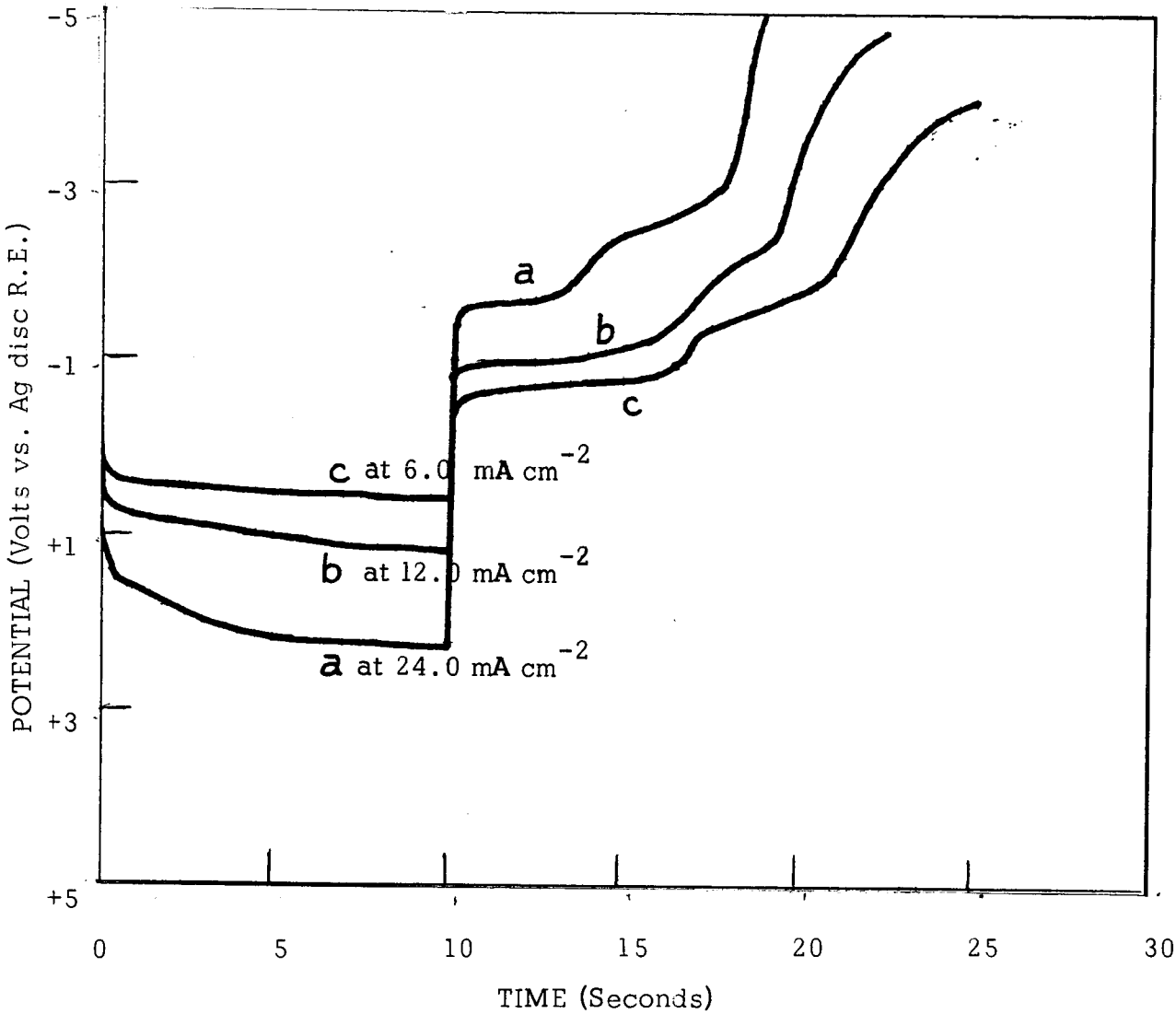

Figure 14: ANODIC-CATHODIC CYCLING ON COPPER IN CHLORIDE MEDIA In propylene carbonate, 0.35 M in $AlCl_3$ and 0.1 M in LiCl. Cycling performed on polished copper electrodes at current indicated.

media. Such behavior is not peculiar to this particular solution but is general to all chloride containing propylene carbonate solutions. That an insoluble film is formed during anodization seems clear from the fact that the cathodic transition time up to the point where the potential rises to that for lithium deposition is about equal to the preceding time of anodization. However, any film formed is slowly soluble in the electrolyte -- if the solution is stirred the amount of evident film recovered on cathodization decreases, and after ten minutes of stirring no recovery is obtained.

A more detailed assessment of the utility of the copper-chloride system was obtained by performing a series of anodic oxidations in a solution, 0.9 M in $AlCl_3$ and 0.8 M in LiCl. Anodizations were performed in quiet solutions in order to diminish the amount of copper salt removed by mechanical agitation. Since it was feared that at low cathodic recovery currents a significant amount of the current might be consumed by background impurities, relatively large cathodic currents, 30 mA cm^{-2}, were employed. At these large currents the iR drop of course is quite large but there appeared a fairly sharp potential break at +1 V versus the lithium electrode which we presumed represented complete film reduction. The results shown in Table 4 were obtained by anodizing polished copper electrodes at the current indicated for the time required to give the total deposition indicated. Following anodization the current supply was changed to 30 mA cm^{-2} and the current reversed. A period of only a few seconds elapsed between the completion of anodization and the commencement of cathodization. The percent recovery was obtained by dividing the total coulombs of cathodization by the total coulombs of previous anodization.

Table 4

Cathodic Efficiency of Copper Films Formed in Chloride Media

Anodic Current ($mA\ cm^{-2}$)	Total Deposition ($mC\ cm^{-2}$)	% Recovery at 30 $mA\ cm^{-2}$
15	150	75.0
	600	58.5
	1200	55.0
	1800	50.8
	2700	57.0
60	150	60.0
	600	48.5
	1200	70.5
	1800	79.3
	2700	76.8
150	150	73.0
	600	65.0
	1200	69.0
	1800	73.0
	2700	71.0

Such behavior is not considered satisfactory, particularly when compared with the Ag/AgCl electrode where essentially 100% recoveries would be obtained for all of the electrolysis conditions shown in Table 4 and attempts were made to improve the cycling characteristics of the copper electrode by varying the composition of the electrolyte.

A propylene carbonate solution, 0.5 M in $AlCl_3$ and 0.6 M in KPF_6, was prepared. (Note: The particular concentrations chosen were arbitrary, dictated by experimental convenience.) Anodizations were performed at

relatively high currents. As shown in Figure 15 an initial potential plateau was observed for a period of time after which the potential increased to large positive values. Arbitrarily, anodizations were discontinued when the potential had reached +12 V (versus a silver disc electrode in the same solution). Anodizations were performed at different currents but all subsequent cathodizations were performed at 6 mA cm^{-2}. A typical cycle, as shown in Figure 15, differs from those shown in Figure 14 in that, on cathodization, the ratio between the time elapsed during the first potential plateau to that of the second plateau (at -.4 and -1.4 V respectively) is considerably larger for the cycle shown in Figure 15. The complete results obtained in this solution are shown in Table 5 below. Anodizations were performed at the current indicated until the potential rose to +12 V. The recovery was calculated by observing the time required for reduction at 6 mA cm^{-2} before the potential rose to -1 V. (Note: This is only the time for the first cathodic potential plateau.)

Table 5

Cathodic Efficiency of Copper Films Formed in KPF_6-$AlCl_3$ Solution

Anodic Current (mA cm^{-2})	Time of Anodization (sec.)	Total Anodization (mC cm^{-2})	Recovery (%)
15	49	735	93
30	18	540	87
45	6.6	297	91
60	4.3	258	84

The results shown in Figure 15 and Table 5 show some improvement over the performance typified by Figure 14 and Table 4. However, we feel this improvement is marginal and the variation in results is of interest primarily in demonstrating that changes in electrolyte composition do influence the cycling performance of electrodes. The ability to proceed in a logical manner

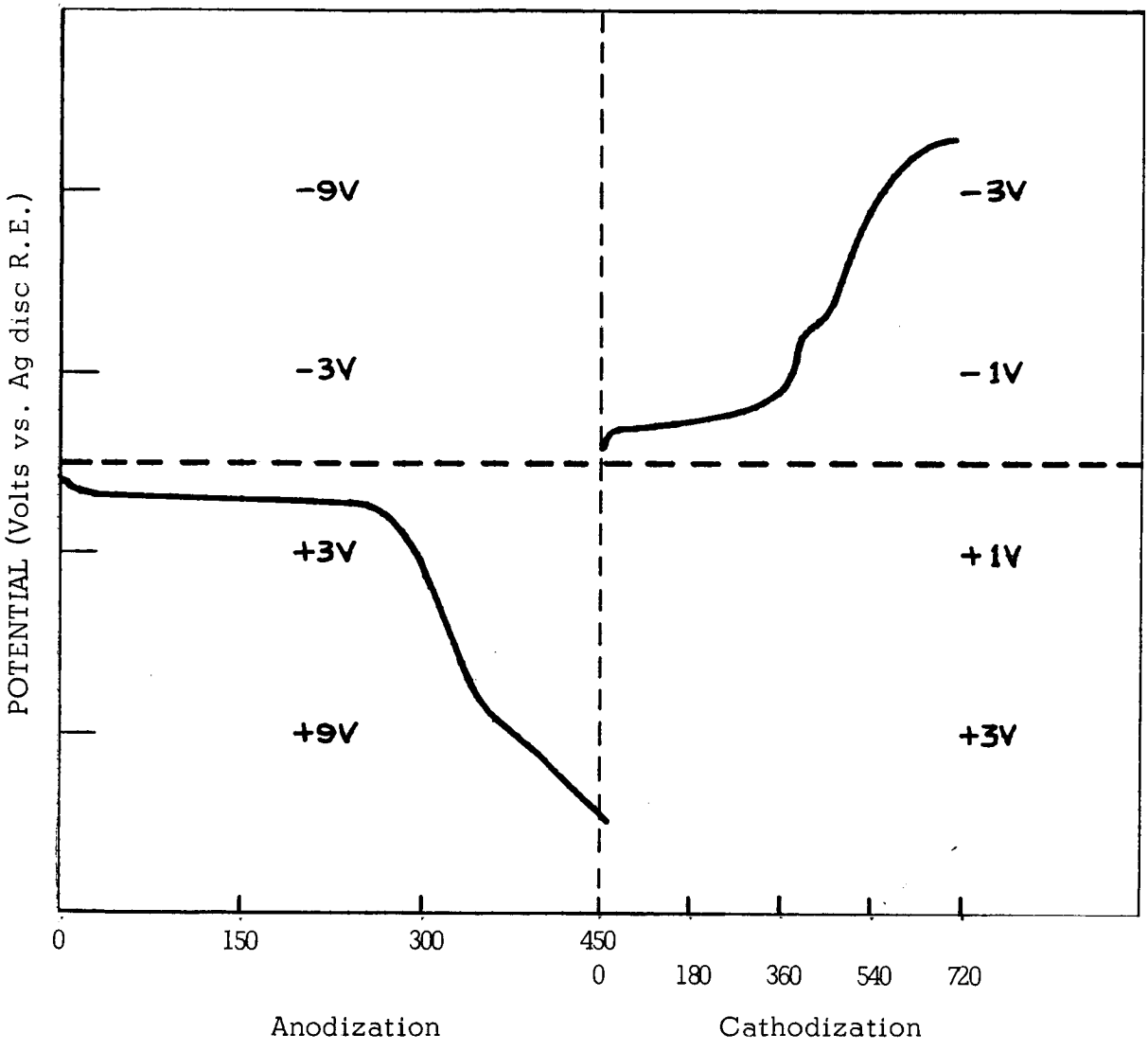

Figure 15 ANODIC - CATHODIC CYCLING OF COPPER IN CHLORIDE MEDIA

In propylene carbonate, 0.6 M in KPF_6 and 0.5 M in $AlCl_3$. Anodization performed at 30 mA cm^{-2} in quiet solution followed by immediate cathodization at 6 mA cm^{-2}. Note difference in potential scales.

towards modifying the cycling performance of electrodes through variations in electrolyte composition depends on a more detailed knowledge of the species present in these electrolytes than is yet available.

Further attempts at modifying the performance of the copper electrode were made by performing electrolyses in a solution of propylene carbonate, 0.5 M in $AlCl_3$ and saturated with LiF. Cathodic chronopotentiometry indicated the concentration of lithium ions in the solution to be about 0.05 M. Anodic chronopotentiometry performed on copper gave a reasonably well-defined transition time as shown in Figure 16. The value of $iT^{1/2}$ which, as will be later discussed, should reflect the total concentration of available chloride, was about 220 mA cm^{-2} $sec^{1/2}$. This is about that expected for a 0.5 M $AlCl_3$ solution alone. The behavior shown in Figure 16 did not differ significantly from that observed in the $AlCl_3$/LiCl solutions described by Figure 14 and Table 4. A more detailed investigation of the rate at which anodically formed deposits are removed by stirring was performed in this solution. The results are shown in Figure 17. It can be seen that the presence of the small amount of LiF in solution does not decrease the solubilization of the copper film.

Further examination of the copper electrode was not deemed useful at this time in the absence of more detailed information about the specific nature of the species present and the equilibria extant in these non-aqueous electrolytes.

c. Cobalt, Nickel, and Iron Electrodes. The results obtained on these three electrodes are obscure. This can be seen by a more detailed discussion of typical results shown in Figure 18. The particular examples chosen are for the only solutions in which identical measurements had been made on all electrodes under identical conditions; however, the behavior described is generally observed. Curve a. shows the results obtained when a polished copper electrode is cathodized, without prior anodization. The potential immediately jumps to a negative value (ca. -4.0 V versus a silver disc in the

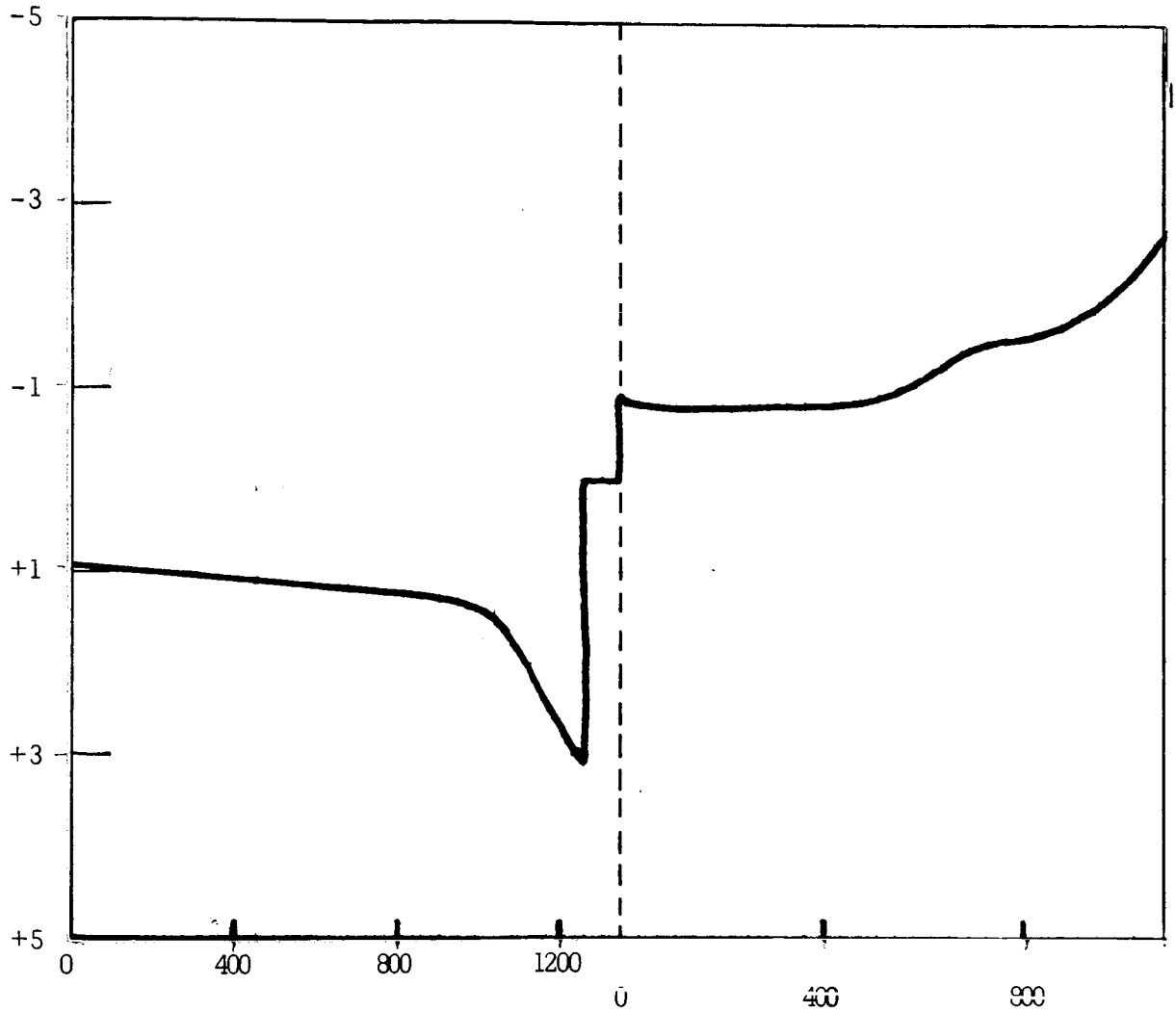

Figure 16 ANODIC-CATHODIC CYCLING OF COPPER IN CHLORIDE MEDIA

In propylene carbonate, 0.5 M in $AlCl_3$ and saturated with LiF (Conc. ca. 0.05 M). Anodization performed at 45 mA cm^{-2}. Subsequent cathodization performed at 6 mA cm^{-2}.

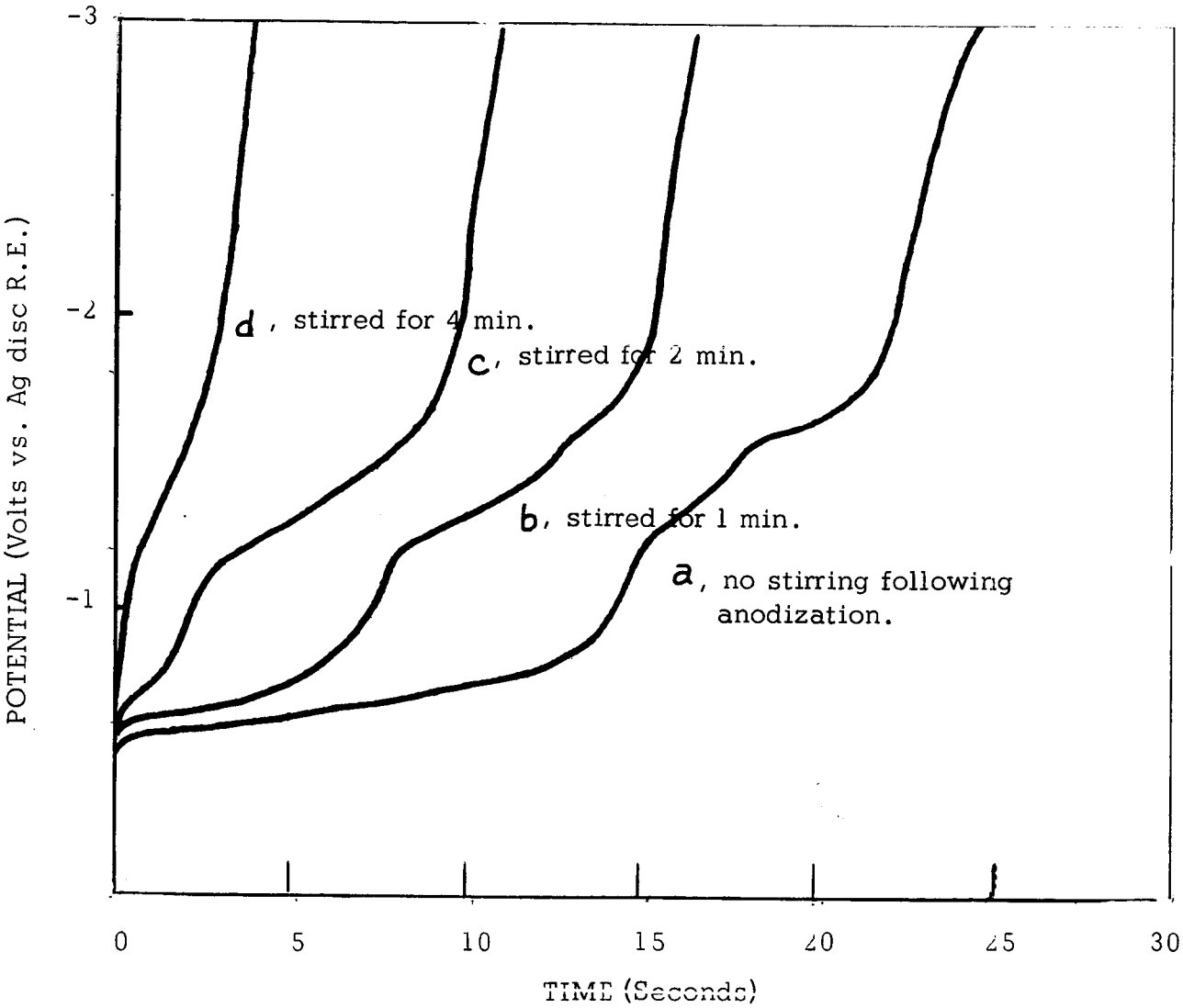

Figure 17 STIRRED REMOVAL OF ANODICALLY FORMED COPPER SALTS

In propylene carbonate, 0.5 M in $AlCl_3$ and saturated with LiF (Conc. ca. 0.05 M).

Anodic film formed by anodization of polished copper at 12 mA cm^{-2} for 10 sec (120 mA cm^{-2}).

Subsequent cathodizations performed at 6 mA cm^{-2}. After anodization solution was stirred for period indicated prior to cathodization.

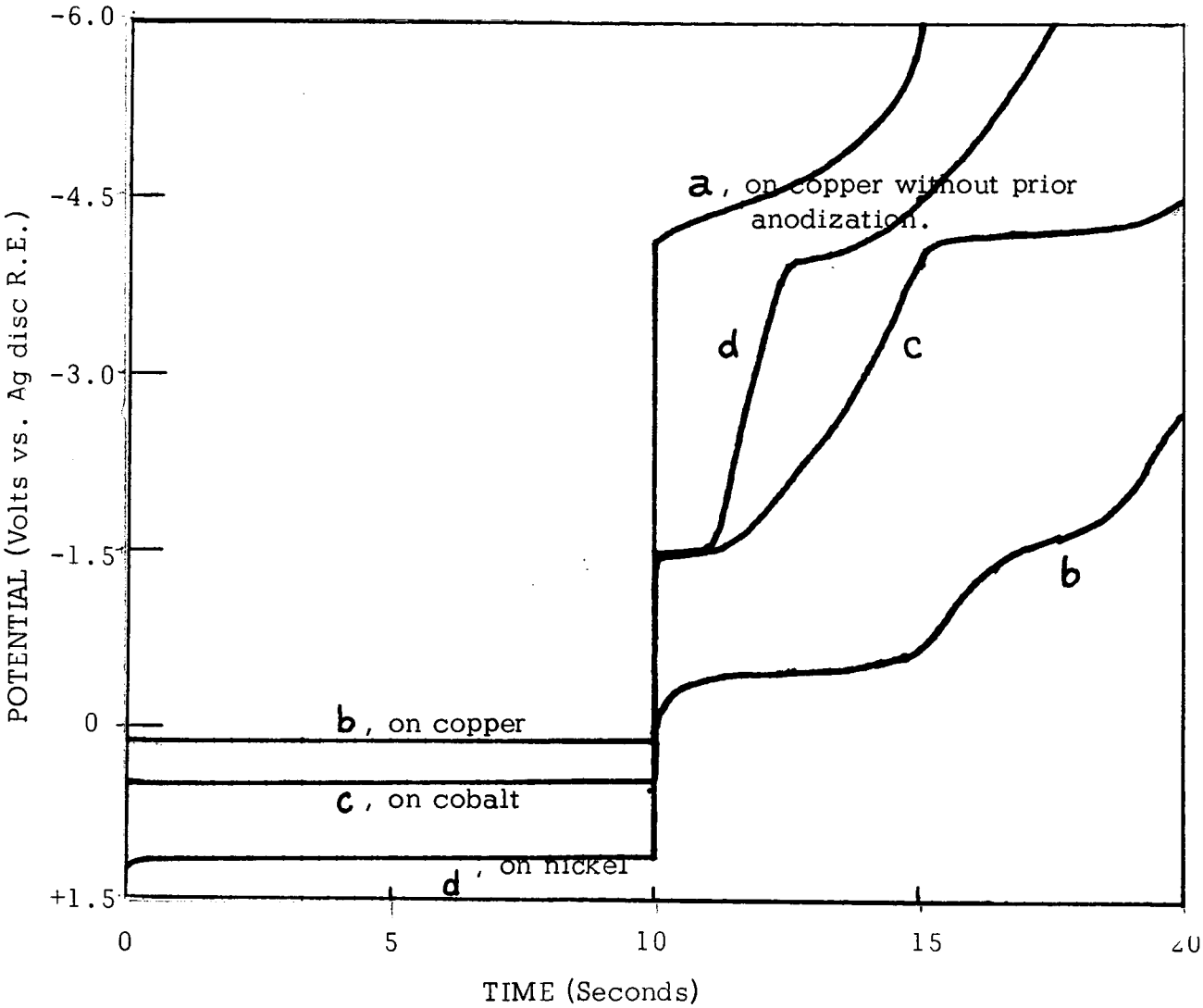

Figure 18 ANODIC-CATHODIC CYCLING ON COPPER, NICKEL, AND COBALT In propylene carbonate, 0.5 M in $AlCl_3$ and saturated with LiF (Conc. ca. 0.05 M). Cycling performed on polished electrodes at 5 mA cm^{-2}.

same solution) at which lithium is deposited. At this current there is no evidence of preliminary reduction before the onset of lithium deposition. When copper is first anodized (curve b.) following which current is reversed two potential plateaus are observed as was earlier discussed; finally the potential slowly rises to that for lithium deposition (not shown for curve b). Curves c. and d. show what happens when cobalt and nickel are oxidized. The potentials for oxidation are positive to that for copper oxidation whereas, thermodynamically, they should be oxidized at potentials negative to copper (both cobalt and nickel are more active than copper, i.e., their oxidation potentials should be closer to the lithium potential than is that for copper). The fact that cobalt and nickel are oxidized at more positive potentials than is copper attests to the well known electrokinetic irreversibility of the Co/Co^{++} and Ni/Ni^{++} couples. When, after anodization of cobalt and nickel, the current is reversed, potential pauses at -1.5 V are observed for both metals, thereafter the potential rises to the negative values at which lithium is deposited. The fact that the cathodic transition times observed from curves c. and d. are approximately one-third the previous anodic time suggests that reduction occurring at -1.5 V is that of the cobalt and nickel ions (supposedly formed during previous anodization) to the metal. This conclusion may be too facile. As shown in Figure 11 when AgCl is cathodically reduced two plateaus are observed on reduction. The first clearly corresponds to complete reduction of AgCl to silver metal. An anomalous plateau is observed at about -1.5 V which is not very significant when polished silver is subjected to cathodization without prior anodization. It may be proposed that this reduction is that of electrolyte, catalytically enhanced by the active surface resulting from the reduction of AgCl, or of by-products produced via the preceding anodization of silver to silver chloride. Since this type of behavior is observed with the silver electrode which in other respects is quite well-behaved it may be concluded that the reduction observed at -1.5 V along curves b, c and d in Figure 18 may also reflect some other process rather than the reduction of copper, cobalt and nickel ions to the metal. Since one cannot be

sure what the reduction process at -1.5 V is, there is little one can state conclusively about the behavior of the cobalt, nickel, and iron electrodes. (Note: Iron behaves similarly to cobalt and nickel in this respect also.)

The anodic behavior of iron, cobalt, and nickel electrodes in propylene carbonate solutions of $LiClO_4$ is interesting. In Figure 19 are shown a series of chronopotentiograms obtained on a polished cobalt electrode in a 1 M solution of $LiClO_4$ in propylene carbonate. Such chronopotentiograms can be obtained repeatedly on the same electrode with excellent reproducibility. Furthermore, even after repeated runs, negligible etching of the cobalt electrode is observed, suggesting that the oxidation process is, indeed, not that of cobalt at all. The oxidation may be that of solvent or of perchlorate ion to the free radical.

Further studies on cobalt and nickel electrodes involved attempts to prepare oxide films of these elements electrolytically from aqueous solution and to discharge these oxides in propylene carbonate solutions. In 25% KOH cobalt may be anodically oxidized at currents of from 2.5 to 10 mA cm^{-2} to give deposits of 750 mC cm^{-2} (at 2.5 mA cm^{-2}) to 250 mC cm^{-2} (at 10 mA cm^{-2}) of $Co(OH)_2$ or CoO before passivation. Such deposits were prepared and then discharged in propylene carbonate, 0.1 M in $LiClO_4$. The discharge was totally unsatisfactory as the potential immediately rose to +0.5 V or more versus a lithium electrode in the same solution, depending on the current. Neither was there evidence for any oxidation of Cobalt (II) oxide or hydroxide to the trivalent state.

Satisfactory deposits of $Ni(OH)_2$ (or NiO) cannot be formed directly by anodic oxidation of nickel metal in aqueous alkali as the potential rapidly rises to high values indicating passivation and subsequent oxygen evolution after only about 40 mC cm^{-2} of anodic current have passed. However, $Ni(OH)_2$ may be deposited by cathodization in aqueous 1 M $NaNO_3$ which is made 0.05 M in $Ni(NO)_3)_2$ and to which is added strong base until the $Ni(OH)_2$ just begins to precipate from solution. On cathodization at 5 mA cm^{-2} the following reaction occurs: $Ni^{++} + 2\ H_2O + 2e^- = H_2 + Ni(OH)_2$ and about 50% of the nickel

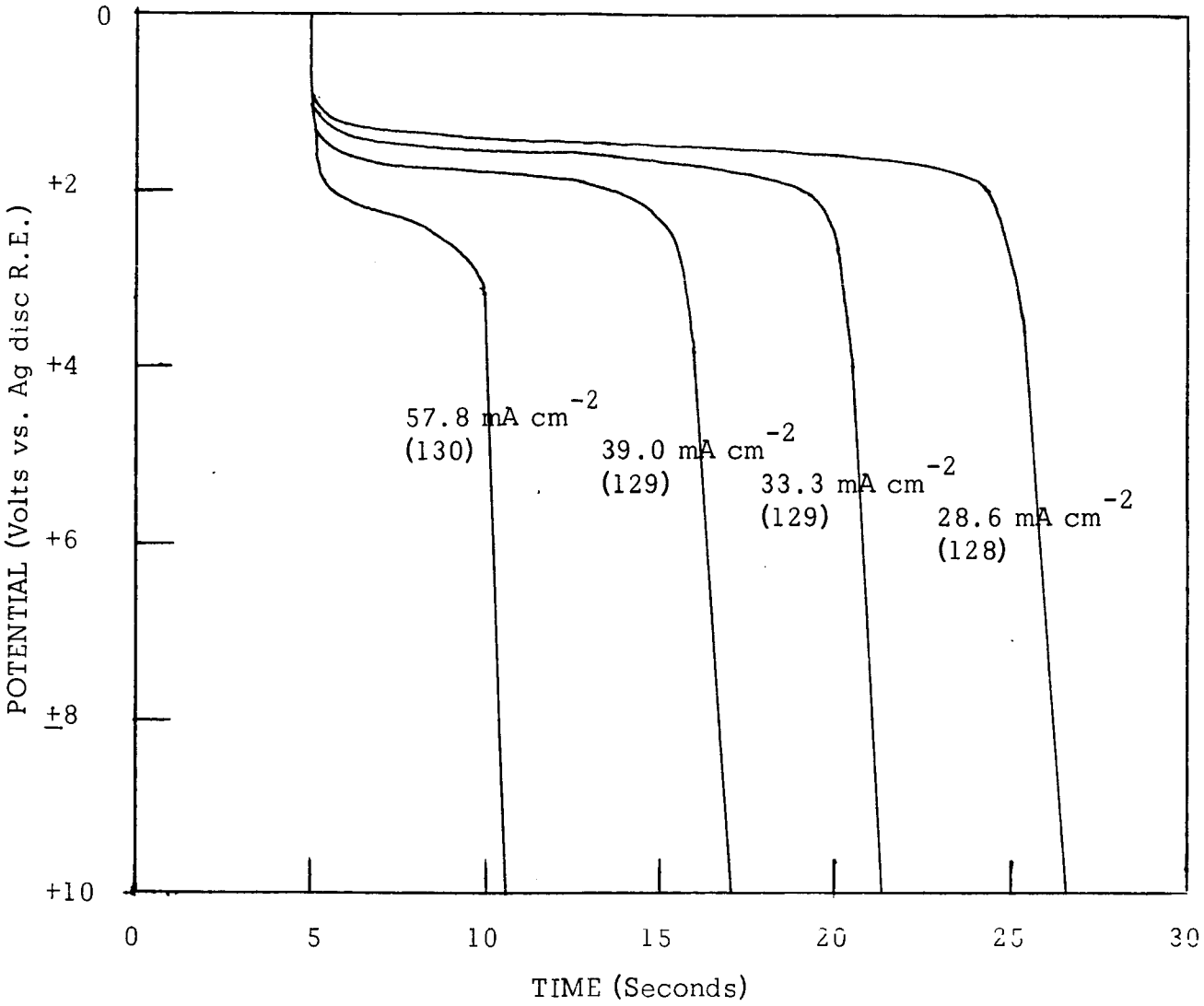

Figure 19 ANODIC CHRONOPOTENTIOMETRY ON COBALT

In propylene carbonate, 1 M in $LiClO_4$. Anodization performed on polished cobalt electrodes at current indicated.

Values for $iT^{1/2}$ in mA cm^{-2} sec$^{1/2}$ are given in parentheses.

hydroxide so formed remains on the electrode. Such films displayed behavior similar to that described above for cobalt hydroxide in that satisfactory reduction or oxidation could not be obtained in propylene carbonate solutions of $LiClO_4$. Films of $Ni(OH)_2$ prepared as described above may be anodically oxidized in strong base to NiOOH. Such deposits could not be successfully reduced in propylene carbonate solutions of $LiClO_4$. These results are to be compared with the unsatisfactory results obtained when attempts were made to discharge Ag_2O in propylene carbonate solutions of $LiClO_4$.

2. Electrolyte Composition and Equilibria

From the preceding discussion concerning the silver, copper, iron, cobalt and nickel electrodes it will be apparent that procedures for the logical development of electrolytes designed to enhance electrode performance cannot be evolved until more is known about the type of situation which prevails in these electrolytes. In this section some of the preliminary experiments, which have been performed in an attempt to characterize the electrolytes, will be described.

a. The Silver-silver Ion Electrode. The potential of a silver electrode in propylene carbonate solution of silver ions was investigated to determine whether the Nernst relationship is obeyed by this system. A conventional H-cell was used. In the counter electrode compartment was placed a propylene carbonate solution, 0.5 M in $AgClO_4$ and a silver coated platinum helix to serve as the reference electrode. In the larger working electrode compartment of the cell was placed propylene carbonate, 1 M in $LiClO_4$, and a silver "lollipop" electrode. To this compartment were added successive increments of a stock solution of $AgClO_4$ in propylene carbonate to give the requisite concentration of $AgClO_4$. The potential of the silver "lollipop" electrode was measured versus that of the silver plated helix in the other compartment. Potentials were measured with an L and N Potentiometer using a Varian G-14 recorder as null indicator so the variation in potential with time could be conveniently recorded without polarizing either electrode. Steady potentials

were established within two minutes after each change in the concentration of $AgClO_4$, and the potentials of the various silver discs in the "lollipop" electrodes did not differ by more than 0.5 mV. The results are shown in Figure 20. The solid line in Figure 20 represents the theoretical Nernstian slope of 0.059 V. The presence of excess $LiClO_4$ minimizes the effects of variations in activity coefficient with concentration of $AgClO_4$. It was observed that measurable diffusion of $AgClO_4$ from the reference electrode compartment was negligible. The absolute values of the potentials shown in Figure 20 cannot be used to determine the standard potential of the Ag/Ag^+ couple because the activity coefficient of $AgClO_4$ in the reference electrode compartment (0.5 M in $AgClO_4$) and the liquid junction potentials are not known.

b. The Silver-silver Chloride Electrode. When $AlCl_3$ is dissolved in a solvent such as propylene carbonate a variety of equilibria involving ionization, disproportionation, and dimerization may be envisaged. As an example the following scheme has been proposed[(2)]:

$$AlCl_3 + Al_2Cl_6 = Al_2Cl_5^+ + AlCl_4^-$$

$$LiCl + AlCl_3 = Li^+ + AlCl_4^-$$

$$LiCl + Al_2Cl_5^+ = Al_2Cl_6 + Li^+$$

$$2\ AlCl_3 = Al_2Cl_6.$$

It was of interest to investigate the potential of a reversible chloride electrode in solutions of $AlCl_3$ to which chloride was added in the form of LiCl and from which chloride was withdrawn through the addition of $AgClO_4$, and see whether any regular pattern of behavior could be found. It was observed that a polished silver electrode immersed in chloride containing propylene carbonate when

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* Lockheed Missiles and Space Co., New Cathode-Anode Couples ASD-TDR-62-837, Dec. 1962, p. 6.

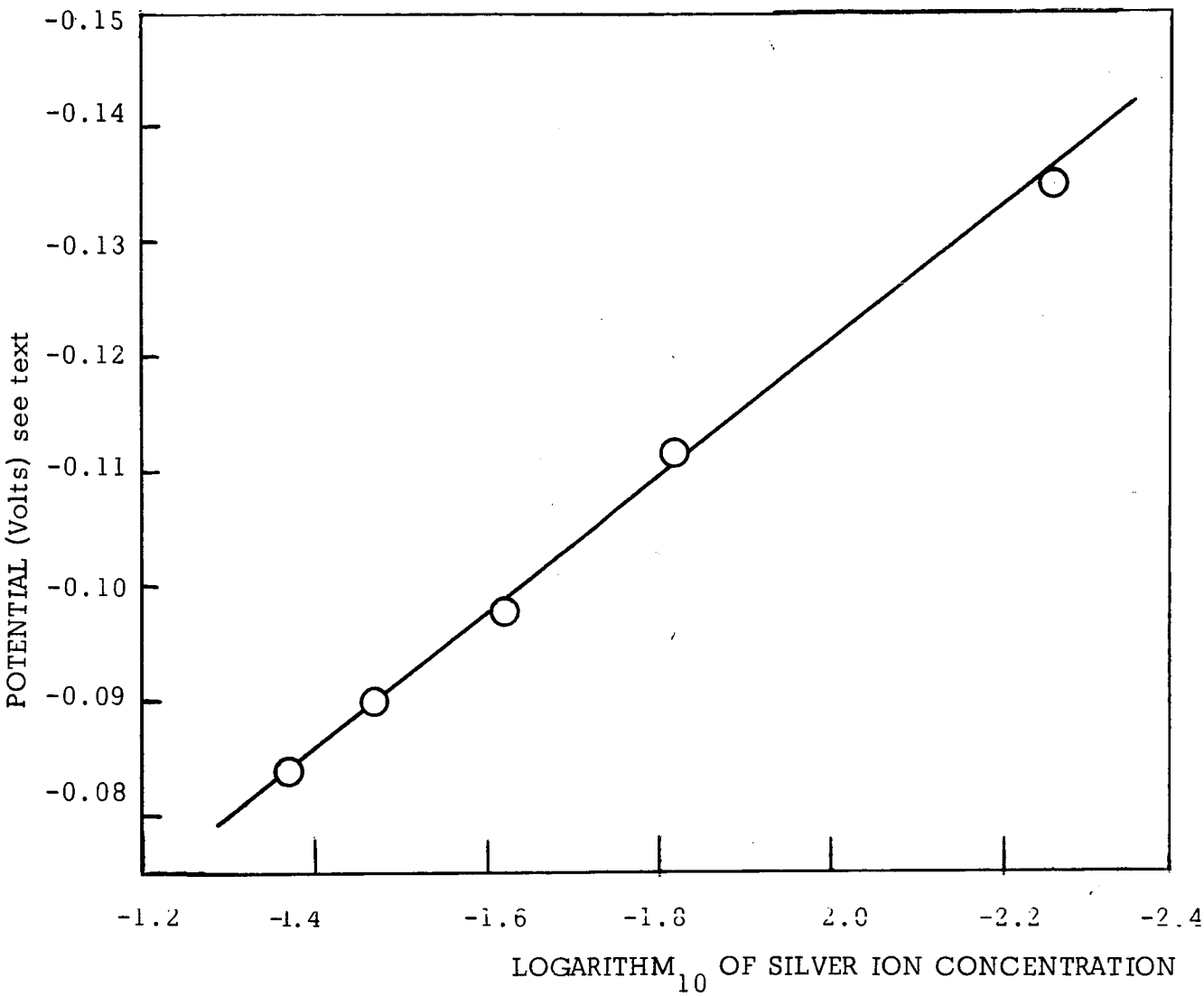

Figure 20 O.C.V. OF SILVER/SILVER ION ELECTRODE VS. CONCENTRATION

In propylene carbonate, 0.5 M in $LiClO_4$, to which amounts of dilute silver perchlorate solution or solid silver perchlorate were added to give concentration indicated.

anodized to give about 500 mC cm^{-2} of AgCl displayed well-poised potentials. Such an electrode was employed in the following experiments as the working electrode. The reference electrode again was a silver plated platinum helix immersed in the counter electrode compartments of the H-cell which contained propylene carbonate, 0.5 M in $AgClO_4$.

Experiment 1: The indicator electrode was immersed in propylene carbonate, 1.0 M in $LiClO_4$, and incremental amounts of a stock solution of $AlCl_3$ in propylene carbonate were added to give the concentration of $AlCl_3$ in the indicator electrode chamber that is shown in Figure 21. Stable potentials were established in reasonable periods of time after each additon of $AlCl_3$ (the time required was somewhat longer than the two minutes or less found on the addition of $AgClO_4$ described above). If the potential of the silver-silver chloride electrode is established by the equilibrium concentration of chloride ions then the potential should become more negative with increasing amounts of $AlCl_3$ -- regardless of the nature of the equilibria. Thus, the maximum observed in Figure 21 for the plot of potential versus concentration of $AlCl_3$ added is disconcerting and indicates that the measured potential does not reflect the final equilibrium composition.

Experiment 2: A similar experiment was performed in propylene carbonate, 0.5 M in $LiClO_4$ and initially 0.025 M in $AlCl_3$. The silver-silver chloride indicator electrode was immersed in the solution and the other conditions were the same as described in experiment 1 above. To the solution were added increments of water giving the concentration indicated in Figure 22. As water was added the potential of the silver-silver chloride electrode became more negative apparently indicating an increased equilibrium concentration of chloride ion, rather than the decreased concentration expected if the effect of water is to remove $AlCl_3$.

Experiment 3: In a further series of experiments solutions of propylene carbonate, 0.5 M in $LiClO_4$, were prepared with varying concentrations of $AlCl_3$. These solutions were then titrated with 0.5 M $AgClO_4$ (in propylene

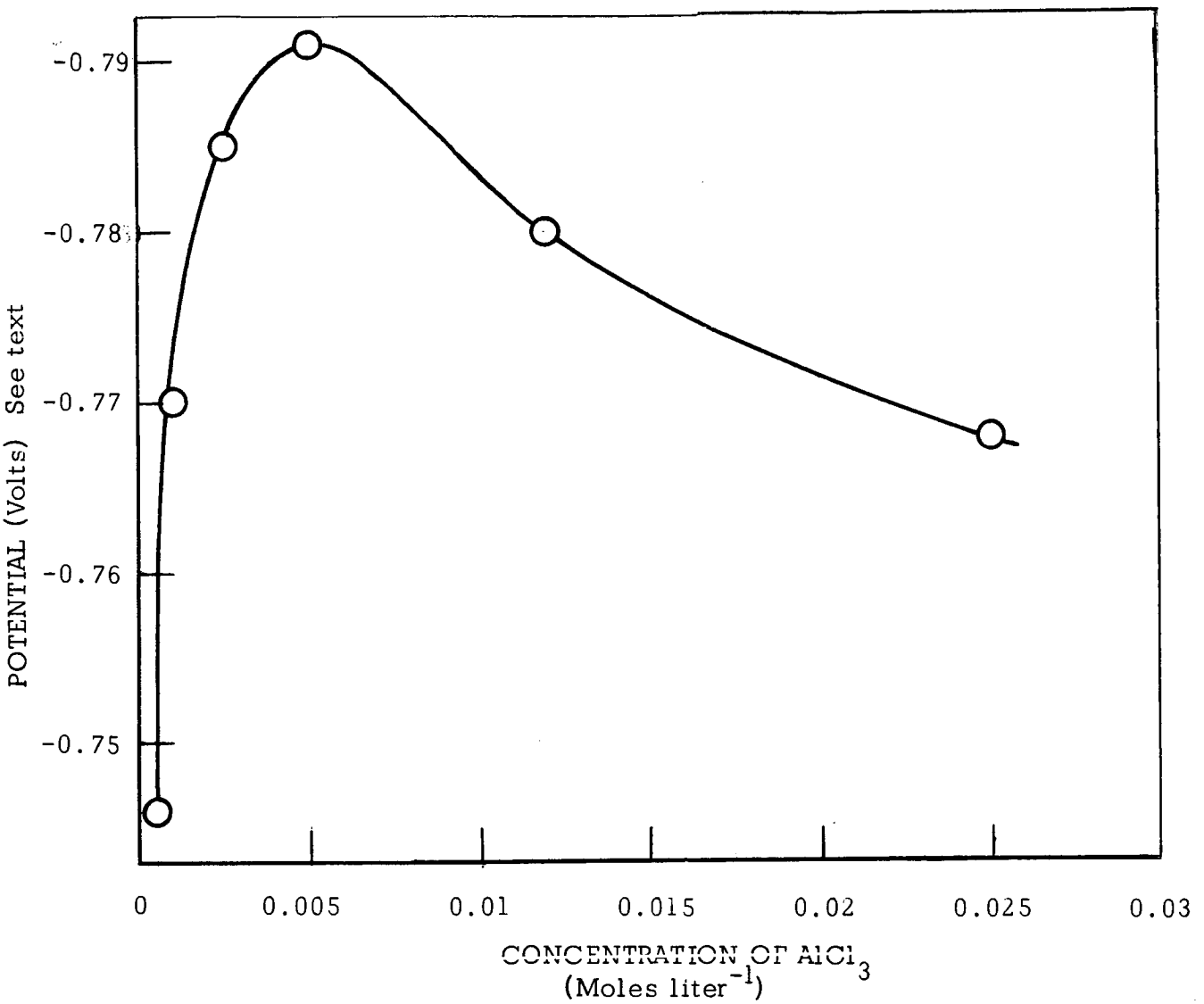

Figure 21 O.C.V. OF SILVER/SILVER CHLORIDE ELECTRODE VS. CONCENTRATION OF $AlCl_3$

In propylene carbonate, 1 M in $LiClO_4$ to which amounts of stock $AlCl_3$ solution were added to give concentration indicated.

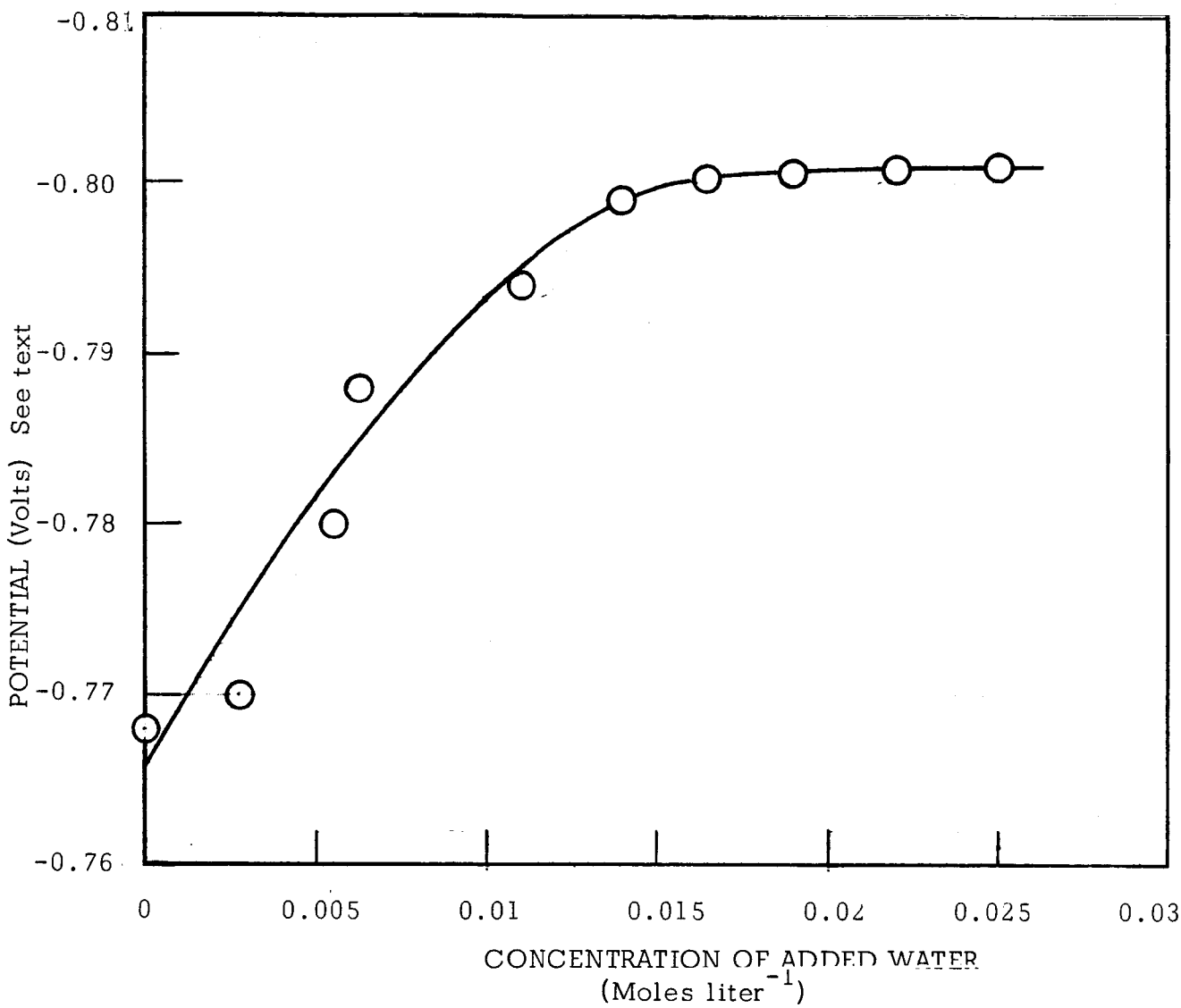

Figure 22 O.C.V. OF SILVER/SILVER CHLORIDE ELECTRODE IN $AlCl_3$ SOLUTION VS. CONCENTRATION OF ADDED WATER

In propylene carbonate, initially 0.5 M in $LiClO_4$ and 0.025 M in $AlCl_3$. Water added to give concentration indicated.

carbonate). The titration curves are shown in Figure 23. The observed variation in potential with added $AgClO_4$ could not be expressed as a function of any simple equilibrium situation.

Experiment 4: A titration, the reverse of that described in experiment 3 above, was performed. Propylene carbonate, 0.5 M in $LiClO_4$, was made 0.0255 M in $AgClO_4$. A dilute stock solution of $AlCl_3$ in propylene carbonate was slowly added and the potential measured. Completion of precipitation was marked by a sharp change in potential to more negative values versus the silver plated helix in the reference electrode compartment. The solution then was essentially $Al(ClO_4)_3$ dissolved in propylene carbonate. This solution was then titrated with a stock solution of propylene carbonate, 0.63 M in $AlCl_3$ and 0.55 M in LiCl. The rationale behind this procedure was to produce a series of solutions in which the ratio of total chloride to total aluminum could be varied in a simple manner. After each addition of titrant the potential was measured. In addition to potential measurements, anodic chronopotentiograms were obtained on polished silver electrodes. The results are shown in Table 6 below. In this table the total concentration of Al^{+3} and of Cl^- have been corrected for dilution resulting from the addition of titrant.

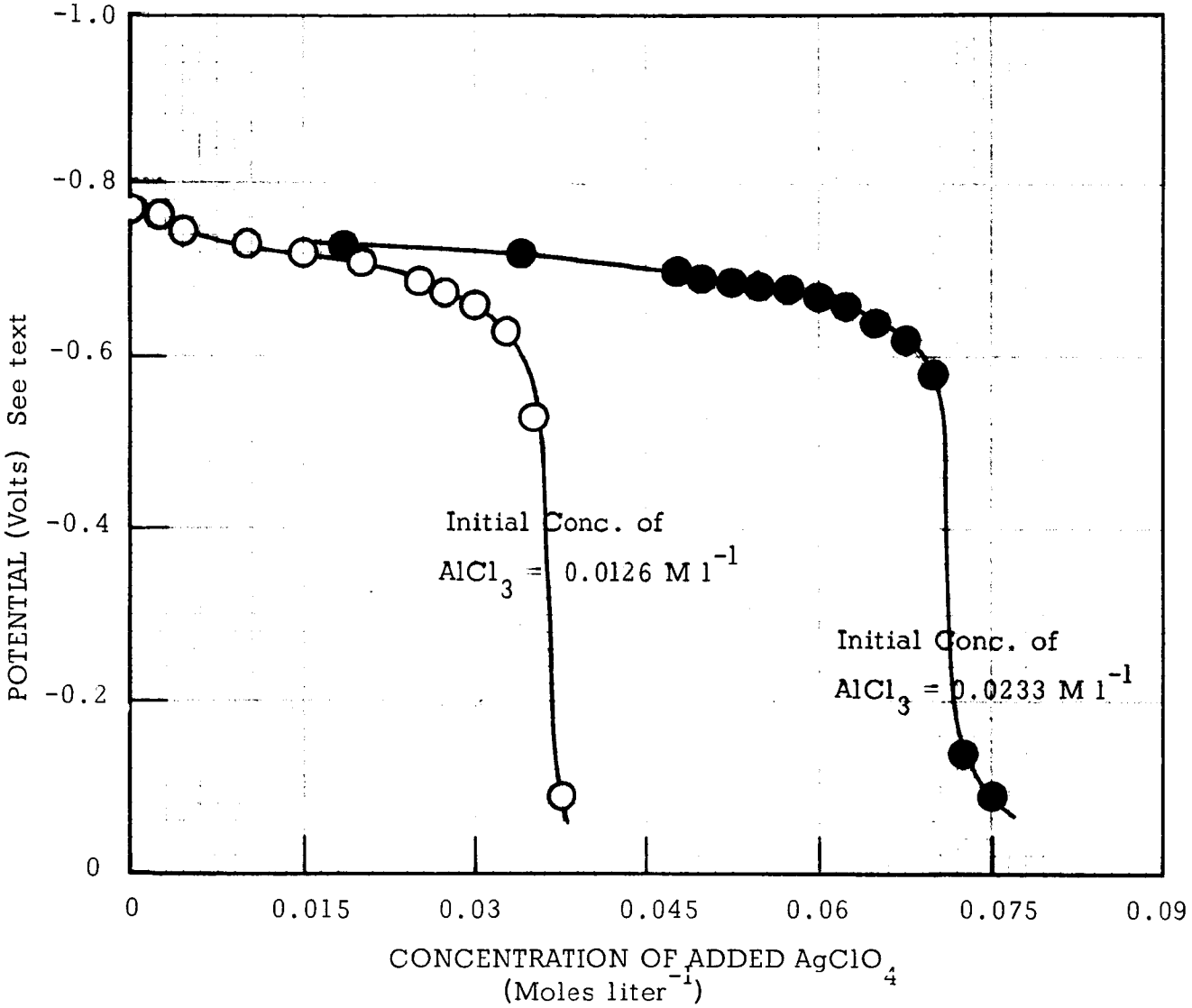

Figure 23 POTENTIOMETRIC TITRATION OF $AlCl_3$ WITH $AgClO_4$
In propylene carbonate, 0.5 M in $LiClO_4$. Initial concentration of $AlCl_3$ as indicated above. Solution titrated with 0.5 M $AgClO_4$ in propylene carbonate. Concentration of added $AgClO_4$ calculated by multiplying the volume of $AgClO_4$ solution added times 0.5 M, and dividing by the final volume of the titrated solution.

Table 6

Variation in $iT^{1/2}$ and Potential with Chloride/Aluminum Ratio

Calculated Total Conc. of Al^{+3}	Calculated Total Conc. of Cl^-	Ratio	$iT^{1/2}$	Potential
(Ml^{-1})	($M\ l^{-1}$)	Cl^-/Al^{+3}	(mA cm^{-2})	(V)
0.0088	0	0	2.06	-0.662
0.0120	0.0095	0.79	3.77	-0.674
0.0151	0.0389	1.25	5.41	-0.680
0.0183	0.0311	1.70	6.88	-0.683
0.0214	0.0433	2.02	8.5	-0.685
0.0245	0.0555	2.27	10.0	-0.686
0.0277	0.0677	2.45	11.4	-0.688
0.0308	0.0800	2.60	13.1	-0.690
0.0340	0.0921	2.71	14.7	-0.691
0.0372	0.104	2.80	16.2	-0.691
0.053	0.165	3.10	24.7	-0.693

It is important to note that $iT^{1/2}$ increases linearly with increasing total chloride concentration and from the slope the value of $iT^{1/2}/C$ (of total chloride) is 140 mA cm $sec^{1/2}$ mM^{-1}. Of course the chloride does not remain in solution uncombined but doubtless exists in various aluminum-chloride species. The linear increase in $iT^{1/2}$ with total chloride concentration suggests that the mobility of these species do not differ markedly, or, less likely, that the relative proportions of the various aluminum-chloride species does not vary with the ratio of total chloride to total aluminum. It will also be observed that there are no marked discontinuities in the relationship

between potential and the ratio of total chloride to total aluminum.

In summary, the results of the potentiometric measurements performed in experiments 1-4 described above indicate that the potential of the silver-silver chloride electrode is not sensitive to the equilibria extant in complex aluminum-chloride media or that the equilibria are more complex and/or more slowly established than would be required for simple elucidation through straightforward potentiometric titrations.

c. Reaction of Aluminum Chloride with Silver Ion. Experiment 3 above, the results of which are shown in Figure 23, established the fact that three equivalents of silver ions are required for each mole of $AlCl_3$, thus the following reaction is indicated: $3\ Ag^+ + AlCl_3 = 3\ AgCl + Al^{+3}$. Although there seemed little cause to question this stoichiometry, further experiments were performed as added verification.

Experiment 1: The proportionality of the chronopotentiometric $iT^{1/2}$ for the reduction of silver ion to the metal was established by adding successive increments of $AgClO_4$ to a solution 0.5 M in $LiClO_4$ (in propylene carbonate). Cathodic chronopotentiograms were obtained on polished silver electrodes. The results are shown in Figure 24. It can be seen that $iT^{1/2}/C$ is 140 mA cm $sec^{1/2}$ mM^{-1}.

Experiment 2: The titration of a solution, 0.043 M in $AgClO_4$, was followed chronopotentiometrically. To the solution were added increments of a stock solution of $AlCl_3$. The concentration of silver ion remaining after each incremental addition of $AlCl_3$ was determined chronopotentiometrically. The results are shown in Figure 25. It will be observed that the concentration of silver ions, as reflected by $iT^{1/2}$, decreases to zero when 1.02 equivalents of $AlCl_3$ have been added per equivalent of $AgClO_4$ initially present, thus verifying the above equation.

d. Decomposition of $AlCl_3$ Solutions. In the course of this work it had been observed that a polished silver electrode immersed in a solution

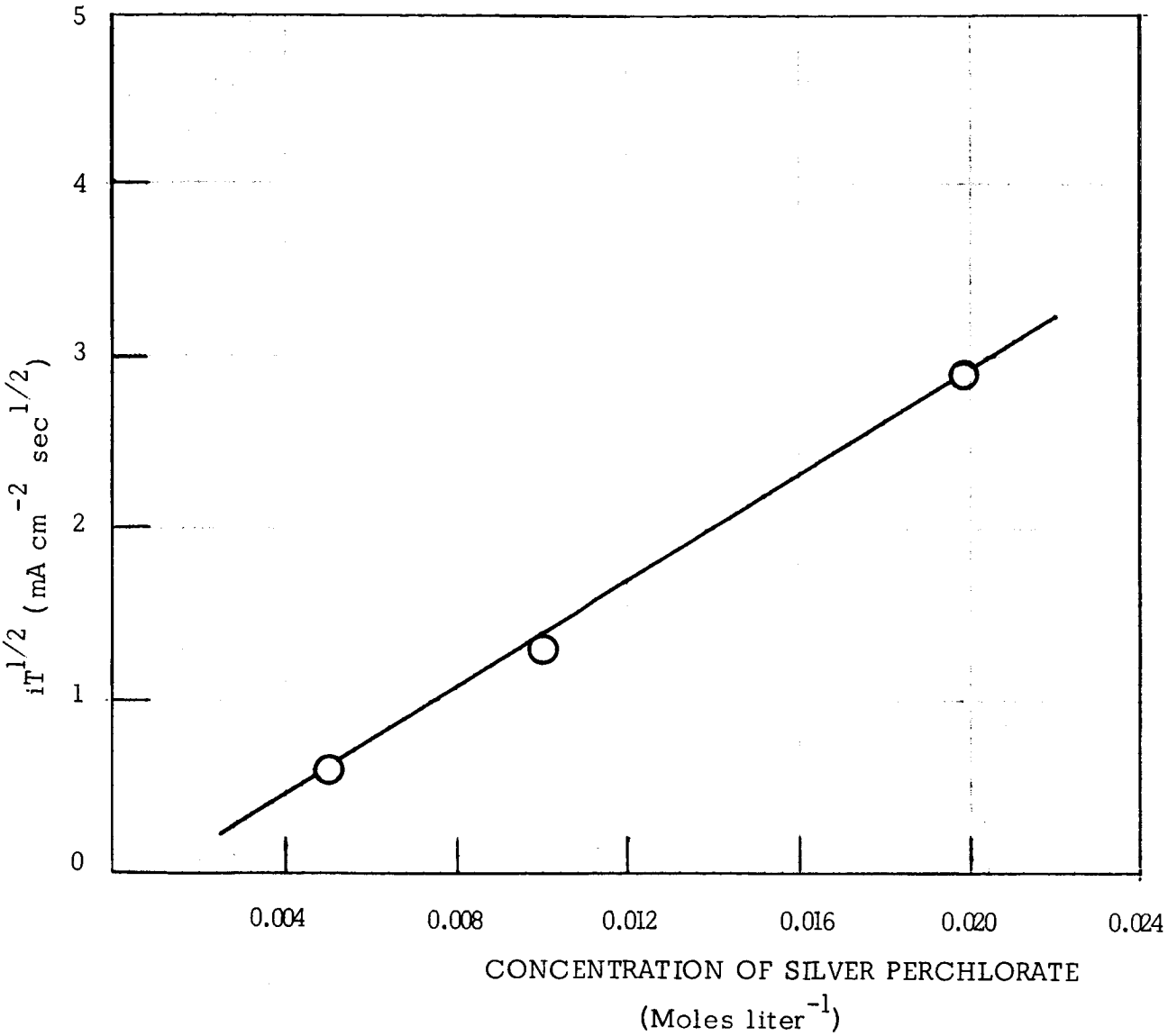

Figure 24 CHRONOPOTENTIOMETRIC $iT^{1/2}$ VS. SILVER ION CONCENTRATION

In propylene carbonate, 0.5 M in $LiClO_4$, to which $AgClO_4$ was added to give concentration indicated. Chronopotentiograms obtained on polished silver electrodes, from which the indicated value of $iT^{1/2}$ was obtained.

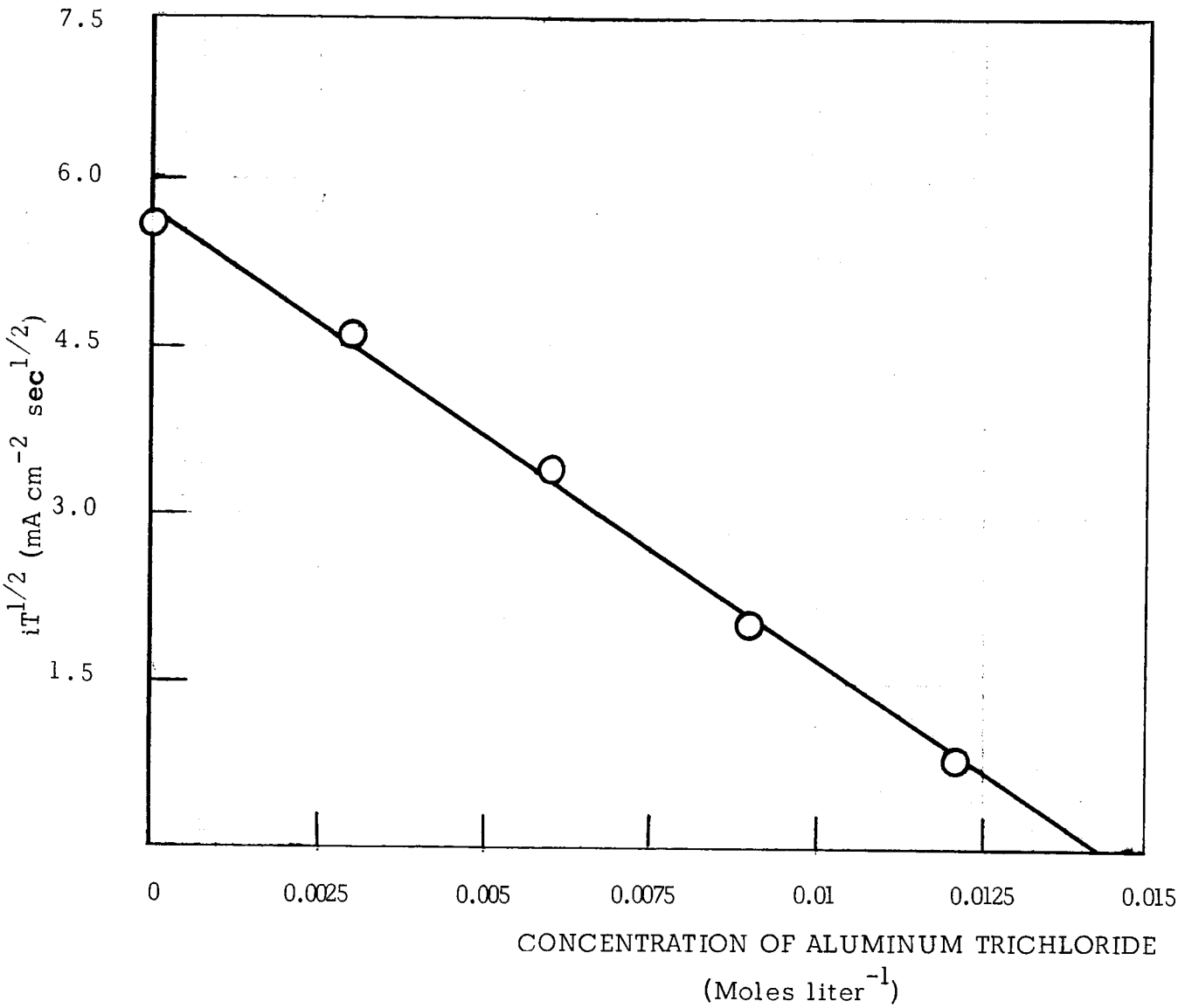

Figure 25 CHRONOPOTENTIOMETRIC TITRATION OF $AgClO_4$ WITH $AlCl_3$ In propylene carbonate, initially 0.043 M in $AgClO_4$ and 0.5 M in $LiClO_4$. Cathodic chronopotentiograms obtained on polished silver electrodes following each addition of an $AlCl_3$ solution. Concentration of added $AlCl_3$ above was calculated by dividing the product of the molarity and volume of the $AlCl_3$ solution added by the total volume of the titrated solution.

containing $AlCl_3$ when anodized at constant current yields well-defined chronopotentiograms which exhibit transition times from which the product $iT^{1/2}$ can be calculated and is found to be proportional to the added concentration of $AlCl_3$. The use of such measurements was shown in Table 6. However, it was often observed that the $iT^{1/2}$ normally decreased as the solution was allowed to stand for extended periods of time. This phenomena was further studied in the following experiments.

Experiment 1: Propylene carbonate, 0.4 M in $LiClO_4$, was made 0.02 M in $AlCl_3$ and anodic $iT^{1/2}$'s determined. The initial $iT^{1/2}$ was 10 mA cm^{-2} $sec^{1/2}$ and decreased to 2.5 mA cm^{-2} $sec^{1/2}$ in four hours. After standing overnight $iT^{1/2}$ had diminished to 1.3 mA cm^{-2} $sec^{1/2}$. Further increments of $AlCl_3$ were added whereupon $iT^{1/2}$ again increased to about the values expected for the constant $iT^{1/2}/C$ = 140 mA cm $sec^{1/2}$ mM^{-1} of total chloride; but, after each addition of $AlCl_3$, $iT^{1/2}$ again slowly decreased with time. If the decay in $iT^{1/2}$ was assumed to be caused by the reaction of $AlCl_3$ with residual water in the electrolyte then the decay in $iT^{1/2}$ should cease when enough $AlCl_3$ had been added to react with all of the water. This expected cessation of decay of $iT^{1/2}$ was not observed even when to the solution had been added a total of 0.1 M i^{-1} of $AlCl_3$.

Experiment 2: Propylene carbonate, 0.4 M in $LiClO_4$, was made 0.1 M in $AlCl_3$. Although anodic chronopotentiograms in this more concentrated solution of $AlCl_3$ were rather ill-defined a value of $iT^{1/2}/C$ of about 180 mA cm $sec^{1/2}$ mM^{-1} of total chloride was observed. To the solution were added increments of water; following each addition, $iT^{1/2}$ was measured with the results shown below:

Table 7

Effect of Water on Removal of $AlCl_3$ by Chronopotentiometry

Conc. of added water ($M\ l^{-1}$)	Anodic $iT^{1/2}$ on polished Ag ($mA\ cm^{-2}\ sec^{1/2}$)
0.00	55
0.05	48
0.10	43
0.15	39
0.25	27
0.30	23
0.35	18
0.40	11

It will be observed that a plot of $iT^{1/2}$ versus concentration of added water extrapolates to zero when about 5.2 moles of water are added per mole of $AlCl_3$. The following reaction is thus suggested:

$$AlCl_3 + 6\ H_2O = Al(H_2O)_6\ Cl_3$$

This hydrated aluminum chloride is well-known. The fact that the extrapolation of the data in Table 7 gives about 5.2 moles of water rather than 6.0 per mole of $AlCl_3$ is not of concern at this time -- more important is the fact that the chloride is removed from solution and that the reaction is not simple hydrolysis:

$$AlCl_3 + 3\ H_2O = Al(OH)_3 + 3HCl.$$

Experiment 4: It seemed likely that the strongly polarizing lithium ion in $LiClO_4$ solutions might effectively complete with aluminum chloride for the water molecules and further investigations were conducted in KPF_6 solutions in propylene carbonate. Each of a series of solutions was made 0.5 M in KPF_6

and to each solution was added the concentration of water shown in Figure 26. To each solution was added enough $AlCl_3$ to make the solution 0.046 M in $AlCl_3$ (this concentration was determined by the convenient addition of an aliquot of a stock solution of $AlCl_3$ in propylene carbonate). Chronopotentiograms were obtained at various times following the addition of $AlCl_3$ with the results shown in Figure 26. The results were not those expected, particularly since the extrapolated $iT^{1/2}$ at t = 0 was, in each case, little more than half that expected. Evidence of much contamination of the solvent by water was, of course, suspected and the solution to which no water had been added was further studied in experiment 5 below.

Experiment 5: The solution to which water had not been added was allowed to stand in the cell overnight. Over the solution was passed a stream of Argon which proceeded through a drying tube containing P_2O_5 before entering the cell. The argon leaving the cell was passed through a collector solution of standard base. After overnight standing it was found that $iT^{1/2}$ had decreased to a negligible value. The standard base was titrated and it was found that the amount of base consumed was exactly equivalent to the amount of chloride initially contained in the solution. Titration of the base indicated that partial neutralization had occurred by a strong acid, there being no evidence of carbonate or the salt of another weak acid in the alkali. Thus the following reaction is assumed to have occurred in the cell, with evolution of HCl

$$AlCl_3 + x\,H_2O = Al(OH)_3.(x-3)H_2O + 3\ HCl.$$

Experiment 6: In this experiment propylene carbonate, 0.5 M in KPF_6 and 0.046 M in $AlCl_3$ was investigated. The rate at which HCl was evolved was determined by titrating aliquots of the alkaline collector solution and the anodic $iT^{1/2}$ was simultaneously determined. The results are shown in Figure 27. These results clearly show that chloride is being removed from solution through hydrolytic formation of HCl.

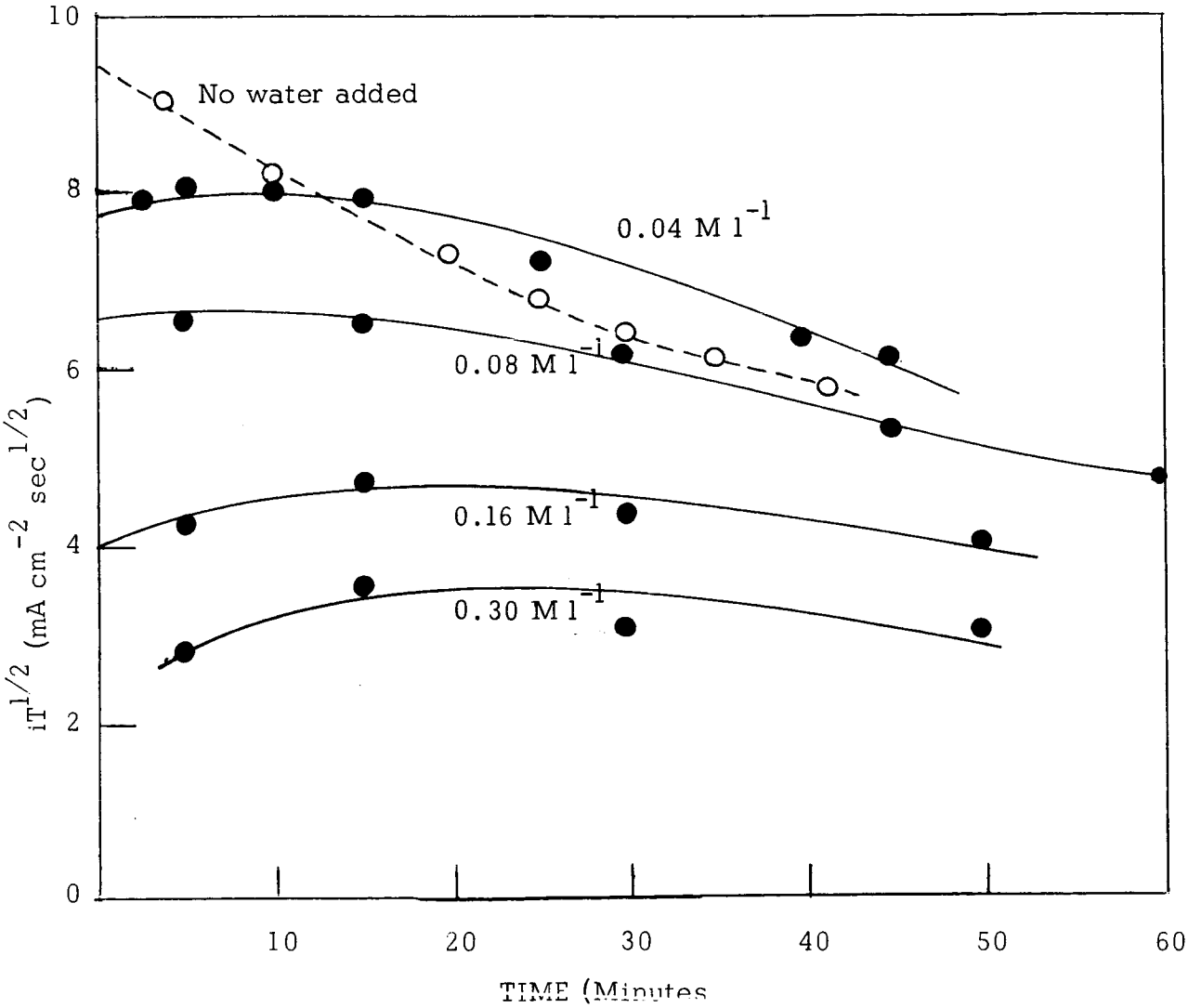

Figure 26 CHRONOPOTENTIOMETRIC $iT^{1/2}$ FOR $AlCl_3$ VS. TIME

In propylene carbonate, initially 0.5 M in KPF_6 and 0.046 M in $AlCl_3$. To four of the five identical solutions was added an amount of water such that the initial concentration of water was that given above. Anodic chronopotentiograms were obtained on polished silver electrodes and the resultant $iT^{1/2}$ is given above.

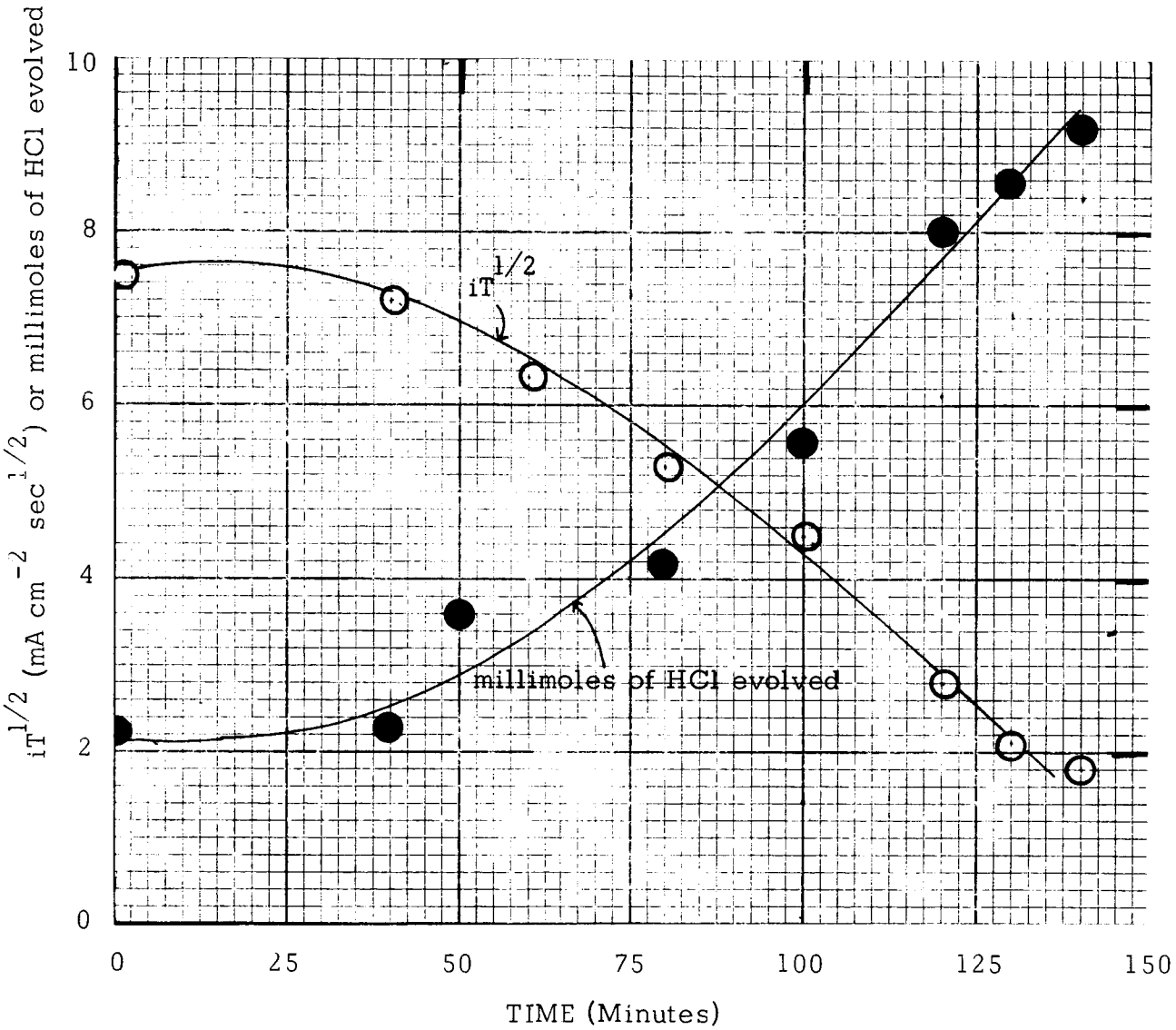

Figure 27 EVOLUTION OF HCl FROM $AlCl_3$ SOLUTIONS

In propylene carbonate, initially 0.5 M in KPF_6 and 0.046 M in $AlCl_3$. Anodic chronopotentiograms obtained on polished silver electrodes.

Evolved HCl collected in standard base and amount determined by back-titration of the excess base.

Experiment 7: Analysis for water by Karl Fisher titration had not indicated the solvent to contain more than about 0.02% water (ca. 0.01 M) and further experiments were performed in the absence of any solute but $AlCl_3$. A stoppered flask containing 0.05 M $AlCl_3$ in propylene carbonate was allowed to stand with deaeration overnight. Back titration of the alkaline collecting solution with standard acid indicated that a negligible amount of HCl had been evolved. In a second experiment a solution, 0.05 M in $AlCl_3$ was made 0.02 M in H_2O. The evolution of HCl was determined by titration of the alkaline collecting solution with the results shown in Figure 28. It will be observed that the amount of HCl evolved after only 300 minutes is nearly three times the equivalent amount of water added.

Experiment 8: To determine the effect of other solutes which might be expected to compete effectively with $AlCl_3$ for water, propylene carbonate solutions, 0.25 M in $Mg(ClO_4)_2$ and 0.05 M in $AlCl_3$, were prepared. The initial anodic $iT^{1/2}$ was 20.4 mA cm^{-2} $sec^{1/2}$ ($iT^{1/2}/C$ = 136 mA cm $sec^{1/2}$ mM^{-1} of total chloride). The solution was then made 0.06 M in water, whereupon $iT^{1/2}$ decreased to 19.0. After standing overnight $iT^{1/2}$ had decreased to 6.7 mA cm^{-2} $sec^{1/2}$, a loss of about two-thirds of the total chloride. The amount of HCl evolved was about equivalent to the amount of water initially added. A second experiment was performed in identical fashion except no water was added to the solution. After overnight standing $iT^{1/2}$ had decreased to about 10 mA cm^{-2} $sec^{1/2}$. The amount of HCl evolved was about the same as that observed from the solution to which water had initially been added.

Experiment 9: A final series of experiments were performed in which various amounts of water were added to a series of solutions, each initially 0.081 M in $AlCl_3$. Upon addition of water a precipitate formed as usual. The solution and suspended precipitate were allowed to equilibrate in rightly stoppered vessels overnight after which they were centrifuged. After pouring

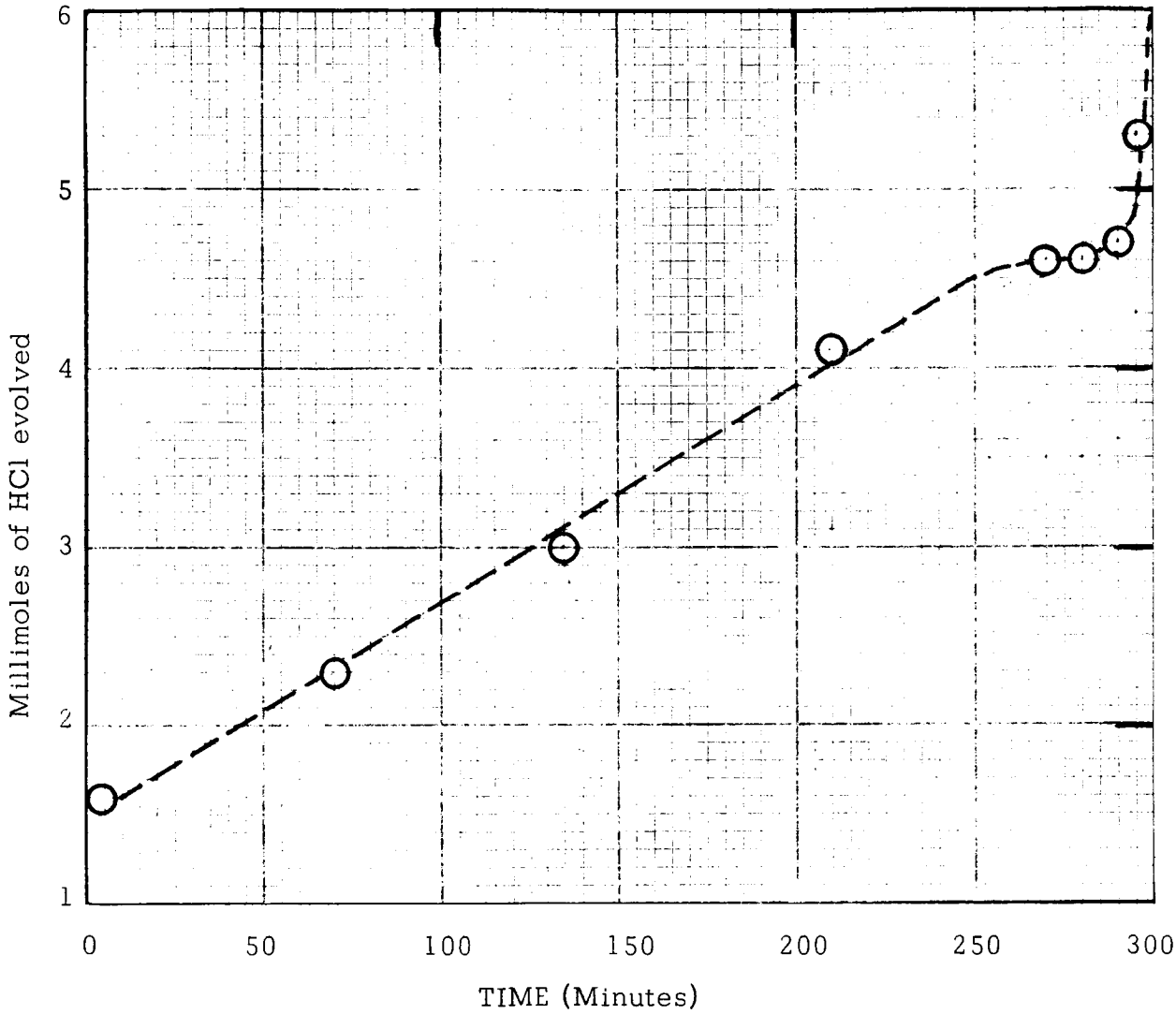

Figure 28 EVOLUTION OF HCl FROM $AlCl_3$ SOLUTIONS

In 100 ml. of propylene carbonate, initially 0.05 M in $AlCl_3$ alone. Two millimoles of water were added and the amount of HCl evolved determined by collecting in standard base and back-titrating aliquots of the base solution with standard acid to determine the amount of excess base remaining.

off the supernatant liquid the precipitates were analyzed for chloride and aluminum. The results are shown in Figure 29. Each solution initially contained 1.62 mM of $AlCl_3$. The maximum amount of precipitate found comprised about 3.7 milliequivalents of $AlCl_3$ or 1.2 mM. The maximum amount of precipitate formed occurs when 7.5 mM of water have been added, about 4.6 moles of water per mole of $AlCl_3$. The results suggest that the hydrated salt, $Al(H_2O)_6.3Cl$ is soluble to the extent of about 0.02 M since 0.42 mM remain unprecipitated in the 20 ml. of solution. With larger concentrations of water the precipitate becomes more soluble and is completely soluble when about twenty-three moles of water have been added per mole of $AlCl_3$. This may reflect solubilization through hydration of the chloride ion.

Conclusions: Experiments 1-9 demonstrate the complexity attending but one chemical reaction in propylene carbonate. The following series of reactions partially explain the data obtained in these experiments:

$$AlCl_3 + 6\ H_2O = Al(H_2O)_6.3Cl \qquad \text{(rapid)}$$

$$Al(H_2O)_6.3Cl = Al(H_2O)_6^{++} + 3\ Cl^- \qquad \text{(slow)}$$

$$Al(H_2O)_6^{+++} + Cl^- = Al(H_2O)_5(OH)^{++} + HCl \qquad \text{(slow)}$$

$$HCl\ (\text{soluble}) = HCl\ (\text{gaseous}) \qquad \text{(slow)}$$

It is clear that the equilibrium situation appropriate to particular concentrations of water and $AlCl_3$ is not rapidly attained, and that our initial hope that this reaction might serve either as the basis for the chemical dehydration of solvent or as a means for the analytical determination of water has not been realized.

D. Summary and Conclusions

The objectives cited in the introduction to Section II have been realized thus:

1. Chronopotentiometric and potentiometric techniques have proven applicable for investigating phenomena in non-aqueous electrolytes both

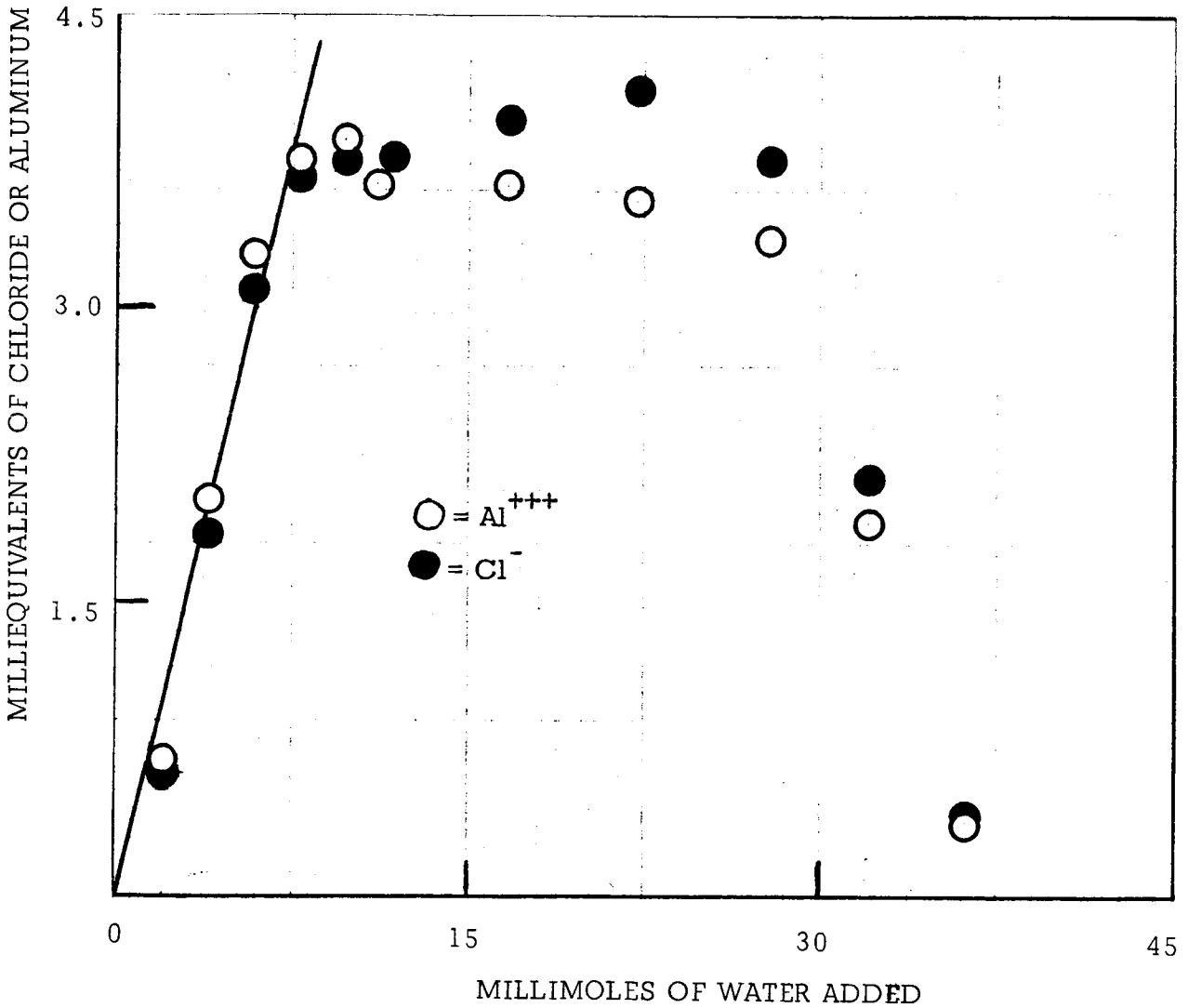

Figure 29 COMPOSITION OF PRECIPITATE FROM $AlCl_3$ - WATER SOLUTIONS

Each of eleven solutions, 20 ml. of propylene carbonate, 0.081 M in $AlCl_3$. To each solution was added the amount of water indicated. After overnight equilibration in sealed vessels, the solutions were centrifuged and the centrifugate analyzed for aluminum and chloride.

Note: The number of milliequivalents of aluminum (III) is three times the number of millimoles.

analytically in reflecting the nature and amount of dissolved species and in yielding information concerning the probable cycling behavior of silver, copper, iron, cobalt and nickel electrodes in various media.

2. Chronopotentiometry and potentiometric titrations indicate that all of the chloride contained in complex aluminum-chloride electrolytes is readily available for combination. Attempts to learn more about the nature of the species in these complex aluminum-chloride electrolytes have not yielded conclusive results. It is inappropriate to pursue studies concerning the nature of the species in solution and the equilibria and reactions which there prevail without more sophisticated procedures for the analytical determination and monitoring of solvent and solute impurities.

3. Cyclic chronopotentiometry has demonstrated the marked superiority of the silver-silver chloride electrode over all other systems. The reactions are electrokinetically reversible and efficient; the ability to anodically form large amounts of adherent deposit per unit area demonstrates the superiority of this electrode in terms of coulombic capacity. Copper is less satisfactory in that the anodic deposits are more soluble. Iron, cobalt, and nickel couples are so irreversible, electrokinetically, that electrode systems employing ion-metal transitions of these elements will have doubtful utility. No evidence has been found for the formation of anodic deposits of any of these three elements.

III. Active Metal Anodes

A. Introduction

The objectives outlined in the introduction to Section II have also guided our work in the investigation of active metal anodes. Thus, the discussion in this section reflects our interest in the use of basic electrochemical techniques, and in the validity and utility of such techniques in learning more about the electrolytes themselves and in disclosing the nature of those basic problems which must be solved before a satisfactory anode can be developed.

Our conclusions will be discussed in more detail at the end of this section but the general problem underlying all of our work with active metal anodes appears to be: The lithium electrode demonstrates the best cycling behavior of any active metal system investigated; however, cathodic efficiency is not 100% because there occurs, during deposition of lithium metal, concurrent electrolytic reduction of solvent, electrolyte or impurities, the effect of which is to diminish the cycling performance of the lithium electrode.

B. Experimental

The experimental procedures outlined in Section II-B have been used in our investigations of active metal anodes.

C. Electrochemical Evidence of Background Material.

We use the term "background material" to describe all substances present in solution, the presence of which in some way influences the basic reaction being studied. We find that there is present in most of the electrolytes we have examined either or both of two types of species which we denote "species A" and "species B", which are inherently suspect of interfering with lithium reduction because of their ability to undergo cathodic decomposition, or to react chemically with electrodeposited lithium. Such species may include solvent, supporting electrolyte (e.g. the perchlorate ion), and unknown impurities including water. At this point it is emphasized that the presence of

water, though obviously undesirable, is not as clearly apparent as would be predicted, and water, if present, does not behave as a simple carrier of active hydrogen. The role of water is even less clean-cut in its effect on the lithium electrode than it is in its reactions with $AlCl_3$ as described in the preceding section.

1. Species A in Propylene Carbonate

Species A comprises all substances reduced more easily than is the lithium ion, that is, all material reducible at potentials positive to the lithium-lithium ion open circuit potential. The presence of species A is evidenced by chronopotentiograms of the type shown in Figure 30. Upon cathodic polarization of flat metal electrodes at constant current in quiet solution the potential rises to and moves along a plateau which is positive to the open circuit potential of an electrodeposited lithium electrode in the same solution. The open circuit potential of such a lithium electrode is about -3 V vs. the silver reference electrode. Variations in the reduction of species A are observed as seen by the difference between curve a and curve b in Figure 30.

Further evidence for species A is obtained "polarographically". We use this term advisedly, recognizing the fact that polarography is normally thought of as being associated with measurements performed on a dropping mercury electrode. Equivalent measurements may be made on solid electrodes, however, by holding the potential of the working electrode constant by means of an electronic potentiostat and measuring the resultant steady state current. In the polarography herein discussed such measurements have been made in stirred solution. A typical "polarogram" is shown in Figure 31. The data represented by each open circle was obtained by holding the potential of the working electrode constant until the steady state current remained constant for a period of at least a minute. Using lollipop electrodes of the type described in Section II-B, operating in conventional H-cells with magnetic stirring of the electrolyte, we find that for well-behaved systems

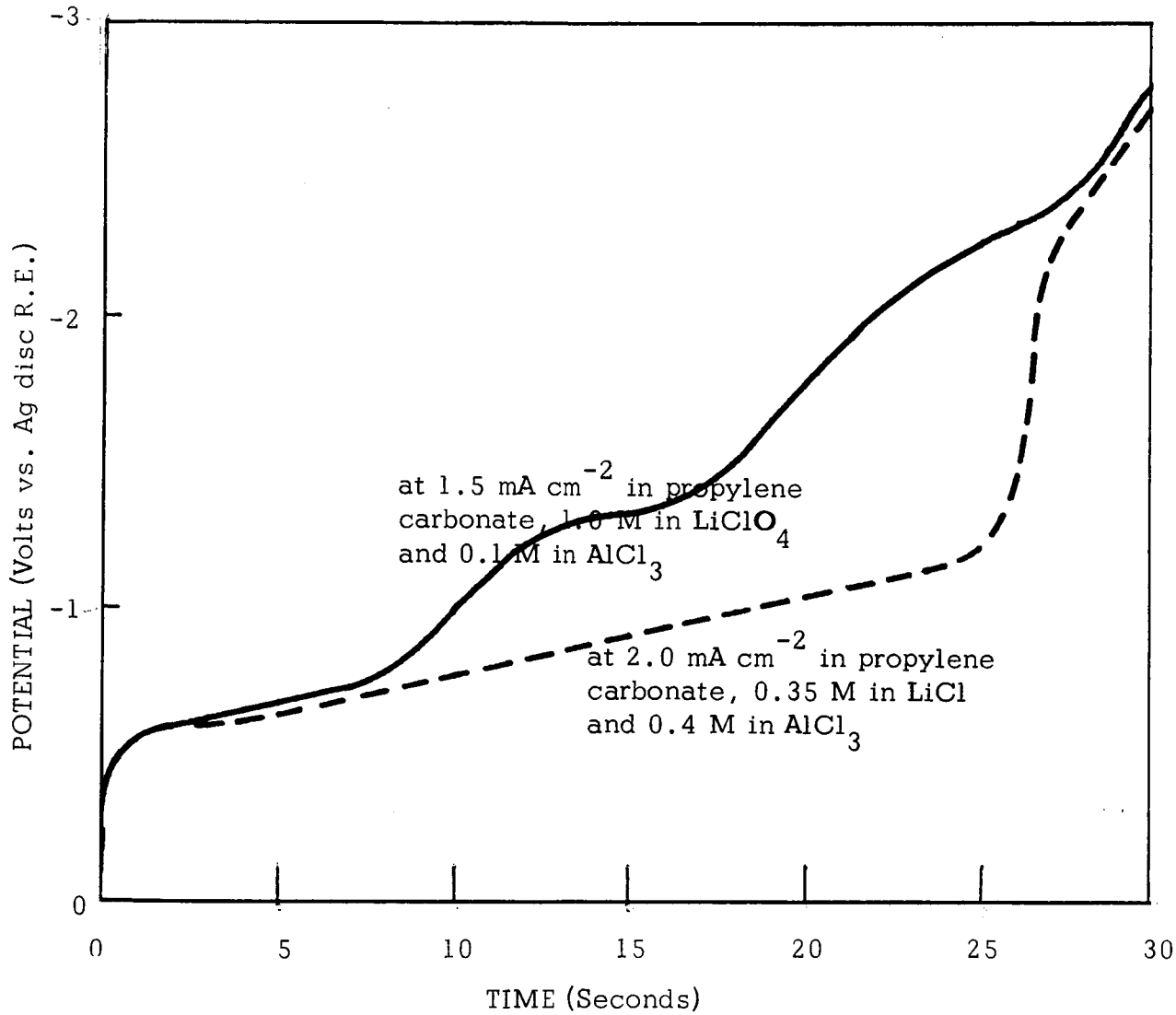

Figure 30 CATHODIC CHRONOPOTENTIOMETRY OF SPECIES A (BACKGROUND)
Chronopotentiograms obtained under conditions indicated on polished cobalt electrodes.

steady state currents are obtained within a few seconds after application of the potential. In other systems we have observed that steady state currents are never attained. Thisreflects important information concerning the nature of the electrode process and will be discussed later. The results shown in Figure 31 reflect a system where true steady state currents were obtained. At potentials more positive than -0.5 V * no current is observed, there being present in solution no species which are reducible at such positive potentials. At -0.5 V reduction of background material commences and the current increases with increasingly reducing potentials. At potentials more negative than -1.6 V the current observed is limited by the rate at which reducible material can reach the electrode. This maximum current is the limiting current, and normally is directly proportional to the to the concentration of reducible material. Finally, at potentials more negative than -3 V the reduction of lithium ions commences and the current again increases.

As stated above, species A may comprise a number of materials and thus variations are observed from solution to solution. The following facts are important in characterizing species A.

a. At any potential more positive than that required for lithium deposition satisfactory steady state currents are observed only in solutions which contain $AlCl_3$. In other solutions (e.g. $LiClO_4$ or KPF_6) the current continuously decreases with time at potentials more positive than about -3 V. The rapidity with which the current decreases depends on the particular potential and the particular electrolyte and is discussed in more detail later.

b. The limiting current observed in $AlCl_3$ solutions at potentials between -1.5 and -3.0 V (see Figure 31) normally varies between 1-5 mA cm^{-2} from solution to solution. Since the magnitude of the limiting current is expected to be directly proportional to the concentration of electroactive species reducible at the potentials bracketing the limiting current plateau, some

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*Unless otherwise stated, potentials are given with respect to the reference silver disc electrode.

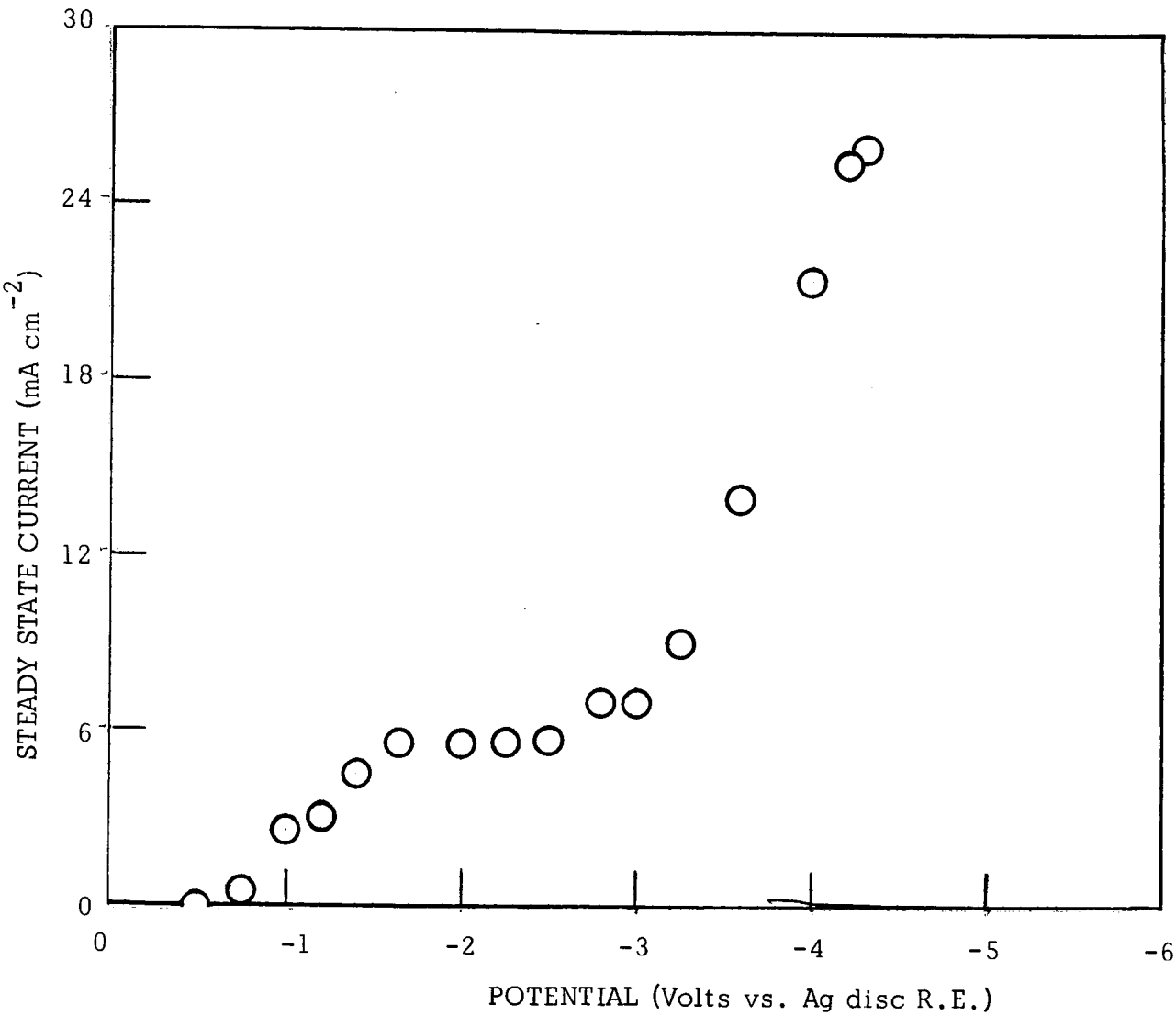

Figure 31 CATHODIC POLAROGRAPHY OF SPECIES A (BACKGROUND) In propylene carbonate, 0.5 M in $AlCl_3$ and 0.21 M in LiCl. Results obtained from potentiostatic measurements in stirred solution on a polished cobalt electrode.

knowledge of the concentration of electroactive species may be deduced from the observed values for the limiting current. In propylene carbonate solutions, and with the geometry prevailing in our electrolytic cells we find that the limiting current (in mA cm^{-2}) is about one hundred times the concentration of electroactive species (in M l^{-1}). Thus limiting currents of 1-5 mA cm^{-2} correspond to concentrations of reducible species of 0.01 to 0.05 M.

c. We do not believe the electroreducible species in $AlCl_3$ solutions to be water, since the deliberate addition of water does not produce a marked enhancement of the limiting current. This may be explained by considering the discussion of the preceding section where it was noted that water is precipitated by $AlCl_3$ with the formation of $Al(H_2O)_6.3Cl$.

d. The appearance of the electrode, as reduction is allowed to proceed at the limiting current for extended periods of time, is instructive. We find that, at potentials between -1.5 and -3V, the electrode becomes coated with a tarry black substance. This substance is insoluble in all mineral acids except aqua regia, and is also insoluble in acetone, benzene, toluene, and carbon tetrachloride. This suggests that the reduction product of species A is, at least partially, an organic polymer. This substance is normally removed by polishing. No gas evolution is observed during the reduction of species A.

e. As described in Section II-B, solutions of $AlCl_3$ in propylene carbonate are normally yellowish to deep reddish-brown. This color may be ascribed to species A because of the fact that when this material is removed by pre-electrolysis, as discussed later in this section, a marked decrease in the limiting current occurs at the same time as the deep color disappears.

f. Species A is capable of chemical oxidation of lithium metal, as discussed later in this section concerning stripping experiments

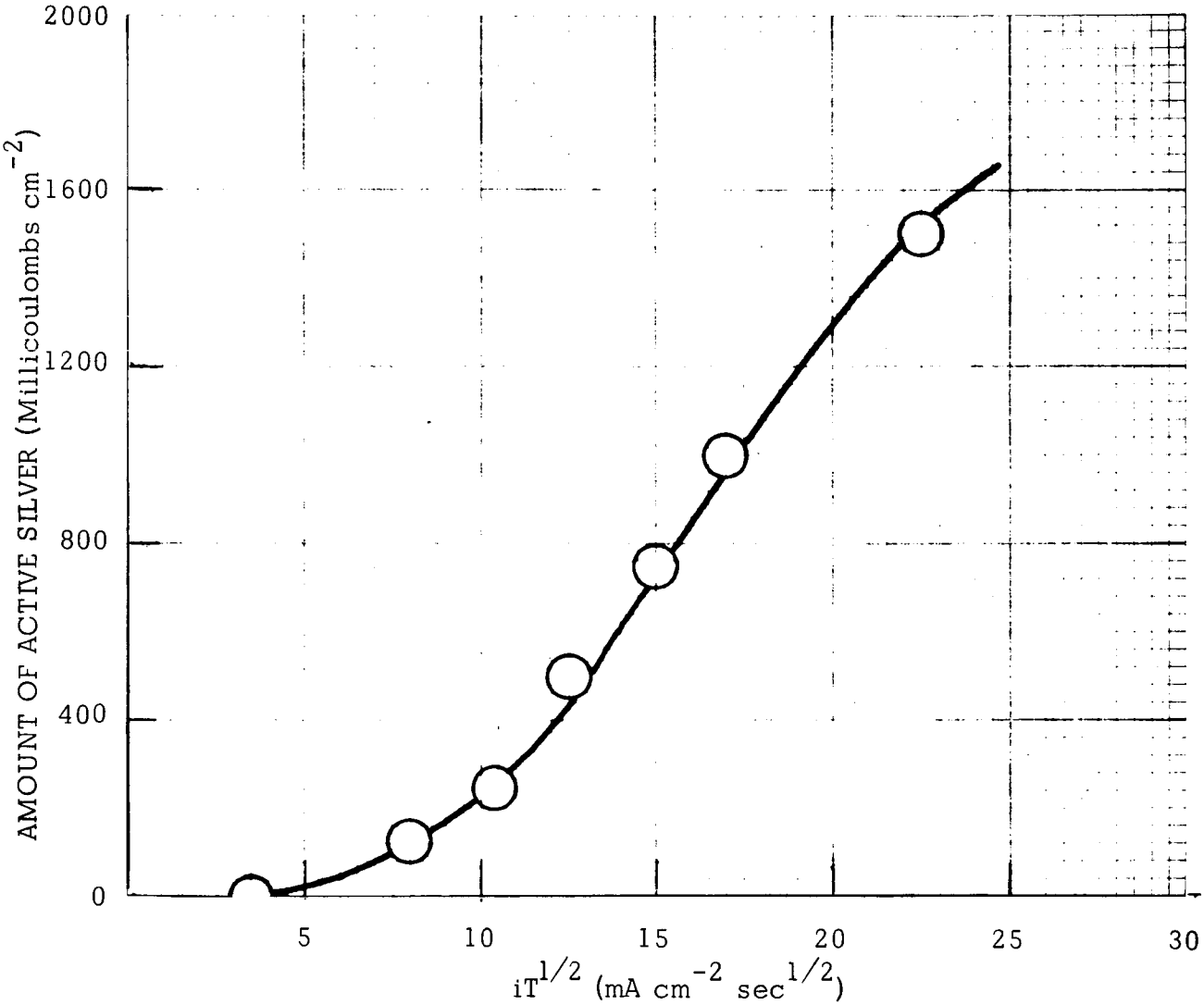

Figure 32 CHRONOPOTENTIOMETRIC $iT^{1/2}$ FOR SPECIES A (BACKGROUND) VS. ACTIVE SURFACE AREA

In propylene carbonate, 0.5 M in $LiClO_4$. Chronopotentiograms obtained at currents yielding transition times between 5 and 15 sec. Chronopotentiograms obtained on active silver electrodes.

performed with lithium, and the rate at which lithium reacts with species A is of the same order of magnitude as the limiting current for species A.

g. In many cases species A may not be observed polarographically since steady state limiting currents are not obtained; the current rapidly and continuously decreases to negligibly small values following the imposition of constant potential at sufficiently reducing values. The presence of species A may be observed chronopotentiometrically in many cases, however. For example, in propylene carbonate solutions of $LiClO_4$ chronopotentiograms similar to curve a in Figure 30 are obtained. The total current passed before the potential reaches that required for lithium deposition is, however, a function of the active surface area. In Figure 32 are shown the values for $iT^{1/2}$ obtained on active silver electrodes prepared as described in Section II-C-1.

h. Finally, and most importantly, it is to be noted that if polarographic and/or chronopotentiometric measurements are to be interpreted in terms of the concentration of species A in solution, the concentration of species A so deduced is far less than that which would be required to account for the inefficiency of lithium deposition. In other words, either the efficiency of the lithium deposition is not limited by concurrent reduction of species A or else the electrochemical measurements previously discussed are not valid reflections of the maximum rate at which species A may interfere with the reduction.

2. Species B in Propylene Carbonate.

Species B represents all material which is reduced with greater difficulty than is lithium, that is, material reduced at potentials negative to the open circuit potential of the lithium-lithium ion electrode. The reduction of species B can be observed in solutions in which lithium salts are not dissolved. In Figure 33 are shown cathodic chronopotentiograms reflecting the reduction of species B.

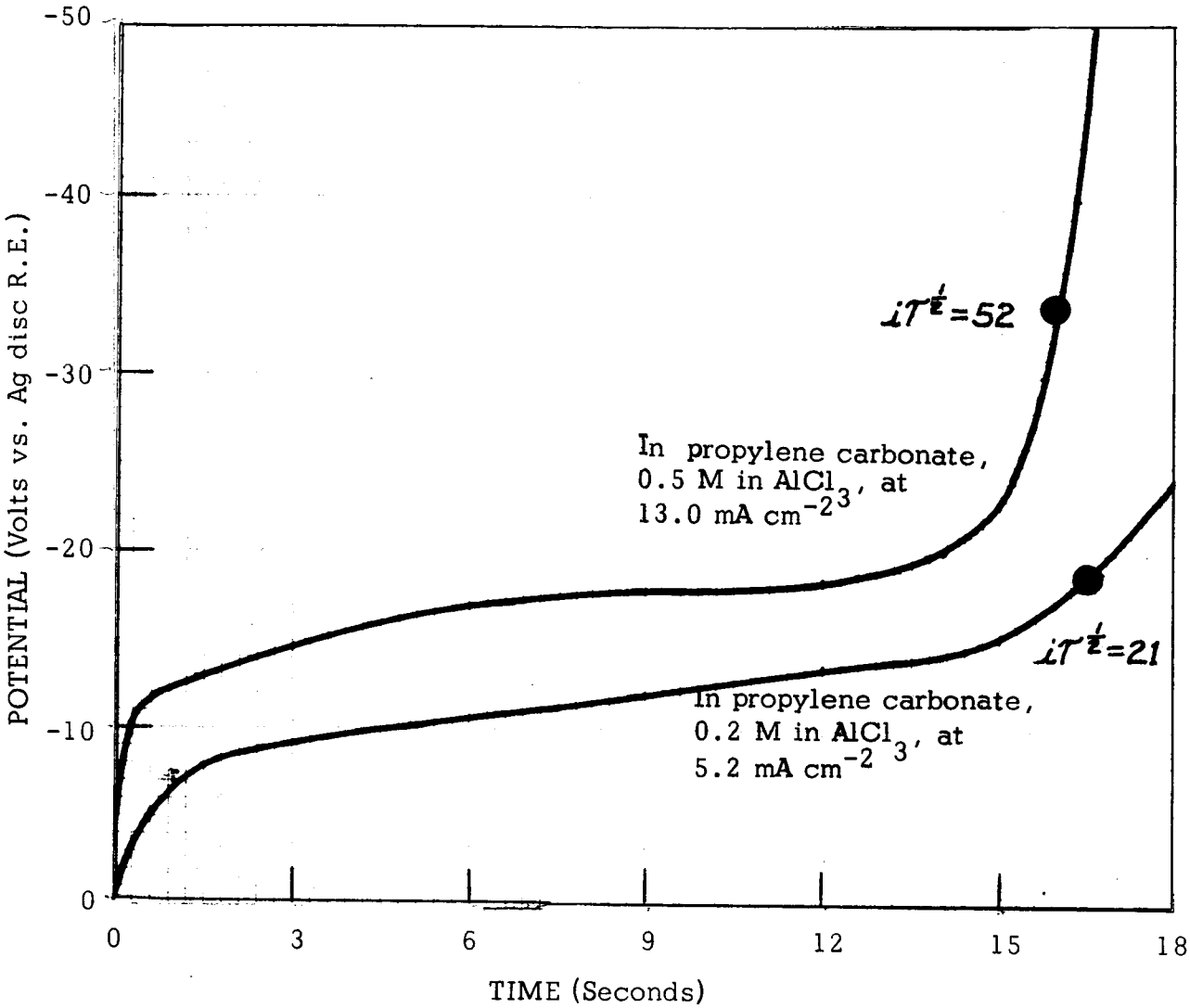

Figure 33 CATHODIC CHRONOPOTENTIOMETRY OF SPECIES B (BACKGROUND)
Chronopotentiograms obtained on polished cobalt electrodes under conditions indicated.

a. The reduction potentials observed are remarkably large. This does not reflect excessive iR drop however. If a series of cathodizations are performed at decreasing currents, a plot of the initial potential versus the current extrapolates to about -7 V at zero current.

b. Reproducible chronopotentiograms for the reduction of species B are readily obtained if the electrode is simply allowed to stand in stirred solution for a few minutes between electrolyses. Thus the products of the reduction of species B do not inhibit successive reductions.

c. The distinction between species A and B can be seen from chronopotentiograms of the type shown in Figure 34. Such chronopotentiograms are quite ill-defined but do show reduction occurring at potentials positive to that for lithium reduction (-3 V) followed by an increase to those negative values at which species B is reduced.

d. It is found that the product, $iT^{1/2}$ is related to the concentration of $AlCl_3$, and is, in mA cm^{-2} $sec^{1/2}$ about one hundred times the concentration of $AlCl_3$ (in M l^{-1}). This suggests that $AlCl_3$ is, in some way, involved in the potential determining process. During the reduction of species B, no visible deposit is formed, and pronounced gassing does not occur until after the transition time. Clearly, the observed reduction is not that of $AlCl_3$ to the metal but most likely involves either reduction of some $AlCl_3$-solvent complex in which the solvent molecule itself is electrolytically decomposed or reduction of uncomplexed solvent molecules in which the reduction products combine with $AlCl_3$ in such a manner as to exhaust electrical charge in the diffusion layer, this exhaustion of charge being signalled by the rise in potential at the transition time.

3. Background Reduction in other electrolytes.

It is of some interest to consider the nature of background reductions observed in other electrolytes. In the experiments to be described, information specifically concerned with evidence for background material was not directly sought and these data were but a by-product of the experiments and doubtlessly

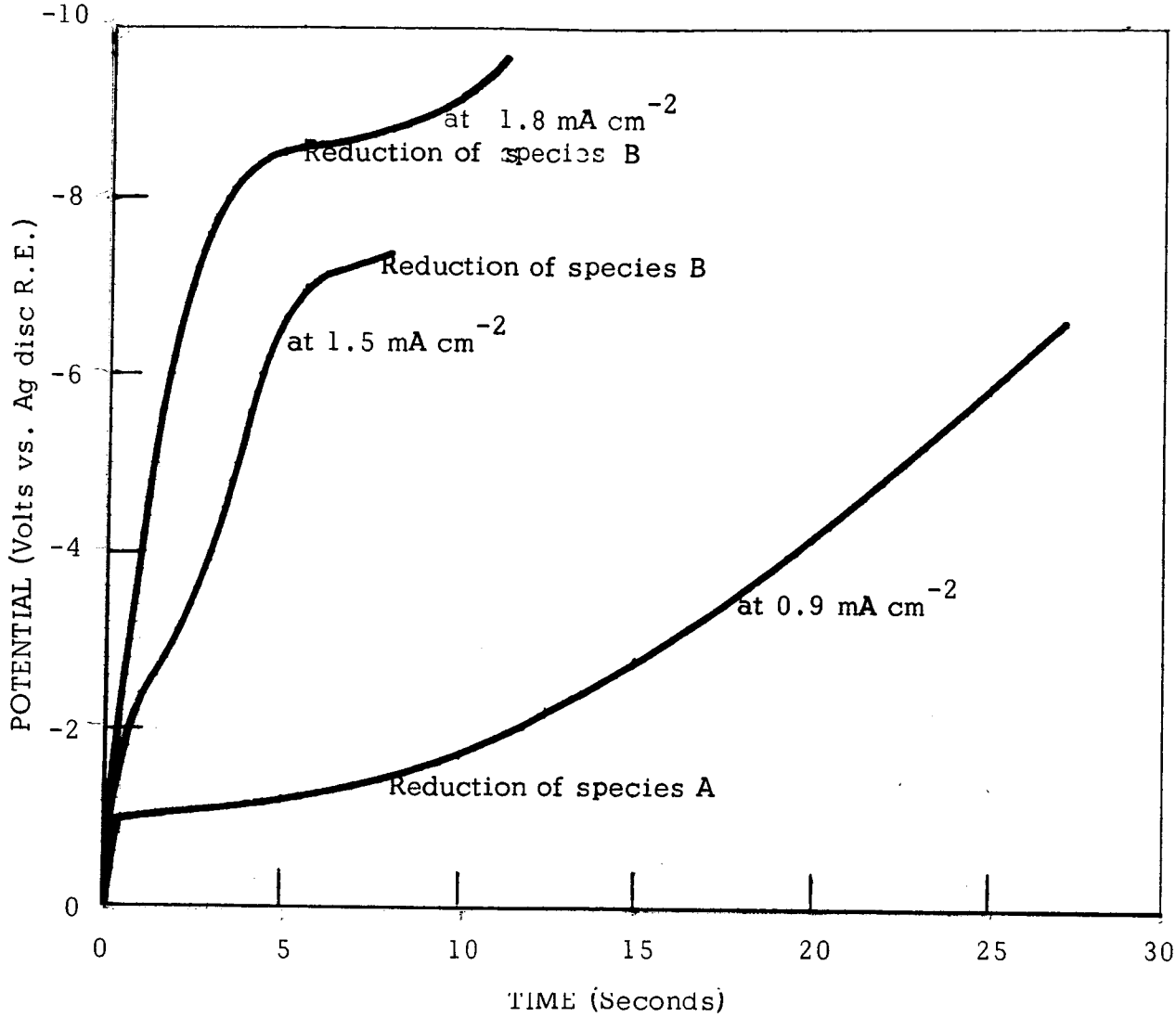

Figure 34 CATHODIC REDUCTION OF SPECIES A AND SPECIES B (BACKGROUND) In propylene carbonate, 0.5 M in $AlCl_3$. Chronopotentiograms obtained on polished cobalt electrodes at current indicated.

give an incomplete picture of the background reduction which transpires in these electrolytes. Since these electrolytes did not prove useful, more detailed investigations of background reductions were not conducted.

a. Propylene carbonate, 0.4 M $AlCl_3$ - 0.4 M $BeCl_2$. On cathodization at 15 mA cm^{-2} the potential immediately rises to -5 V and a somewhat ill-defined potential plateau is observed followed by a transition time appearing after about 10 seconds, corresponding to an $iT^{1/2}$ of about 47 mA cm^{-2} $sec^{1/2}$, close to that which would be observed in the absence of $BeCl_2$. A reduction similar to that of species B in solutions of $AlCl_3$ alone may be presumed. No metallic deposit of either aluminum or beryllium is observed.

b. Acetonitrile, 0.5 M $AlCl_3$ saturated with LiF. At large currents (100 mA cm^{-2}) the potential rose to about -9 V and remained there for as long as 45 seconds. No transition time was observed. At lower currents (2.5 to 4.5 mA cm^{-2}) reduction commenced at -0.5 V, slowly rising to -1.5 V, whereupon a transition time was observed yielding a value for $iT^{1/2}$ of about 10 mA cm^{-2} $sec^{1/2}$. This behavior is similar to that observed for species A in propylene carbonate solution of $AlCl_3$.

c. Propylene carbonate, 0.5 M $AlCl_3$, saturated with NaF. Polarographic evidence for species A ions obtained, a limiting current of about 1 mA cm^{-2} being observed. No search was made for reductions at more negative potentials.

d. Propylene carbonate, 0.15 M KPF_6. On polarization at -3 V the current decayed, within a second, to about 0.1 mA cm^{-2}. At 10 mA cm^{-2} the potential rapidly rose to -9 V, remaining relatively constant during the twenty seconds electrolysis was conducted. At lower currents the potential increased more slowly to -9 V, no intermediate plateau reflecting the possible reduction of potassium was observed. At 20 mA cm^{-2} the potential increased linearly from an initial value of -9 V to -24 V in a period of 20 seconds. No electrochemical evidence for reductions analogous to those of species A or B was observed.

e. Propylene carbonate, 0.2 M $Mg(ClO_4)_2$. At 0.4 mA cm^{-2} the potential immediately rose to -7 V, thereafter continuously increasing with time. At higher currents gassing ensued shortly after commencement of electrolysis. No evidence was observed for reductions analogous to those of species A or B or of the reduction of magnesium ion to the metal.

D. The Behavior of the Lithium Electrode

1. Cathodic Chronopotentiometry

In Figures 35, 36, and 37 are shown typical cathodic chronopotentiograms which reflect the reduction of lithium ions to the metal. The following facts are important:

a. As seen in Figure 35 the addition of a lithium salt (in this case, LiCl) results in the development of a potential plateau at a value of between -3.5 and -5.0V versus a silver disc in the same solution. Increasing the concentration of the lithium salt increases the length of this potential plateau. After the transition time reduction of species B occurs. The subsequent reduction of species B manifests itself in a different way when lithium ions are present. The potential at which reduction occurs is lower (See Figure 35) and this may be largely the decreased iR drop. The shape of the chronopotentiograms is also different (See Figure 36).

b. The shape of the chronopotentiograms obtained in the presence of lithium salts may vary as seen in Figure 37. Nevertheless the transition times observed are always those corresponding to $i\tau^{1/2}/C(\text{of } Li^+)$ = ca. 200 mA cm $sec^{1/2}$ mM^{-1}.

c. After cessation of reduction the potential reverts to a value of about -3 V versus a silver disc reference electrode in the same solution and remains constant at this value for a greater or less period of time as discussed in the next section on chemical stripping experiments.

d. After cessation of reduction the electrode is covered with a gray to black deposit. When the electrode is removed from solution and placed in water, vigorous gas evolution ensues. This demonstrates that at

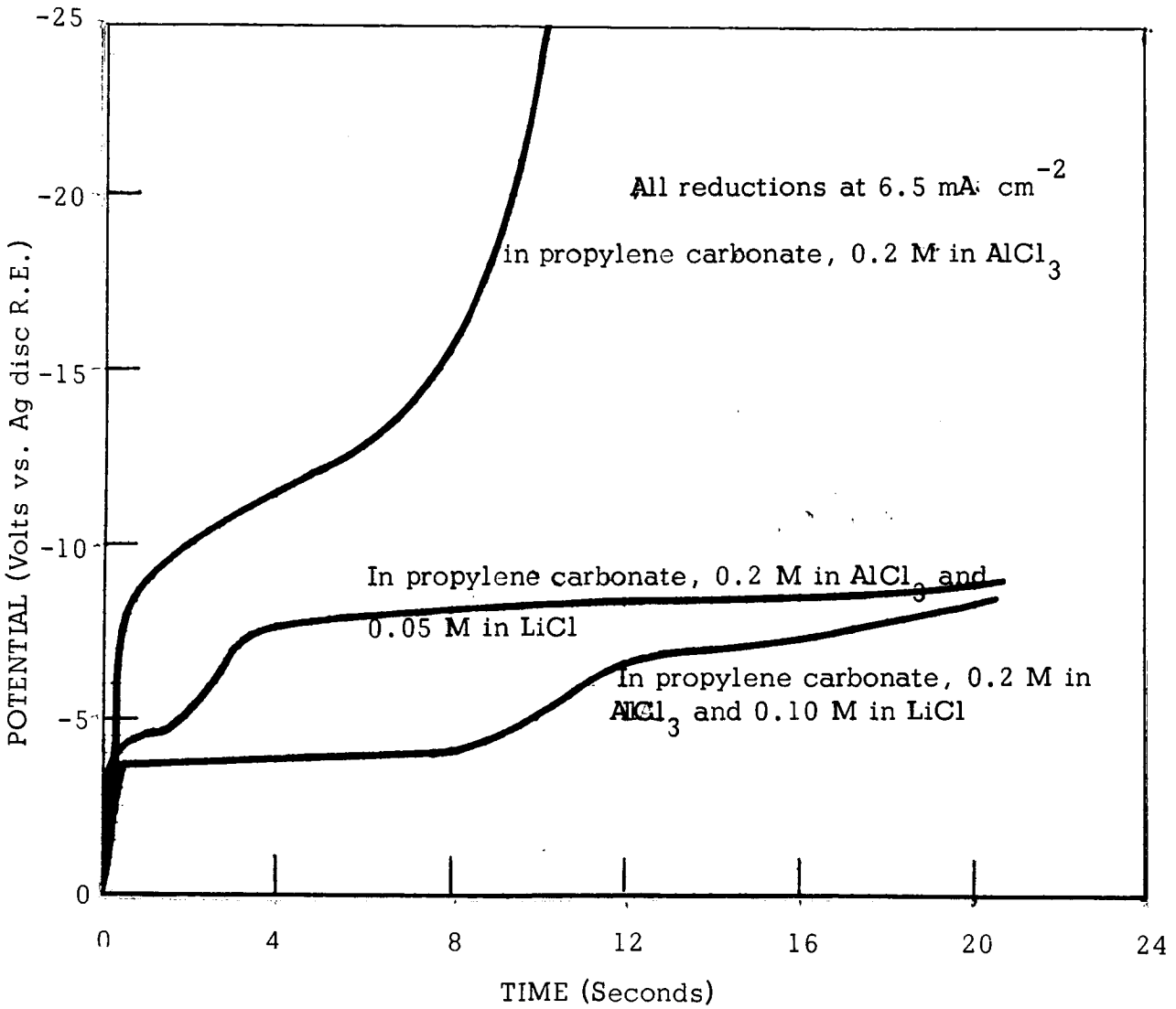

Figure 35 CATHODIC REDUCTION OF LITHIUM AND SPECIES B

Chronopotentiograms obtained on polished cobalt electrodes.

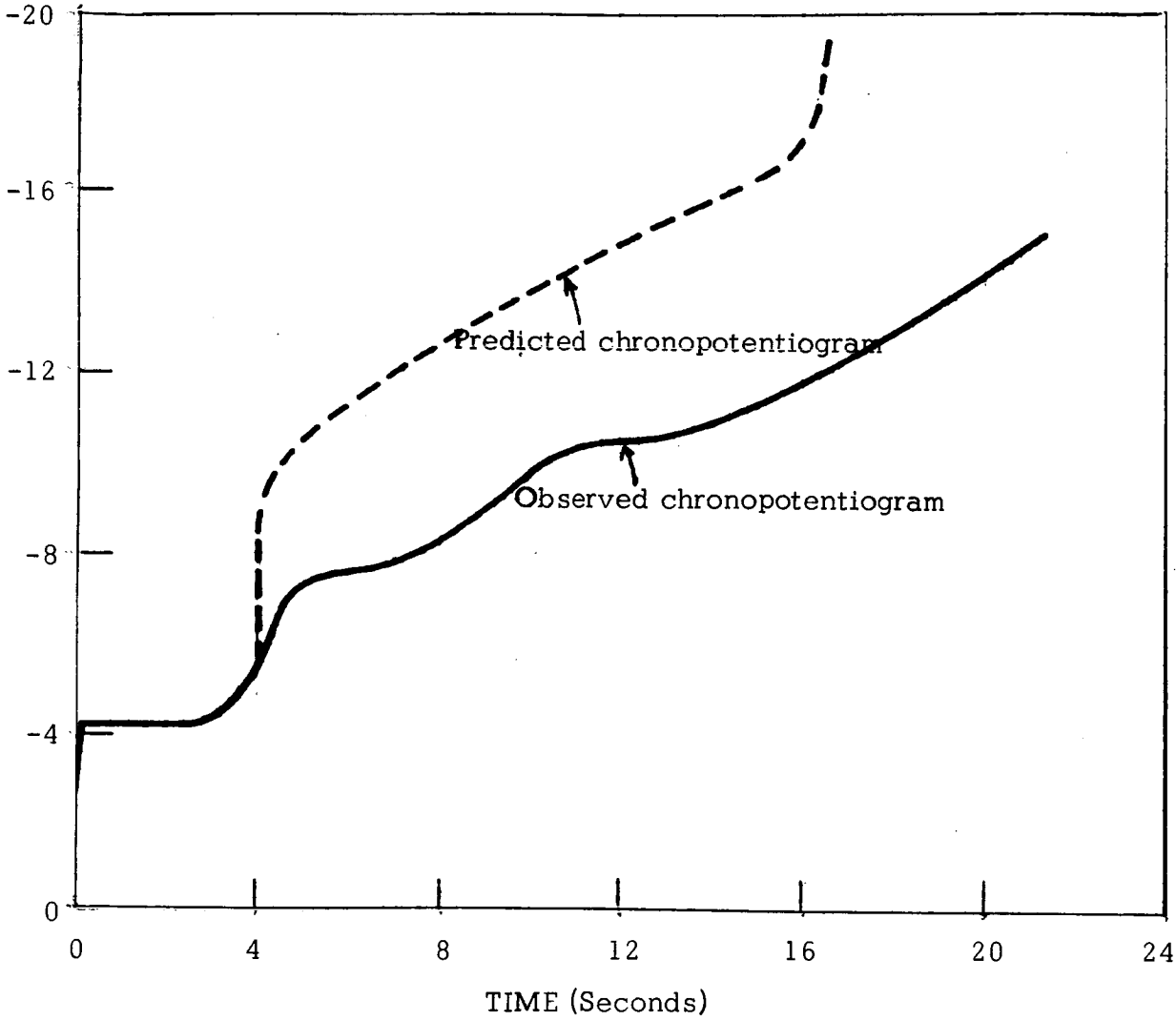

Figure 36 CATHODIC CHRONOPOTENTIOMETRY OF LITHIUM AND SPECIES B In propylene carbonate, 0.2 M in $AlCl_3$ and 0.1 M in LiCl. Chronopotentiogram obtained on polished cobalt electrode at 10.4 mA cm^{-2}.

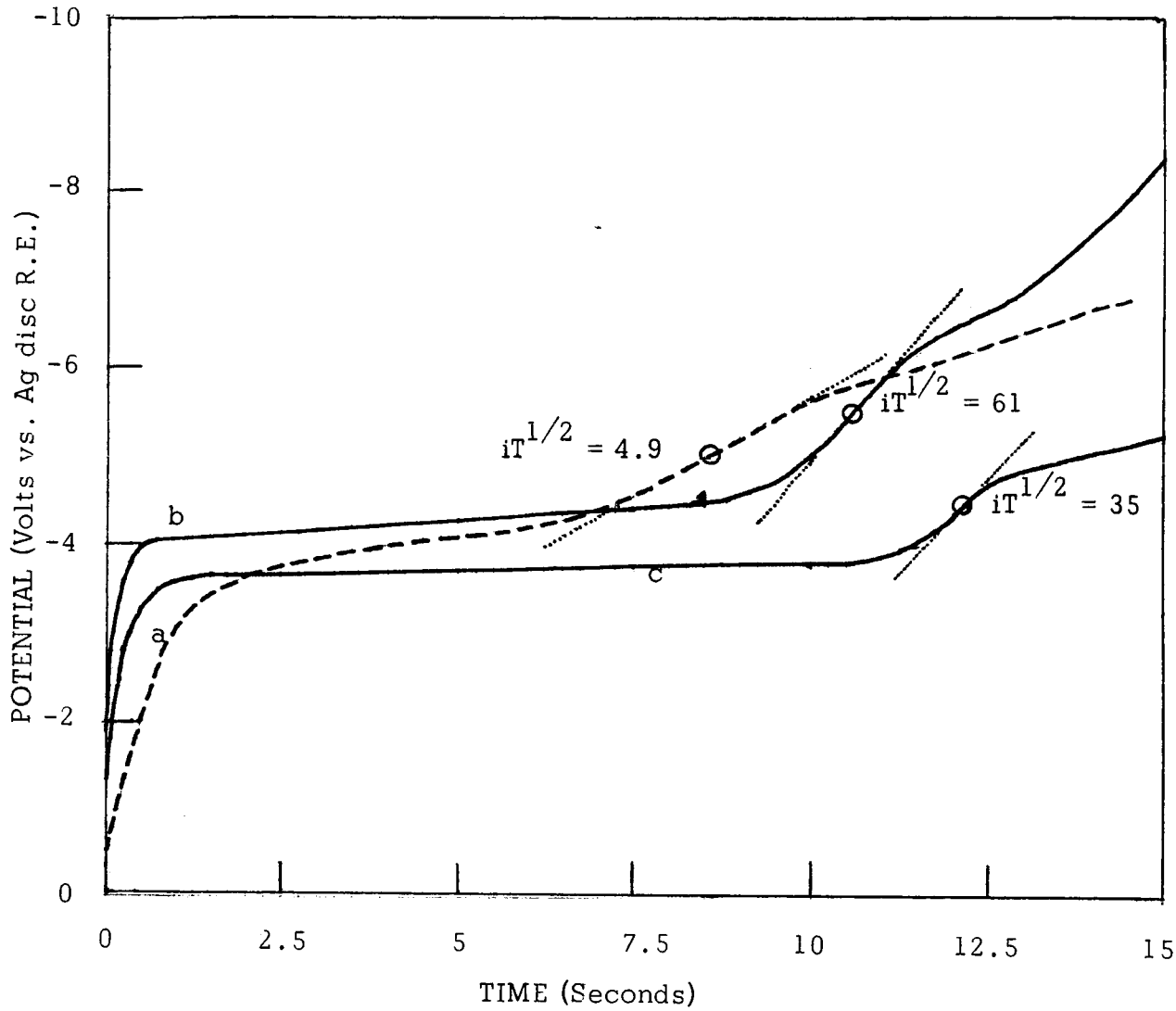

Figure 37 CATHODIC CHRONOPOTENTIOMETRY OF LITHIUM

On polished cobalt electrodes under conditions indicated below. The transition time is taken to be the point of inflection as indicated in the figure by the dotted lines and open circles. The calculated value of $iT^{1/2}$ is in mA cm^{-2} $sec^{1/2}$.

Curve a: in propylene carbonate, 0.5 M in $AlCl_3$ and 0.038 M in LiCl, at 1.7 mA cm^{-2}

Curve b: in propylene carbonate, 0.5 M in $AlCl_3$ and 0.3 M in LiCl, at 18.7 mA cm^{-2}.

Curve c: in propylene carbonate, 0.2 M in $LiClO_4$, at 10 mA cm^{-2}.

least part of the deposit is lithium metal.

e. The reproducibility of chronopotentiograms is excellent if performed on freshly polished electrodes. Successive reductions on the same electrode without some intermediate pre-treatment are not normally reproducible.

Thus cathodic chronopotentiometry gave clear evidence of lithium reduction occurring in a straightforward manner by analogy to chronopotentiograms obtained for the reduction of metal ions in aqueous solution. Other evidence disclosed this was not, in fact, the case.

2. Chemical stripping of Lithium.

Chronopotentiometric measurements having suggested that the reduction of lithium ions to the metal in propylene carbonate should occur in satisfactory fashion, it was of interest to investigate the chemical stability of lithium deposits so formed. These experiments indicated that lithium is chemically attacked not by solvent but by small amounts of impurities in solution.

After lithium is deposited on a flat polished electrode, the open circuit potential of the electrode remains at about -3 V versus a silver disc reference electrode for varying periods of time. After a period of time it is normally observed that the potential quite suddenly changes to more positive values. This behavior is shown in Figure 38. In these runs cathodization was imposed at the currents indicated in stirred solution for 2 minutes and the potential recorded as shown in the figure. The open circuit potential after cessation of electrolysis was then continuously recorded. The constancy of the open circuit potential as shown in Figure 38 is to be noted, and the sharpness of the ultimate potential break. It is also observed that following the potential break no lithium remains on the electrode, although there may be a slight haziness to the initially polished electrode surface. The length of the open circuit potential pause as shown

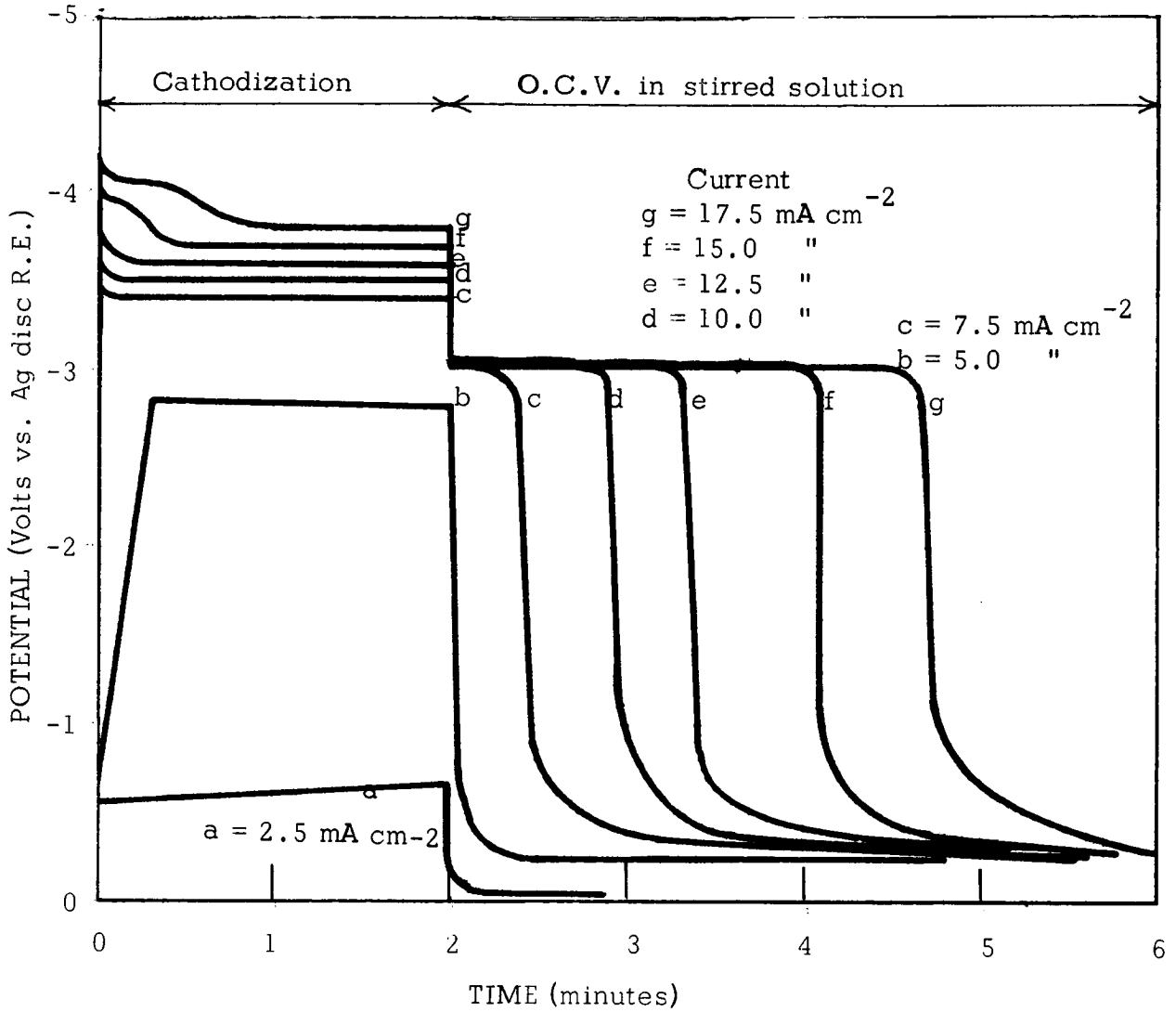

Figure 38 STIRRED REMOVAL OF ELECTRODEPOSITED LITHIUM

In propylene carbonate, 0.5 M in $AlCl_3$ and 0.152 M in LiCl. Polished cobalt electrode cathodized at current indicated for 2 min. in stirred solution. After cessation of cathodization O.C.V. of electrodeposited lithium electrode recorded with time in stirred solution.

in Figure 38 is dependent on the amount of lithium previously deposited. These results suggest that lithium is being chemical ly oxidized and thus removed from the electrode at an approximately constant rate. The results shown in Figure 38 are presented in Table 8 below:

Table 8

Chemical Stripping of Lithium

A Total Cathodic Current Passed ($mC\ cm^{-2}$)	B Time required for Chemical Stripping (sec)	Equivalent Stripping Current (Column A Divided by Column B) ($mA\ cm^{-2}$)
300	0	No lithium
600	0	No lithium
900	24	37
1200	54	22
1500	84	18
1800	126	14
2100	162	8

A better measure of the equivalent stripping current is obtained by plotting Column B of Table 1 versus Column A. A linear plot is obtained the slope of which is 8.3 mC cm^{-2} sec^{1} (8.3 mA cm^{-2}). The plot extrapolates to zero stripping time when the amount of deposit equals 750 mC cm^{-2} which, divided by 120 seconds (2 min.), gives 6.2 mA cm^{-2}. These results clearly suggest that in the solution in which the experiments shown in Figure 38were conducted, lithium is not deposited at currents below 6.2 mA cm^{-2} because of reduction of species A. (Note: Species A is defined as all material reduced more easily than the lithium ion.) The effective stripping current of 8.3 mA cm^{-2} is sufficiently close to 6.2 mA cm^{-2} to suggest that the chemical stripping of lithium also occurs through the oxidative action of species A.

It will be recalled that these currents are of the same order of magnitude as the polarographic limiting current for species A as shown in Figure 31 (ca. 1-5 mA cm^{-2}).

It was found that the results of stripping current measurements performed as described above were somewhat questionable because it was clearly observed that the last traces of deposit were stripped at a slower rate. More accurate measurements were obtained by a more involved procedure the results of which are shown in Figure 39. In these experiments deposition was performed in stirred solution on polished cobalt electrodes at currents of 5 and 30 mA cm^{-2}. After electrolysis the electrode upon which lithium had been deposited was allowed to stand in stirred solution for varying periods of time following which the electrode was anodized. Upon anodization the metallic lithium remaining on the electrode was discharged and the completion of discharge was marked by a sharp change in potential to more positive values. The anodic discharge curves are essentially identical to the open circuit potential plots shown in Figure 38. Each of the points shown in Figure 39 represents one complete run. All of the four or five points along a single solid line represent a series of runs in which deposition was conducted under identical conditions (i.e. the same current density for the same length of time). Each such point along a single solid line differs from others along the same line only in the amount of time which had elapsed following deposition and prior to anodization.

The extrapolations of the straight lines back to a stirring time of zero seconds yields the amount of lithium metal on the electrode prior to any chemical oxidation. It will be observed that the amount of lithium so found is less than the total amount of deposition current. Curves a and b represent total deposition of 150 mC cm^{-2}; the extrapolation yields only about 85 mC cm^{-2} or 57%. Curves c and d represent a total deposition of 600 mC cm^{-2}; the extrapolation yields only about 365 mC cm^{-2} or 61%. The slope of the straight lines yields the effective stripping current (mC cm^{-2} sec^{-1} = mA cm^{-2}) and the values obtained are: curve a: 0.4 mA cm^{-2},

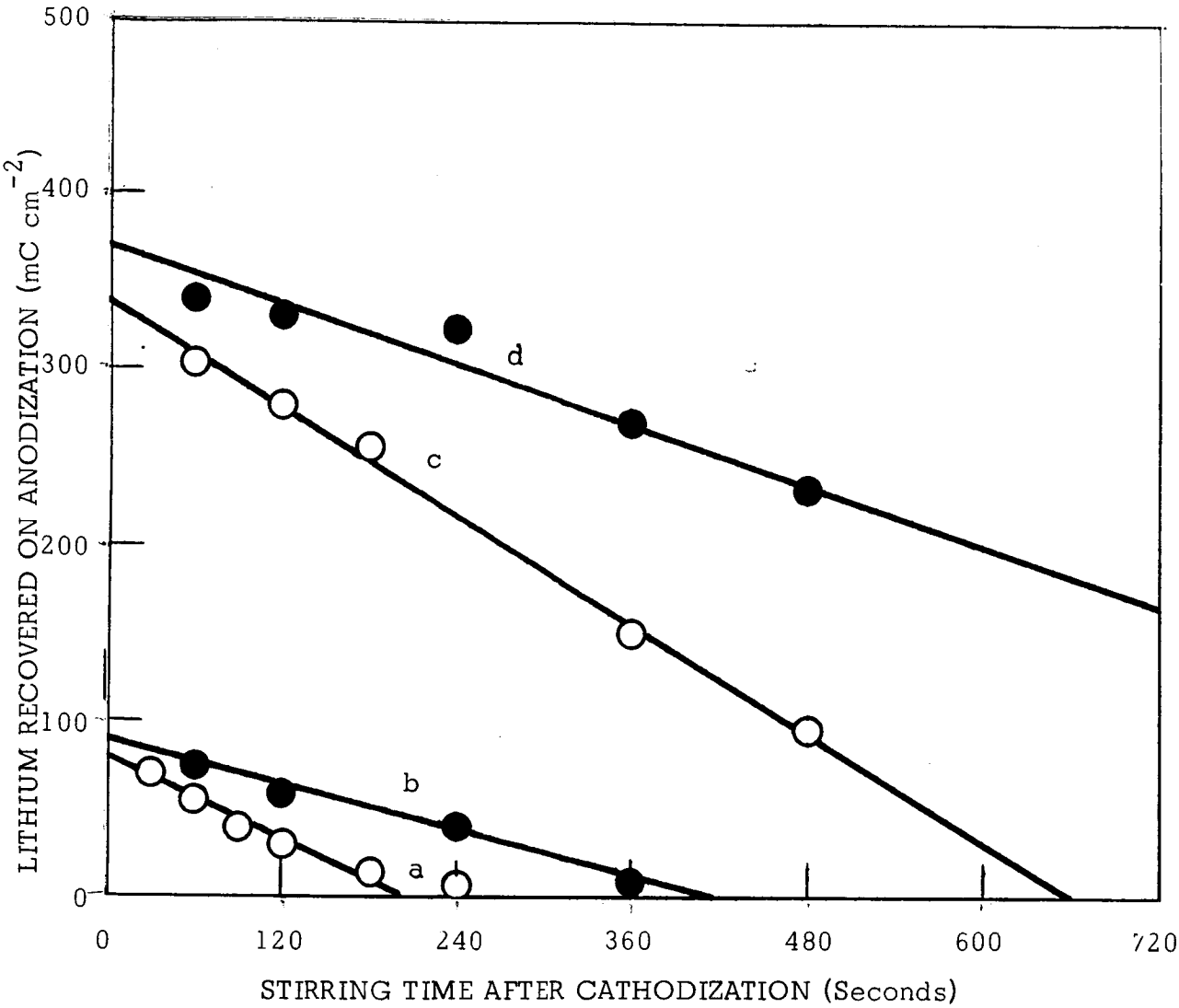

Figure 39 STIRRED REMOVAL OF ELECTRODEPOSITED LITHIUM

In propylene carbonate, 0.5 M in $AlCl_3$ and 0.35 M in LiCl. Lithium initially deposited on polished cobalt under conditions indicated below. The electrode was then allowed to stand in stirred solution for the time indicated above, following which the amount of lithium remaining on the electrode was determined by anodization at 5 mA cm^{-2}.

Curve a: Cathodization at 5 mA cm^{-2} for 30 sec. (150 mC cm^{-2})

Curve b: Cathodization at 30 mA cm^{-2} for 5 sec. (150 mC cm^{-2})

Curve c: Cathodization at 5 mA cm^{-2} for 120 sec. (600 mC cm^{-2})

Curve d: Cathodization at 30 mA cm^{-2} for 20 sec. (600 mC cm^{-2})

curve b: 0.2 mA cm^{-2}, curve c: 0.5 mA cm^{-2}, and curve d: 0.3 mA cm^{-2}. These stripping currents are much lower than those described by the results shown in Figure 38. The reason is simply that this solution had been pre-electrolyzed while the solution in which the results shown in Figure 38 were obtained had not been so treated. In the solution, the results of which are shown in Figure 39, it had been found that the polarographically determined limiting current for species A was only about 0.25 mA cm^{-2} after pre-electrolysis.

Thus far the conclusion was inescapable that species A was deleterious in effecting the chemical stripping of lithium. The fact that a marked decrease in the polarographically determined limiting current for species A as well as the decrease in stripping current attended pre-electrolysis seemed to indicate that solvent reaction with lithium was minimal. If this were not so the results traceable to species A would be completely obscured by the rate of solvent reaction with the lithium.

It was disconcerting to observe that the efficiency for lithium deposition nonetheless was so low (57-61%). Furthermore, the efficiency was as low at 6 mA cm^{-2} as at 30 mA cm^{-2}. This clearly proves that species A is <u>not</u> primarily responsible for the low efficiency of lithium deposition.

Another series of experiments were performed as follows in the same solution in which the results shown in Figure 39 were obtained, namely pre-electrolyzed propylene carbonate, 0.5 M in $AlCl_3$ and 0.35 M in LiCl. In these experiments depositions were performed at varying currents but for a period of time required to give a total of 150 mC cm^{-2} of total cathodization. Following each deposition the deposited electrode was allowed to stand in stirred solution for 30 seconds. The amount of lithium remaining on the electrode was determined by anodization. As seen in Figure 39 the recovery following 30 seconds of stirring does not differ seriously from the

extrapolated value at zero seconds stirring. The solid circles in Figure 40 represent the experimental results.

The dotted lines in Figure 40 represent calculated results expected for two types of reduction behavior. Curve a represents the results expected if there exists in solution an amount of background material, more easily reducible than lithium, in such concentration that the limiting current for the reduction of this material is 0.5 mA cm^{-2}. At currents less than 0.5 mA cm^{-2} no lithium will be deposited -- all of the current will be consumed by reduction of the background material (species A). As the current is increased above this value the efficiency for lithium deposition will continuously increase as the current increases, since the fraction of the total current consumed by background reduction (0.5 mA cm^{-2}) will continuously decrease. The efficiency for lithium deposition will be given by:

$$\text{Efficiency} = \frac{i\ (\text{mA cm}^{-2}) - 0.5\ (\text{mA cm}^{-2})}{i\ (\text{mA cm}^{-2})} \times 100$$

This is represented by curve a.

Curve b in Figure 40 represents a more complicated situation. Here we suppose there exists in solution the same background material with a limiting current of 0.5 mA cm^{-2}; but we also suppose that the lithium reduction is inherently inefficient. If it be assumed for example that the inherent efficiency for lithium reduction is 50%, then the net efficiency for lithium deposition will be given by:

$$\text{Efficiency} = \frac{0.5\ (\ i(\text{mA cm}^{-2}) - 0.5\ (\text{mA cm}^{-2})\ )}{i(\text{mA cm}^{-2})} \times 100$$

This is represented by curve b.

It can be seen that the experimental results reflect behavior more similar to that described by curve b than by curve a. It must be emphasized that it has been consistently observed that lithium reduction in propylene

carbonate is always of the type described by curve b -- that is, the results always suggest an inherent inefficiency in the lithium reduction rather than simply the presence of impurities, interfering in a straightforward way.

Stripping current measurements have been performed in many solutions with essentially similar results. In Figure 41 are shown results obtained in a more dilute solution of lithium. This solution had not been pre-electrolyzed and the polarographically determined limiting current for species A was about 2.5 mA cm^{-2}. In these experiments cathodization was conducted at the currents indicated for one minute. The electrode was then allowed to sit in stirred solution and the open circuit potential recorded until a sharp change in potential signalled the complete chemical dissolution of lithium. The slope of the straight line in Figure 41 between 5 and 10 mA cm^{-2} yields a stripping current of 2.3 mA cm^{-2}, in close agreement with the polarographically determined limiting current for species A. These results simply confirm those previously described for more concentrated solutions of lithium salts.

3. Chemical Analysis of Lithium Electrodeposits.

The deposition of lithium has also been studied by chemical analysis. In this procedure the electrodeposited electrodes were removed from the propylene carbonate solutions and immersed in aqueous solution, whereupon it was presumed the following reaction would occur: $Li^{o} + H_2O = 1/2\ H_2 + LiOH$. It was supposed the base so released could be titrated and thus the efficiency of lithium deposition chemically determined.

In the actual experiments the six working electrode discs contained in a single lollipop electrode were connected together and current passed through all six electrodes simultaneously. Relatively large amounts of deposit were formed in order to give a subsequent accurate titer, normally 5000 to 20,000 mC cm^{-2} yielding 0.05 to 0.2 millimoles of base on reaction with water.

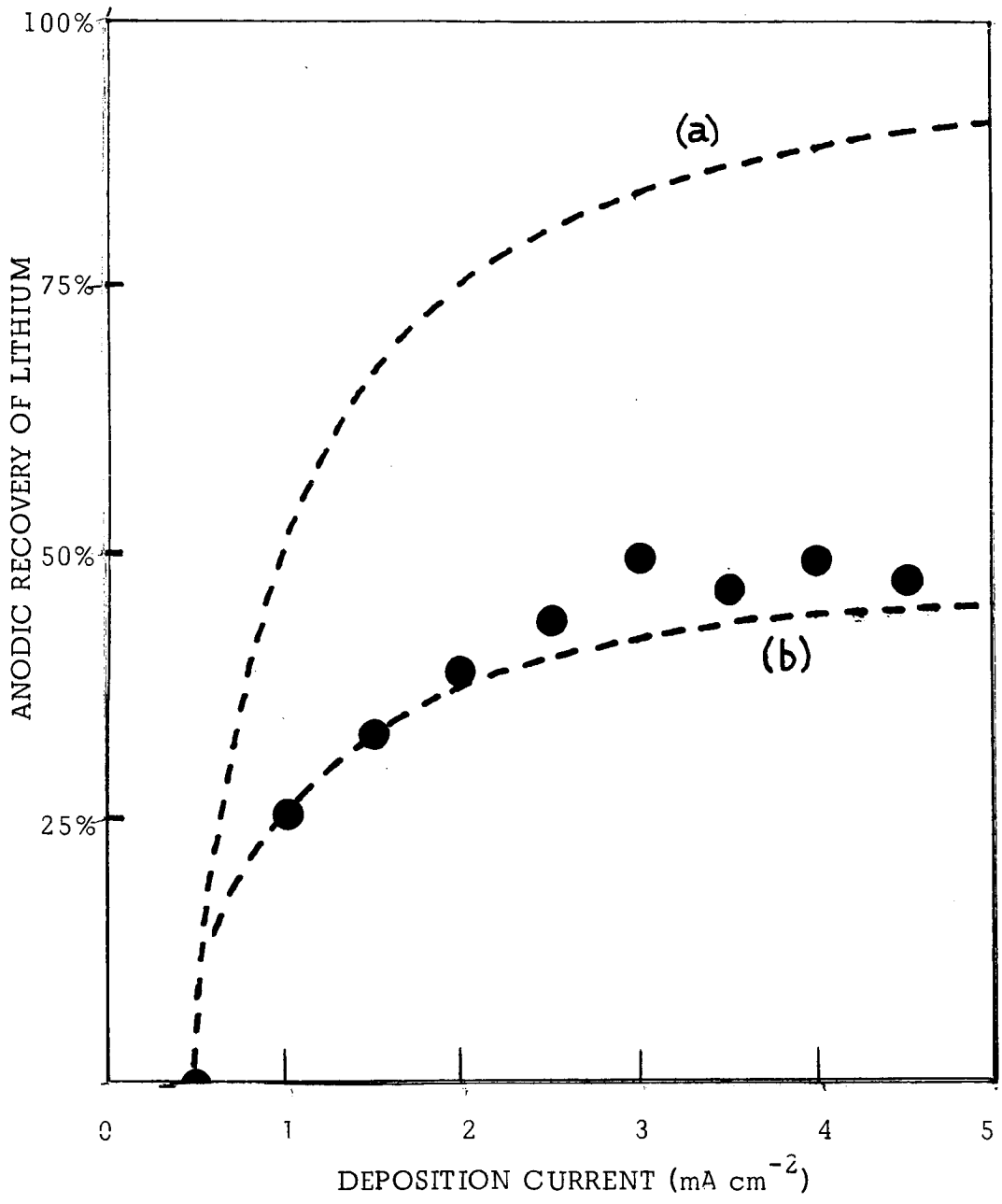

Figure 40 STIRRED REMOVAL OF ELECTRODEPOSITED LITHIUM

In propylene carbonate, 0.5 M in $AlCl_3$ and 0.35 M in LiCl. Lithium deposited on polished cobalt at current indicated for an amount of time required to give a total of 150 mC cm^{-2} of cathodization. After 30 sec. standing in stirred solution, the amount of lithium remaining on the electrode was determined by anodization at 5 mA cm^{-2}.

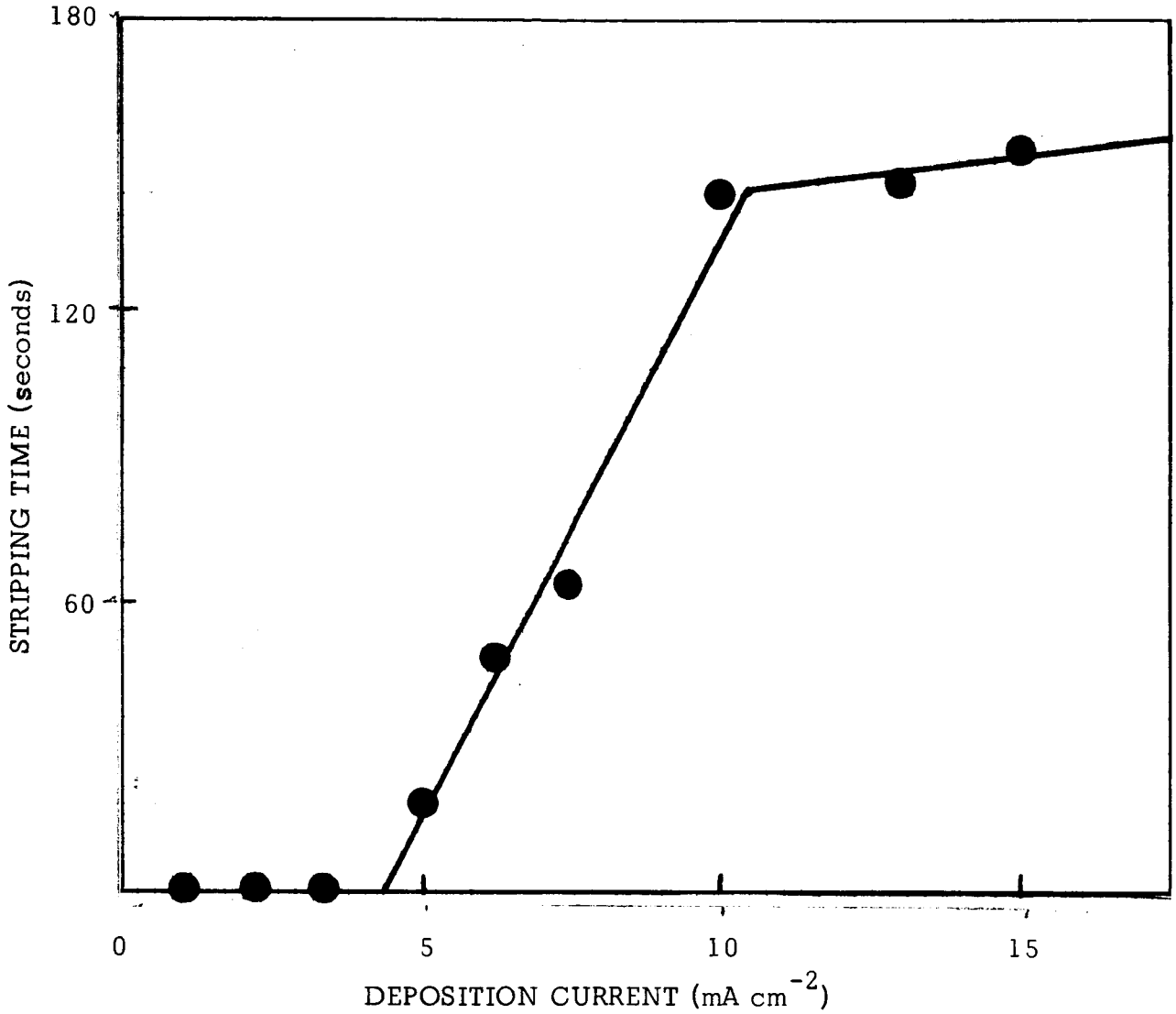

Figure 41 STIRRED REMOVAL OF ELECTRODEPOSITED LITHIUM

In propylene carbonate, 0.5 M in $AlCl_3$ and 0.08 M in LiCl. Lithium deposited on polished cobalt at current indicated for 60 sec. in stirred solution. After deposition the O.C.V. was recorded with time in stirred solution. The "stripping time" is the time elapsed after cessation of cathodization when the removal of lithium from the electrode was signalled by a sudden potential change (see figure III-9).

When the only species in the propylene carbonate solution was a lithium salt ($LiClO_4$), the deposited electrode was directly immersed in water following deposition. In solutions containing $AlCl_3$ a more involved procedure was required because of the hydrolysis of the aluminum ion. Thus, if the electrode removed from propylene carbonate solutions had on it a film of electrolyte containing $AlCl_3$ in addition to electrodeposited lithium, the following reactions would occur when the electrode was immersed in water:

$$Li^{O} + H_2O = 1/2\ H_2 + LiOH$$

$$AlCl_3 + 3\ LiOH = Al(OH)_3 + 3\ LiCl$$

and the subsequent titer would be in error because of the removal of hydroxide ions by aluminum. For this reason electrodes formed in solutions containing $AlCl_3$ were rinsed with freshly distilled propylene carbonate prior to immersion in aqueous solution. Furthermore, to prevent the hydrolysis of the aluminum ion the aqueous solution contained in excess of standard acid.

In Figure 42 are shown typical titration curves obtained when a deposited electrode had been immersed in excess standard acid and the resultant solution titrated with standard base. The solid line represents the results obtained when only lithium is present in the deposit. The dashed curve represents the results obtained when aluminum was present in the deposit. The pH plateau at about 5.5 pH units represents the reaction: $Al^{+3} + OH^{-} = Al(OH)_3$. The stoichiometry of this reaction has been established by titrations on solutions containing known amounts of aluminum. Thus the full titration curve furnishes a convenient method for analyzing for aluminum content. It should be emphasized that this is not a highly accurate procedure for aluminum analysis but was satisfactorily valid at the concentrations of species which obtained in our experiments.

In general, chemical determinations of efficiencies were unsatisfactory in $LiCl/AlCl_3$ solutions. Typical results are shown in Figure 43. The total

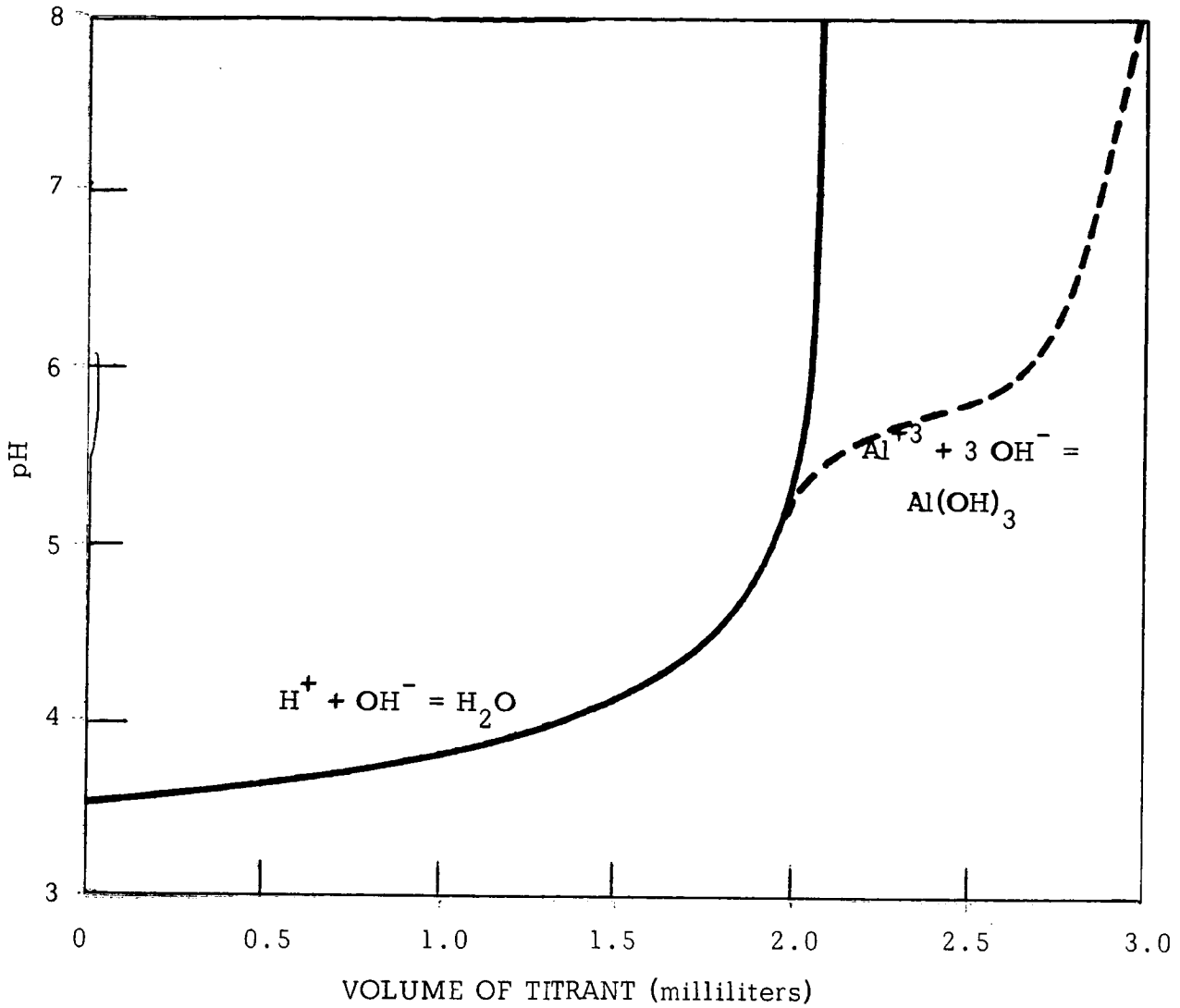

Figure 42 TITRACTION CURVE FOR DETERMINATION OF ALUMINUM IN LITHIUM ELECTRODEPOSITS.

The figure shows the effects observed in the absence of aluminum (solid line) and in the presence of aluminum (dashed line) when the electrodeposit is dissolved in an excess of standard acid and the resultant solution titrated with standard base. Normally, the total volume of solution was about 50 ml. and the normality of base, 0.05 M.

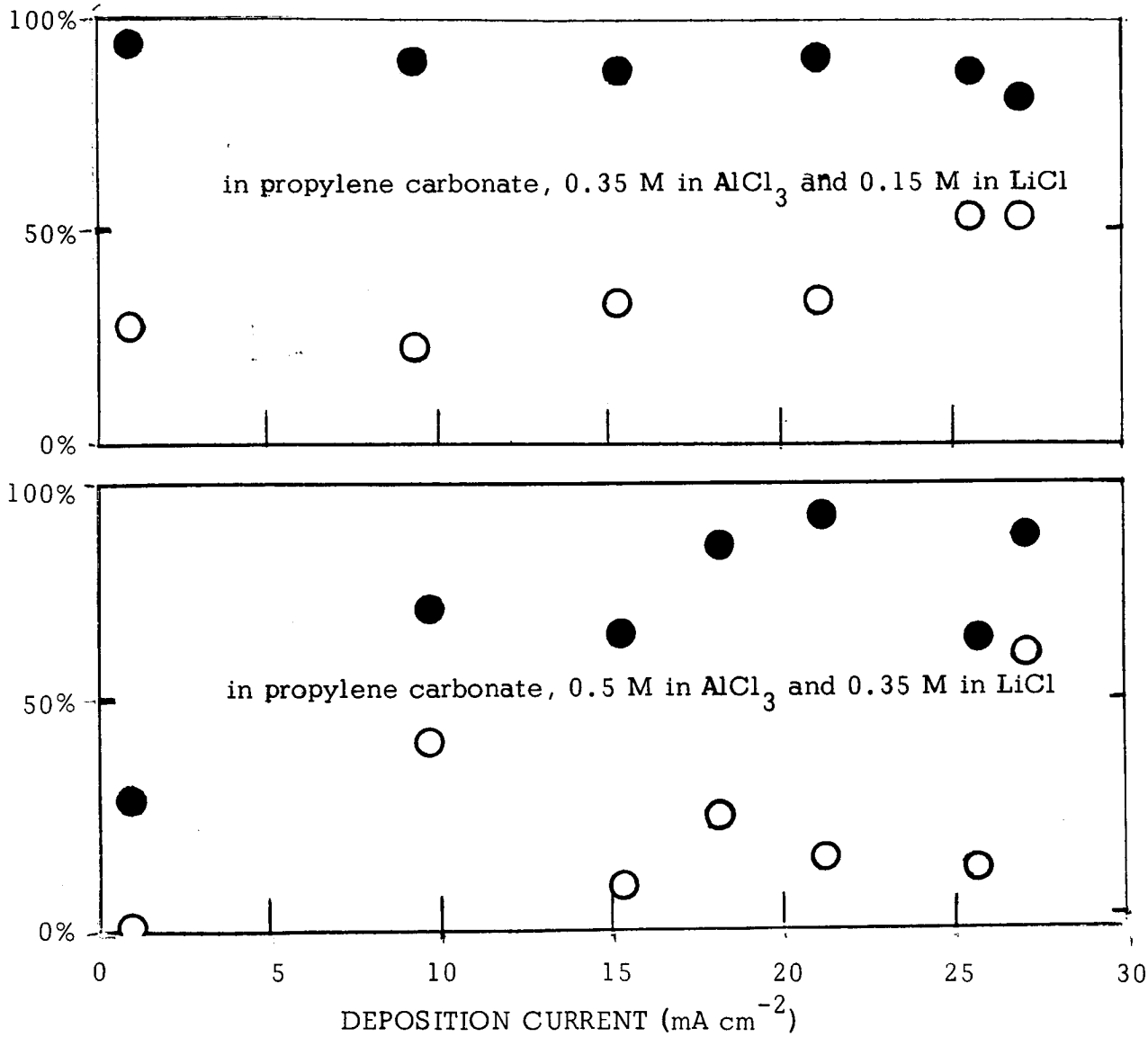

Figure 43 CHEMICAL ANALYSIS OF CATHODIC ELECTRODEPOSITS:

All depositions performed on polished silver electrodes at current indicated for an amount of time required to give a total of 8800 mC cm^{-2}, which, divided by the faraday, is 9.1×10^{-5} milliequivalents cm^{-2}. Deposits analyzed by immersion in excess standard acid and back-titration of the solution.

Solid circles: $\% = \frac{\text{milliequivalents of excess acid consumed per cm}^2}{9.1 \times 10^{-5} \text{ milliequivalents per cm}^2} \times 100$

Open circles: $\% = \frac{\text{milliequivalents of aluminum found per cm}^2}{9.1 \times 10^{-5} \text{ milliequivalents per cm}^2} \times 100$

cathodic efficiency was calculated by assuming that the acid consumed when the electrodeposited electrodes were immersed in standard acid represented the reactions:

$$Li^{O} + H^{+} = Li^{+} + 1/2\ H_2$$

$$Al^{O} + 3\ H^{+} = Al^{+3} + 3/2\ H_2$$

The equivalents of acid consumed as determined by titration to pH = 5 to pH = 7. The aluminum content shown in Figure 43 was obtained by dividing the equivalents of aluminum, found by titration, by the total equivalents of current passed during deposition.

The results shown in Figure 43 are obviously quite erratic and reflect, we believe, the tendency for fine dendritic deposits to form in chloride media which are easily dislodged from the electrode surface.

Chemical recoveries obtained following deposition in propylene carbonate solutions of $LiClO_4$ were much better and the deposits were much more adherent when formed from such electrolytes. For example, in a solution only 0.1 M in $LiClO_4$ depositions were performed at from 1.3 to 30 mA cm^{-2} and the deposits analyzed as described above. Recoveries of 100% were obtained in all cases.

The chemical determination of deposition efficiency was discontinued when it was observed that deposits of Li_2O or LiOH form on the electrodes. Such deposits consume hydrogen ions with the same equivalent stoichiometry as do the metallic deposits. Since titrimetric analysis does not distinguish between the two types of deposits, it is invalid as a means of assessing current efficiency.

4. Anodic Efficiency of Lithium.

As stated in the introduction to this section, the primary problem with the lithium electrode is the fact that anodic efficiencies are low. In Figures 44 and 45 are shown typical results obtained in $LiCl/AlCl_3$ solutions.

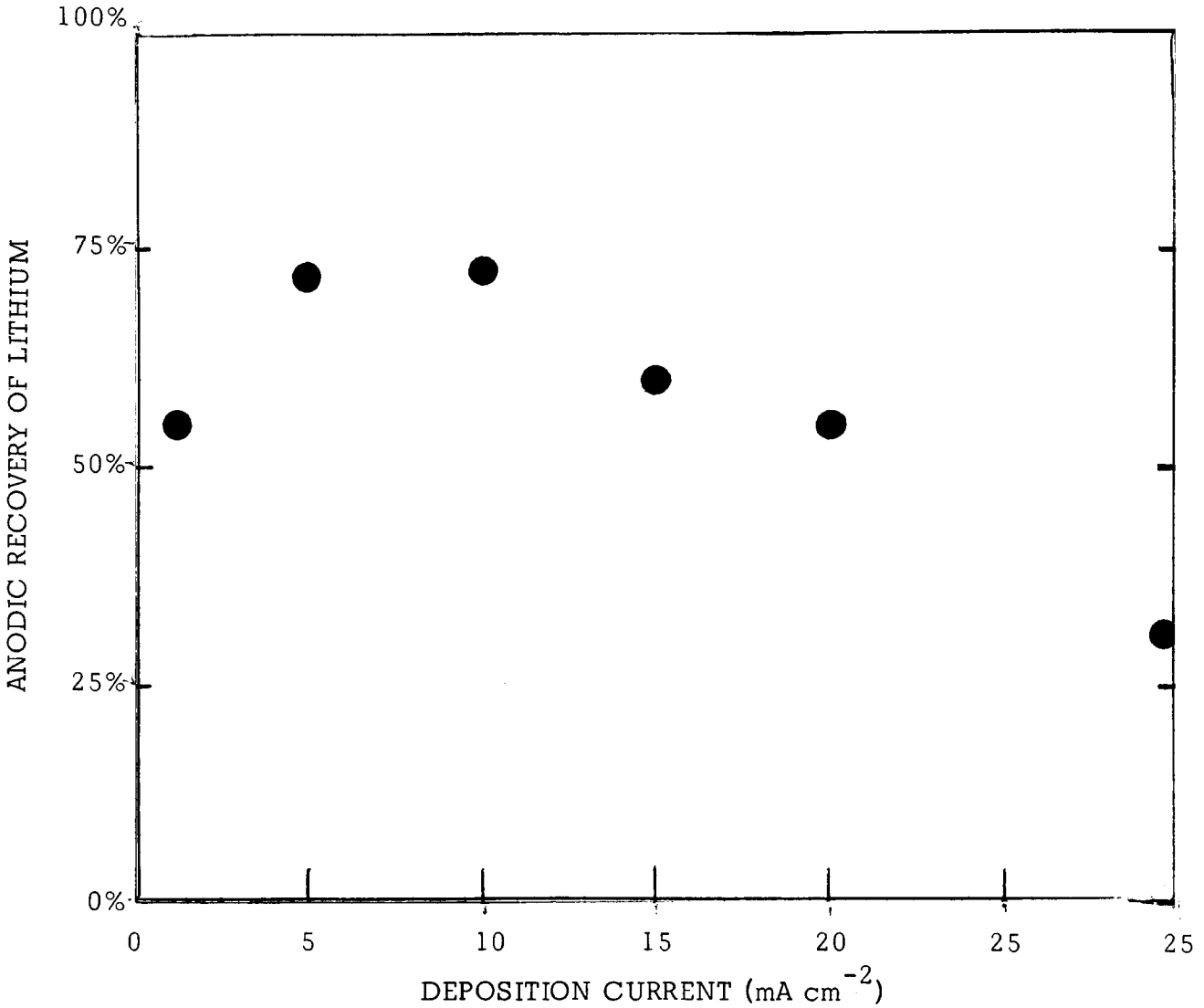

Figure 44 ANODIC RECOVERY OF ELECTRODEPOSITED LITHIUM

In propylene carbonate, 0.9 M in $AlCl_3$ and 0.5 M in LiCl. Deposition performed on polished silver electrodes for an amount of time required to give a total of 150 mC cm^{-2} of cathodization. Anodic recovery determined at 5 mA cm^{-2}.

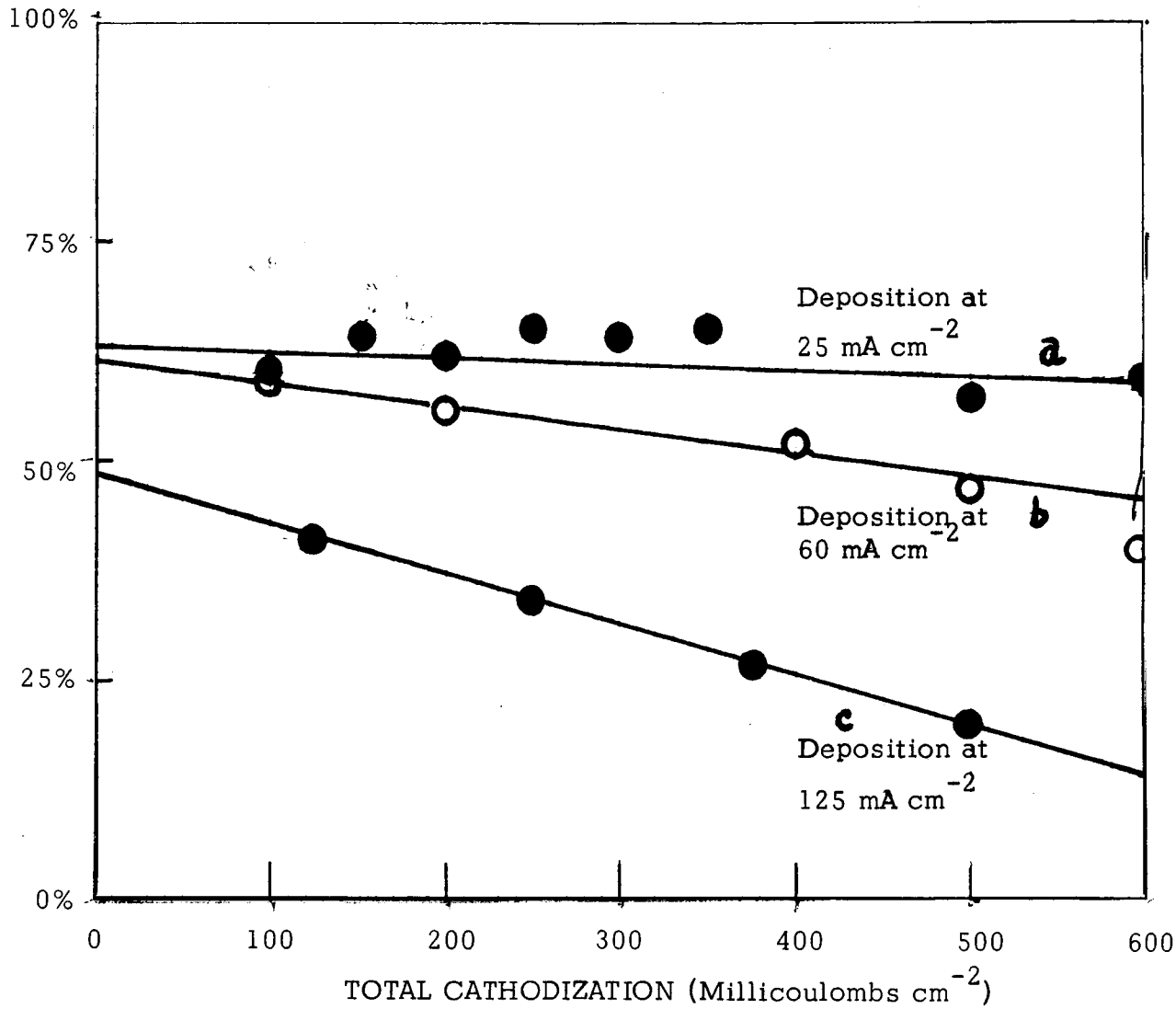

Figure 45 ANODIC RECOVERY OF ELECTRODEPOSITED LITHIUM

In propylene carbonate, 0.9 M in $AlCl_3$ and 0.8 M in LiCl. Depositions performed on polished silver electrodes at current indicated and for an amount of time required to give the total cathodization indicated. Subsequent anodic recovery of lithium determined at 5 mA cm^{-2}.

In Figure 46 are shown results typical of those obtained in $LiClO_4$ solutions. The general pattern of behavior displayed in Figures 44, 45, and 46 was consistently observed and the following facts are important:

a. Anodic efficiency is not a sensitive function of the conditions of anodization. When electrodeposition is conducted under constant conditions subsequent anodic recovery of lithium metal may be determined by oxidation at constant current or at constant potential. On constant current anodization the potential of the working electrode remains quite constant at some value positive to the lithium open circuit potential by an amount dependent on the current (iR drop). Completion of anodization is marked by a sudden jump in potential to values +3 to +4 volts positive to the lithium open circuit potential. The efficiency is determined by the product of the current and the time elapsed before this potential jump is observed. Efficiencies do not significantly vary with the current of anodization. Potentiostatic anodizations are performed by holding the potential of the working electrode positive to that of the lithium open circuit potential. Anodic currents were observed and continuously recorded. The magnitude of the current was dependent on the preset potential since the potentiostat "sees" iR drop as well as the potential across the double layer. The currents observed on potentiostatic anodization remain quite constant until a sharp decay in current to negligible values signaled the complete anodization of lithium. Integration of the current-time curves yields anodic efficiencies. Anodic efficiencies do not vary significantly with the potential at which anodization is conducted.

b. We believe the independence of anodic efficiency with anodic currents suggests inherent anodic efficiency is 100% with respect to the degree to which metallic lithium can be anodically oxidized. However, in this report we consider anodic efficiency in the sense that it reflects the degree to which the total cathodic current passed can be recovered on subsequent anodization. Thus, an anodic efficiency of 50%

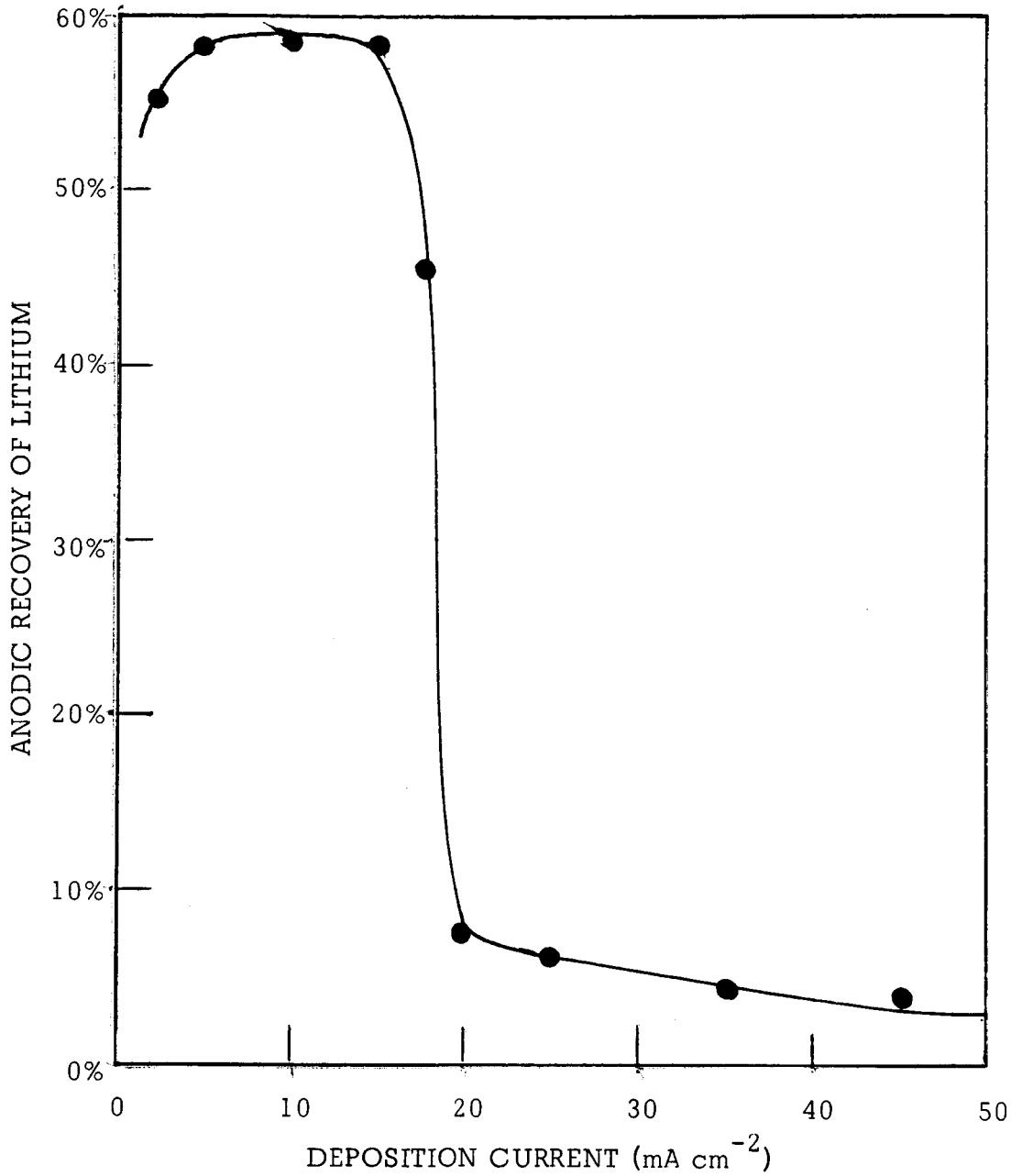

Figure 46 ANODIC RECOVERY OF ELECTRODEPOSITED LITHIUM In propylene carbonate, 0.1 M in $LiClO_4$. Deposition performed on polished copper electrodes at current indicated for an amount of time required to give a total of 1000 mC cm^{-2} of cathodization. Subsequent anodic recovery was done potentiostatically by anodizing the electrode at -2.0 V vs. the silver disc R.E., recording the resultant anodic current, and integrating to give the total millicoulombs recovered.

means that if a total of 1000 mC cm^{-2} of cathodic current were passed, only 500 mC cm^{-2} could be recovered on subsequent anodization. The evidence to date indicates that anodic efficiency in this sense actually reflects efficiency of the preceding cathodic process.

c. Constant values of anodic efficiency are normally obtained over a range of cathodic deposition currents. As seen in Figure 46, at sufficiently high currents approximating the expected limiting current for the lithium ion there results a sharp decrease in anodic efficiency.

d. Anodic efficiency is not a sensitive function of the concentration of lithium salt. Maximum anodic efficiencies of 70% were obtained in 0.1 M $LiClO_4$ as well as in 1 M $LiClO_4$.

e. As previously discussed, anodic efficiencies are not direct functions of the evident concentration of species A.

f. Anodic efficiency decreases with increasing total coulombs of cathodization.

5. Effect of Water on the Behavior of the Lithium Electrode.

Experiments were performed in which water was deliberately added to solutions of $LiClO_4$ and the effect of water assessed by an examination of the chronopotentiometry for lithium reduction, and by electrochemical and chemical analysis of the resultant deposits.

In Figure 47 are shown typical results obtained when water is added to a solution of propylene carbonate, 0.2 M in $LiClO_4$. The solid line represents the chronopotentiogram obtained before the addition of water. The dotted line represents the chronopotentiogram obtained after the solution had been made 0.42 M in water. Intermediate concentrations of water yielded chronopotentiograms intermediate in appearance between the two shown in Figure 47. In the solution to which water had not been added a transition time of about 18 seconds is observed, as shown in Figure 47. This yielded a value

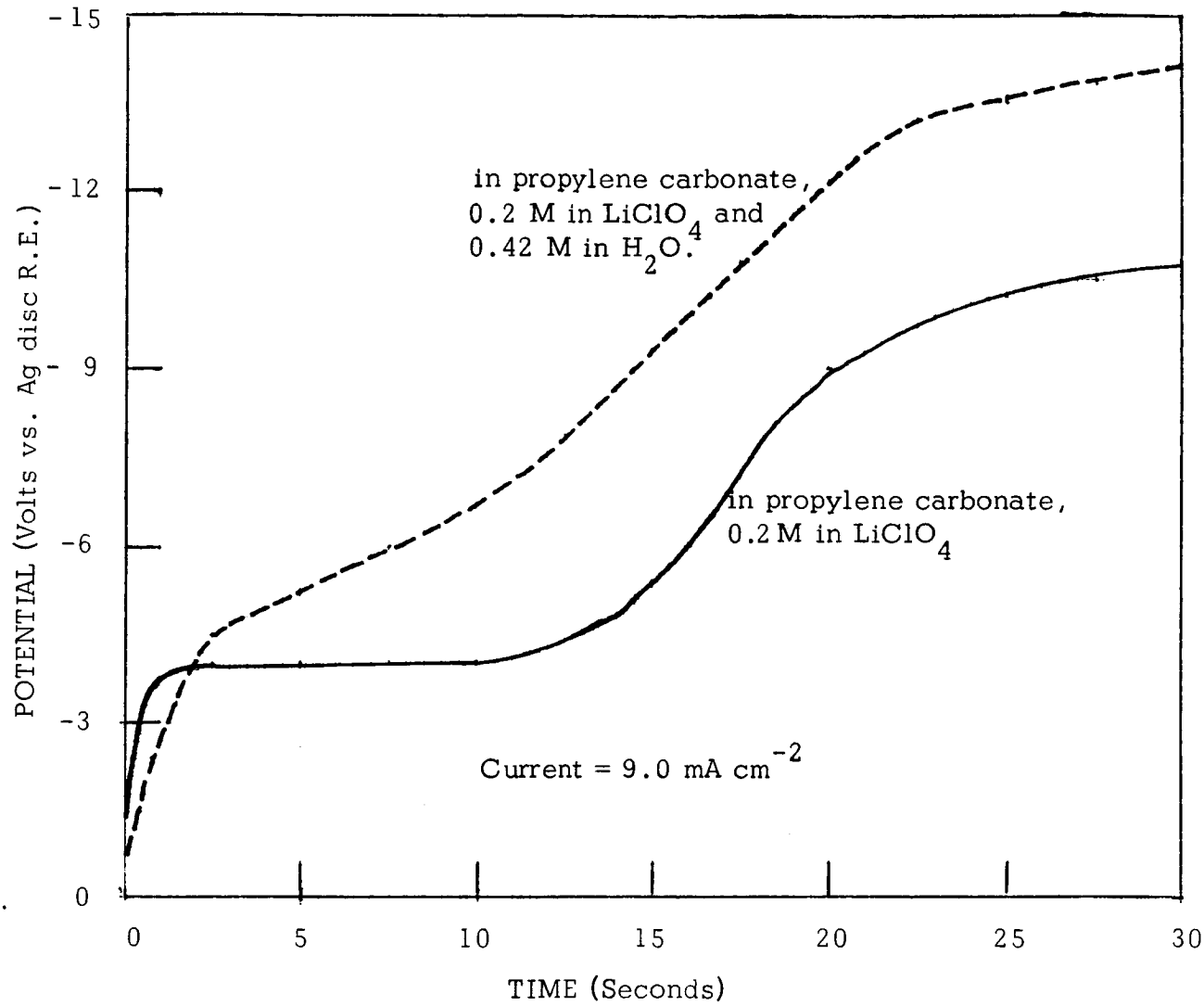

Figure 47 CATHODIC CHRONOPOTENTIOMETRY OF LITHIUM (EFFECT OF WATER)

Cathodizations performed on polished copper electrodes.

for $iT^{1/2}/C$(of $LiClO_4$) of about 210 mA cm $sec^{1/2}$ mM^{-1}, which is the value found for all lithium salt solutions. If water were capable of undergoing reduction before lithium and if the mobility of water were the same as for the lithium species a 0.42 M water solution should give an $iT^{1/2}$ of about 175 (assuming a two-electron reduction to H_2). At 9 mA cm^{-2} this should give a transition time of about 380 seconds. The results shown in Figure 47 give no indication of the reduction of water at potentials positive to that for lithium reduction. It will also be observed that, although the dashed line chronopotentiogram is quite ill-defined, an approximate transition time, not markedly different from that obtained in the absence of water, is observed.

In Table 9 are shown the complete results obtained in this series of measurements. Following each addition of water cathodic chronopotentiometry was performed to determine the $iT^{1/2}$ given in the table. Finally depositions were conducted at 5 mA cm^{-2} for 30 seconds and anodic efficiency was determined by reversing the current and measuring the time required for complete oxidation of lithium.

Table 9

Effect of Water on the Anodic Efficiency of Lithium

Total Conc. of water added ($M\ l^{-1}$)	$iT^{1/2}$ ($mA\ cm^{-2}\ sec^{1/2}$)	Anodic Efficiency (%)
0.00	35	50
0.01	33	45
0.02	--	43
0.04	35	42
0.08	33	32
0.12	33	33
0.22	ill-defined	27
0.32	"	22
0.42	"	18
0.51	"	8
0.61	"	5
0.86	"	negligible

Further experiments were performed in propylene carbonate, 0.2 M in $LiClO_4$, in which prolonged depositions were conducted following each addition of water and the deposits chemically analyzed as discussed in the preceding section. The limiting current for lithium should be about 20 to 40 mA cm^{-2} in stirred solution. Depositions were conducted at currents considerably larger than this -- at 60, 120, and 180 mA cm^{-2}. Cathodization was continued for such time as to yield a total of 15,000 mC cm^{-2} of total current. At such high currents the efficiency for lithium deposition should be small -- indeed, vigorous gassing occurred. However, black, adherent deposits formed on the electrodes. These deposits were directly immersed in water and the amount of base released titrated. Negligible gas evolution occurred when the electrodes were immersed in water. Most surprisingly, it was found that the equivalents of base found in the aqueous solution was exactly equal to the total equivalents of current which had passed in the preceding cathodization. Furthermore the shape of the titration curves demonstrated that the basic constituent was a strong base rather than a weak base such as carbonate. The only cation in solution being the lithium ion it was concluded that the deposit consisted of Li_2O or LiOH. Such experiments were performed in solutions varying all the way up to 0.8 M in water. The results were the same. During deposition the potential varied with time as shown in Figure 48. This behavior is characteristic of processes involving the formation of poorly conductive films.

It may be presumed that water is strongly complexed with lithium ion, and in this state its reduction is not kinetically favored over that of lithium, but that both processes are intimately related and occur simultaneously, the products being lithium metal, lithium oxide or hydroxide and hydrogen by the reactions:

$$Li^+ + e^- = Li^o$$

$$Li^+ + H_2O + e^- = LiOH + 1/2\ H_2$$

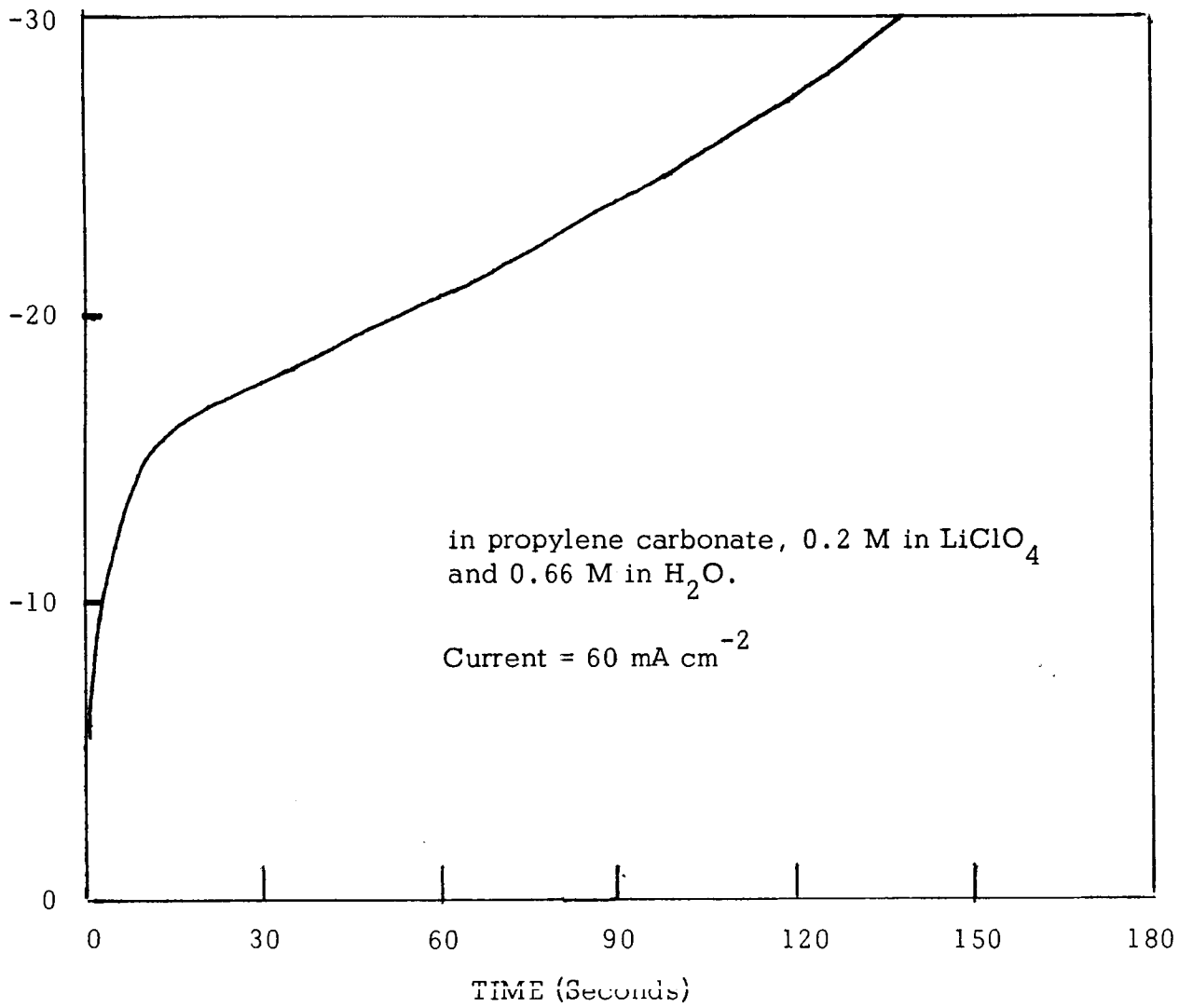

Figure 48 CATHODIC CHRONOPOTENTIOMETRY OF LITHIUM (EFFECT OF WATER)

Cathodization performed on polished copper electrode.

Since the addition of water appears to result in the codeposition of lithium and lithium oxide or hydroxide, it may be expected that better performance would be obtained following the addition of material expected to more strongly bind the water than does the lithium ion. Since $AlCl_3$ is expected to behave in this fashion, experiments were performed in which water was added to a solution of propylene carbonate, 0.4 M in $AlCl_3$ and 0.35 M in LiCl. Following the addition of water chronopotentiograms were run at sufficiently low currents as to give a transition time for the reduction of species A. Anodic efficiencies were also determined by cathodizing the electrode in stirred solution at 20 mA cm^{-2} for 20 seconds followed by immediate current reversal. The results are shown in Table 10 below.

Table 10

Effect of Water on the Concentration of Species

Concentration of added water ($M\ l^{-1}$)	$iT^{1/2}$ for Species A ($mA\ cm^{-2}\ sec^{1/2}$)	Anodic Efficiency (%)
0.00	5.0	68
0.05	5.0	50
0.10	5.7	50
0.15	6.3	40
0.25	6.8	28
0.35	7.2	26
0.50	7.6	23
0.65	8.3	21
0.8	9.0	21
1.0	9.3	negligible

In going from 0 to 1 M l^{-1} of water, $iT^{1/2}$ for species A increases by only 4.3 units. A 1 M solution of material with the same mobility undergoing a one-electron reduction should have an $iT^{1/2}$ of about 200. Clearly, species

A is not water. It will also be observed that the decrease in anodic efficiency with increasing amount of water is somewhat less than described in Table 10 but not so marked as to indicate that $AlCl_3$ is an effective dehydrating agent in solution.

6. Pre-purification of Electrolytes.

In an earlier section the presence of deleterious impurities comprising species A was discussed. Initial attempts at removing this material consisted of prolonged electrolysis. Reference is made to the cathodic polarogram shown in Figure 31. It is clear that if reduction is imposed at potentials along the limiting current plateau (-1.8 to -3 V) for extended periods of time, the reducible material should, in time, be completely removed from the solution. In the procedure normally employed a copper coil with a total surface area of about 100 cm^2 was immersed in 200 ml. of the solution to be pre-electrolyzed. (Note: It is necessary to have solute present for successful pre-electrolysis to provide conductivity.) The Wenking Potentiostatic was used to hold the potential of this copper coil electrode at -2.5 V versus a silver disc in the same solution. Electrolysis was normally continued overnight in stirred solution with constant deaeration with argon. In figure 49 is shown a plot of the natural logarithm of the measured total current (not current density) versus the elapsed time of electrolysis. After pre-electrolysis the polarographic limiting currents for species A of course decreased. More important is the effect of the pre-electrolysis on the anodic efficiency of lithium. In Table 11 are shown results obtained in propylene carbonate, 0.4 M in $AlCl_3$ and 0.35 M in LiCl. Anodic efficiencies were determined by performing cathodizations at the current indicated for 20 seconds, followed by immediate current reversal. The solution was then electrolyzed potentiostatically overnight, following which $iT^{1/2}$ for species A had diminished from about 7.5 mA cm^{-2} $sec^{1/2}$ to 3.4 mA cm^{-2} $sec^{1/2}$. Anodic efficiencies were again determined under the same conditions described above.

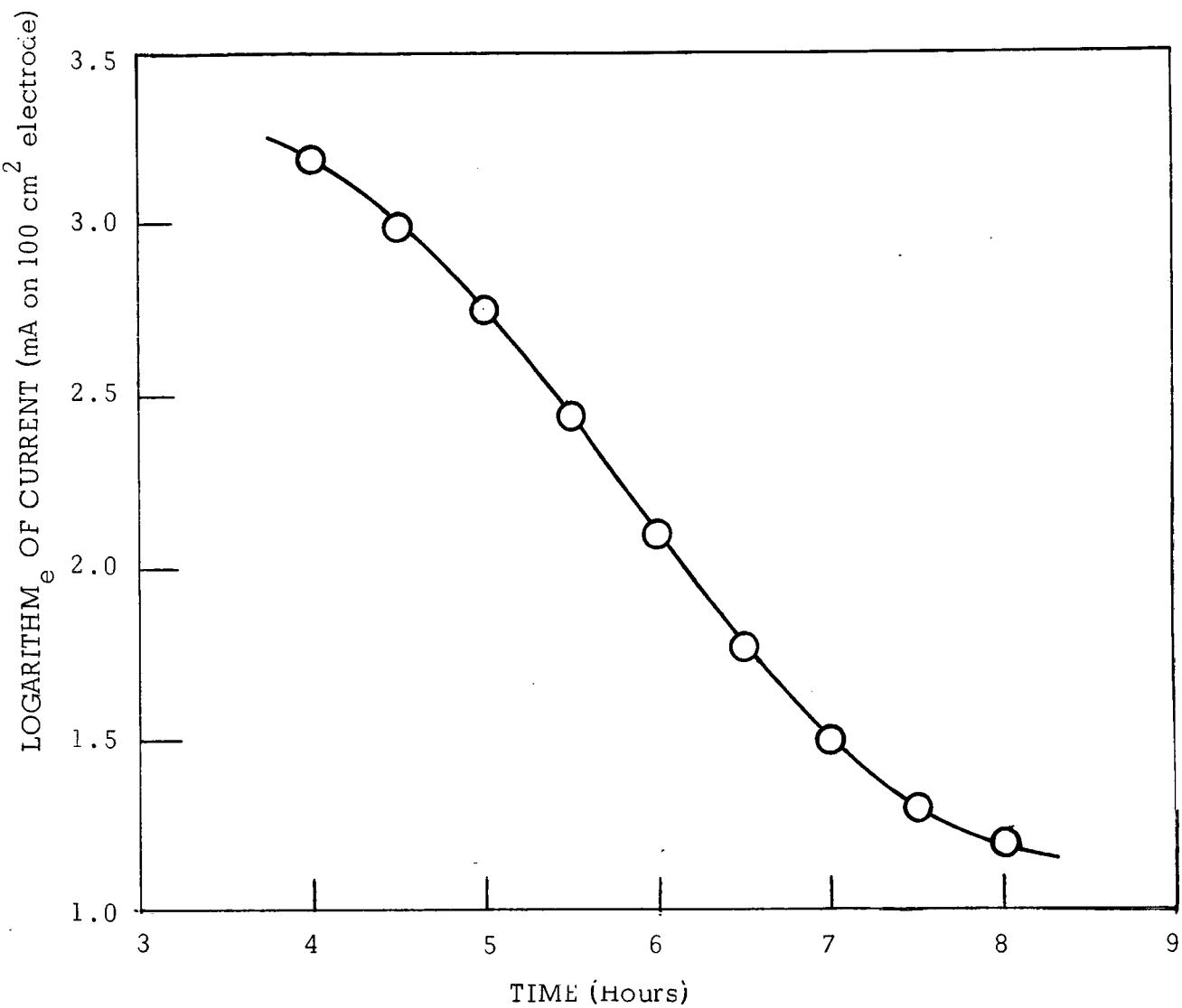

Figure 49 PRE-ELECTROLYTIC PURIFICATION

In propylene carbonate, 0.225 M in $AlCl_3$ and 0.2 M in LiCl. Electrolysis conducted on 100 cm^2 copper coil potentiostatically, at -2.5 V vs. silver disc R.E. in same solution.

Table 11

Effect of Pre-electrolysis on Lithium Anodic Efficiency

Current of electrolysis ($mA\ cm^{-2}$)	Total current passed on cathodization ($mC\ cm^{-2}$)	Anodic efficiency without pre-electrolysis (%)	Anodic efficiency after pre-electrolysis (%)
1.25	25	None	5
5	100	None	40
10	200	None	50
15	300	25	65
20	400	27	68
25	500	40	70
30	600	50	73
35	700	50	78
40	800	40	negligible

The same solution was subjected to further pre-electrolysis overnight but no further improvement was observed either in a significant diminution of $iT^{1/2}$ for species A or increased anodic efficiency. In general it is found that ultimate limitations exist to the efficacy of pre-electrolysis and prolonged pre-electrolysis over a weekend, for example, is no better than overnight pre-electrolysis.

It should be noted that the rate at which material diffuses through the sintered glass disc separating the counter and working electrode compartments is quite low. To insure that the limitations to pre-electrolytic efficacy did not arise from so simple a cause as diffusion of counter-electrode compartment contaminants into the working electrode compartment, the counter electrode compartment was routinely flushed and replaced with fresh solution several times during the course of pre-electrolysis.

In Section II-B, describing the experimental procedures followed in our work, an auxiliary method for the synthesis of propylene carbonate solutions was described. It will again be noted that such solutions exhibited characteristics essentially identical to those of pre-electrolyzed solutions. The deep reddish-brown color characteristic of impure propylene carbonate solutions of $AlCl_3$ slowly appeared with time in both the pre-electrolyzed solutions and the solutions prepared by the more involved synthetic procedure referred to. The rate at which discoloration occurred was of the order of weeks but the phenomenon was not investigated in detail.

Pre-electrolysis was possible only in solutions containing $AlCl_3$. In other solutions the current rapidly decayed to negligible values. A different procedure for pre-electrolysis of $LiClO_4$ solutions in propylene carbonate was employed. A one-liter, four-necked round-bottom flask was filled with 200 ml. of 0.1 M $LiClO_4$ solutions (equivalent to 2×10^6 millicoulombs). A copper coil of 100 cm^2 area was used as the cathode and a lithium sheet electrode was used as the anode. Under these conditions it was presumed that any impurities removed by reduction at the cathode would be replaced by lithium ions formed at the anode. Very high currents were used (100 mA total) and lithium was observed to deposit on the copper anode. The results of anodic efficiency measurements after pre-electrolysis are shown in Figure 50. It will be noted that after electrolysis at 100 mA for 7238 sec. the total current passed during pre-electrolysis (0.7×10^6 mC) is about one-third the equivalents of lithium perchlorate initially present. Such results indicate that the problems presented by the lithium electrode are not so easily solved by electrolytic pre-treatment.

Although the auxiliary electrolysis studies described by the results shown in Figure 50 essentially eliminated water as the perpetrator of background currents there still existed the possibility that other chemical species might be present in propylene carbonate such as propylene oxide and propylene glycol which could account for the observed phenomena. It was therefore important to determine lithium anodization efficiencies in a solvent other than

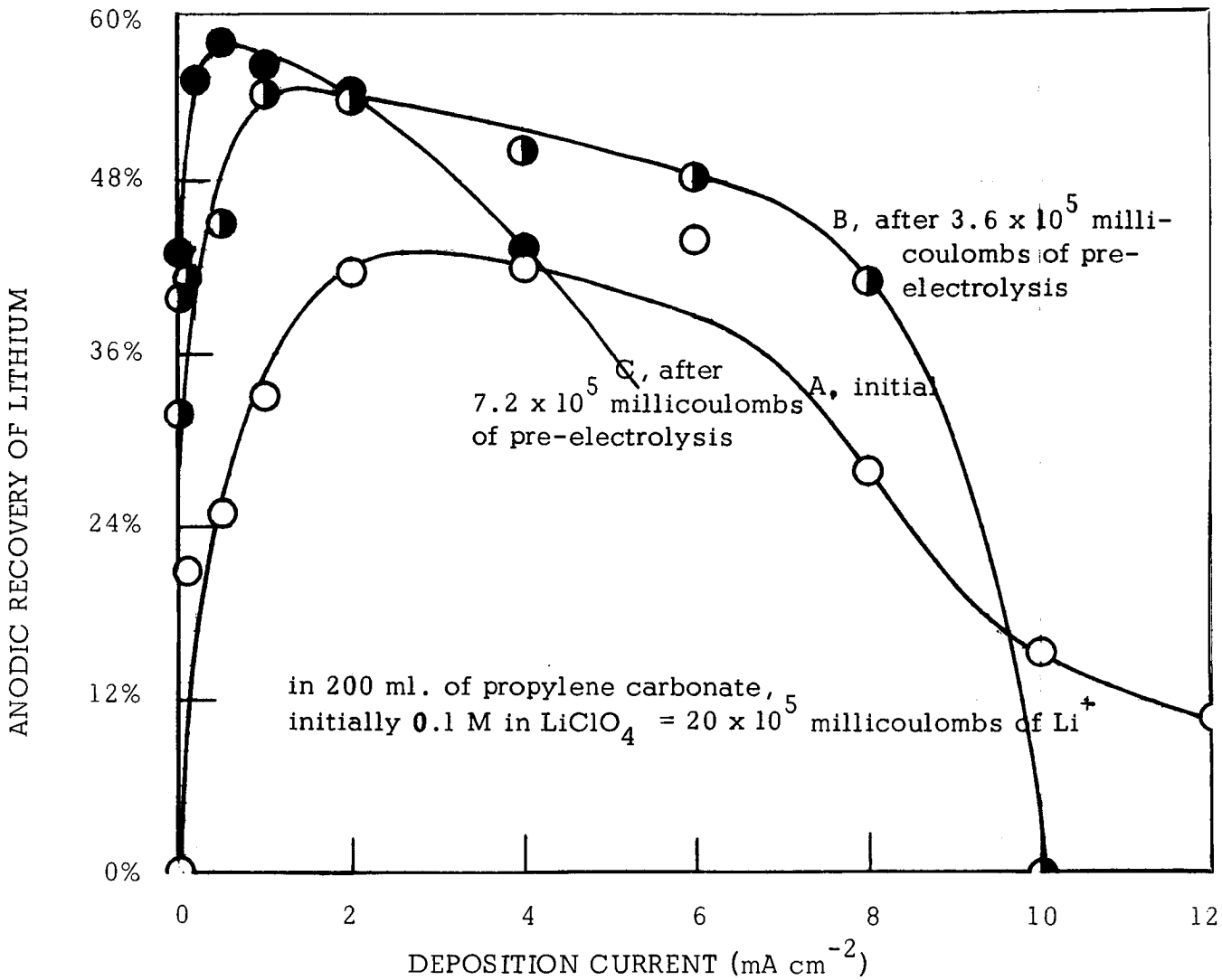

Figure 50 PRE-ELECTROLYTIC PURIFICATION

Anodic recovery determined on polished copper electrodes at current indicated for an amount of time required to give a total of 100 mC cm^{-2} of cathodization. Subsequent anodic recovery determined at same current as preceding cathodization.

propylene carbonate. Tetrahydrofuran was selected for this purpose after preliminary tests indicated that lithium perchlorate is sufficiently soluble in it to prepare solutions of the required concentration.

A chronopotentiometric examination of a 0.1 M solution of $LiClO_4$ in tetrahydrofuran was made. Background reduction, analogous to that for species A in propylene carbonate, was observed at low currents with an $iT^{1/2}$ of about 0.28 mA cm^{-2} $sec^{1/2}$. Reanodization efficiencies for lithium were then determined with the results shown in Table 12.

Table 12

Anodization Efficiency of Lithium in Tetrahydrofuran

Current of cathodization ($mA\ cm^{-2}$)	Total Current passed during cathodization ($mC\ cm^{-2}$)	Current of Anodization ($mA\ cm^{-2}$)	Efficiency (%)
5	30	5	36
5	60	5	34
5	60	2.5	35
5	60	10	37
5	60	20	46
10	60	10	42
10	120	2.5	32
10	120	20	55
15	90	15	31
15	180	20	54
20	120	20	42
25	150	25	37

E. Summary and Conclusions.

Chronopotentiometry and polarography have been extensively employed in the investigation of a number of propylene carbonate solutions. The results demonstrate the usefulness of such techniques even though the con-

ditions under which they are used are not the conditions which must prevail for rigorous interpretation of the results in classical fashion. The results provide useful information regarding the impurity levels and the effects of impurities and give a clear qualitative picture of the behavior of the lithium electrode.

It has not been demonstrated that the lithium electrode is unsatisfactory; it has been demonstrated that the behavior of the lithium electrode is critically sensitive to impurities. It has been demonstrated that conventional methods of purification, in particular vacuum distillation, are not sufficient in themselves. It has been further demonstrated that water alone is not the only deleterious impurity and that, if present, it does not behave in a simple fashion as though it were only a carrier of active hydrogen.

The characterization of unknown systems with respect to their eventual incorporation in secondary cells is not easy. As a result of our intensive studies into but a few systems we are convinced that adequate characterization is best made by the simplest possible basic techniques and that data obtained in the absence of such characterization is totally inadequate in providing a preliminary assessment of the utility of any given system.

IV. Organoberyllium Complex Salt Electrolytes

A. Introduction

It was apparent during our initial literature survey pertaining to non-aqueous battery systems that the low conductivities reported for various salt/organic solvent combinations of interest could present a serious problem in the construction of practical cells. Although internal resistance losses can be minimized by proper design and engineering of electrode and separator structures, the potential value of a non-aqueous electrolyte system possessing exceptionally high conductivities was readily apparent. The highest specific conductivities for organic electrolytes reported in previous investigations[1] were in the range of 10^{-3} to 10^{-2} ohm^{-1} cm^{-1}, whereas a typical aqueous system -- 35% sulfuric acid -- has a value of 7×10^{-1} ohm^{-1} cm^{-1} and a typical fused salt -- liquid potassium nitrate -- has a value of 6.8×10^{-1} ohm^{-1} cm^{-1}.

Although fused salt mixtures afford the highest ionic conductivities that can be achieved, the high operating temperatures associated with such systems severely limits their consideration for portable secondary batteries. It is known, however, that certain organic-inorganic salt mixtures form eutectics which are liquid at room temperature -- for example the ethyl pyridinium bromide/aluminum chloride electroplating baths -- and furthermore that these eutectics form at stoichiometric ratios where chemical complexes are formed by ion transfer reactions. The idea was therefore conceived of attempting to "design" a non-aqueous electrolyte that would be a liquid at or very near room temperature and, in addition, would possess the high specific conductivities normally associated with fused salts.

Our acquaintance with the literature indicated that one of the most likely candidates to fulfill these requirements was the complex salt formed between an alkali metal halide and a dialkyl or diaryl beryllium compound. A comprehensive study of the preparation and characterization of such salts was reported by Strohmeier[2], [3] who found that the melting points of the

potassium cyanide, rubidium fluoride, and cesium fluoride salts when complexed with beryllium dialkyl or diaryl compounds were 52°, 61° and 29° respectively, and that the tetraethyl ammonium chloride salt was a viscous, clear liquid. These materials were also reported[4] to possess conductivities approaching those of conventional fused salt baths.

It was considered that increasing the size of the alkyl groups attached to beryllium would lower the melting points of subsequently prepared complex salts and reduce their sensitivity to oxidation. Consequently, a program was initiated and carried out which consisted of the following three areas of effort: (1) The preparation of a series of dialkylberyllium compounds with increasingly large organic groups. The compounds selected were dimethyl, diethyl, di-n-propyl, di-isopropyl, dibutyl, and diphenyl beryllium. (2) The attempted preparation of complex salts of the above beryllium compounds with selected halides or pseudohalides such as sodium fluoride, cesium fluoride, potassium cyanide, beryllium chloride, and tetraethylammonium chloride. (3) The measurement of melting points and specific conductivities of complex salts successfully prepared followed by compatability and electrochemical studies of any that looked promising.

B. Synthesis of Dialkyl and Diaryl Beryllium Compounds

1. Discussion

Although the preparation of beryllium dialkyls is reported as early as 1860 by Cahours[5], much of this early work has been discredited by the later investigations of Gilman[6], [7] around 1927, whose preparations differed in many physical properties from those of Cahours. Beryllium diaryls can also be prepared by the procedure of Ramsden[8] from beryllium chloride and arylmagnesium chloride in tetrahydrofuran. The best method for the synthesis of diethylberyllium and the one used in this work is due to Goubeau[9], who employed ethylmagnesium bromide and beryllium chloride in ethyl ether.

2. Experimental Techniques

a. Dimethylberyllium

Dimethylberyllium was prepared using the procedure and apparatus recommended by Gilman[6]. Anhydrous beryllium chloride was prepared first by dissolving the appropriate quantity of flake beryllium metal in ethyl ether saturated with a continuously flowing stream of dry hydrogen chloride admitted through a fritted bubbler. Simultaneously, a solution of methyl magnesium iodide was prepared in the three-necked flask part of the special apparatus shown in Figure 51. The ether solution of beryllium chloride was degassed with nitrogen under vacuum to remove excess hydrogen chloride and added dropwise to the Grignard reagent with stirring. The mixture was then refluxed at 200° and continuously cycled through the apparatus for twenty-four hours in order to accumulate the volatile dimethylberyllium etherate in the receiving flask. The contents of the receiving flask were then forced into the storage flask with nitrogen pressure. The entire operation was carried out under a dry nitrogen atmosphere. The product was obtained as the ethereal solution which was used directly in this work. If the pure dimethylberyllium is desired it can be obtained by careful heating of the distillate to expel ether, followed by sublimation of the white crystalline product. Using this procedure, 50% yields of dimethylberyllium were obtained.

b. Diethylberyllium

The ether solution of beryllium chloride was prepared as described above. Tetrahydrofuran was then added to the solution whereupon the beryllium chloride tetrahydrofuranate precipitated and the ether was distilled off. The precipitate was then placed in a 2-liter, 3-necked round bottom flask along with a calculated amount of magnesium metal turnings and the mixture covered with tetrahydrofuran. The flask was equipped with a sealed magnetic "Lew" stirrer, a reflux condenser, and an addition funnel and the entire assembly was flamed out under dry nitrogen before each run.

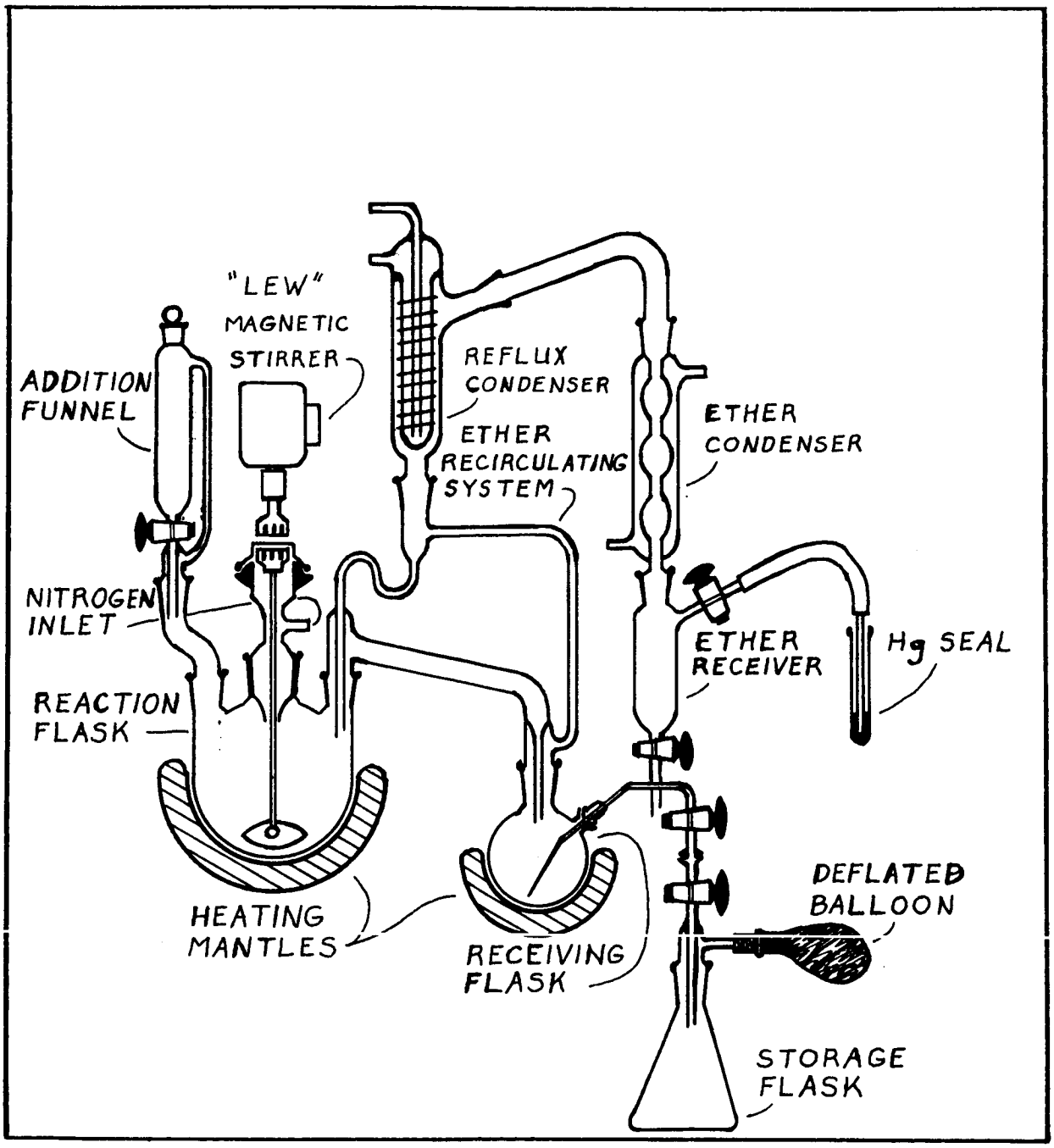

Figure 51 APPARATUS FOR SYNTHESIS OF DIMETHYLBERYLLIUM

A tetrahydrofuran solution containing the calculated stoichiometric amount of the desired alkyl bromide was then added dropwise with stirring. The beryllium chloride reacted with the Grignard reagent as rapidly as it formed giving the desired dialkylberyllium compound. The mixture was refluxed for about 24 hours and then forced with nitrogen pressure through a fritted glass filter stuck into a distilling flask. The residual magnesium salts were washed several times with fresh tetrahydrofuran, filtered, and the filtrates combined with the solution in the distilling flask. Vacuum distillation was then carried out in the apparatus shown in Figure 52 using nitrogen bleed. After removing the excess tetrahydrofuran, the dialkylberyllium was distilled at 2-5 mm of mercury. Due to the soluble magnesium salts carried over during filtration, the distilling temperatures required were quite high -- sometimes to the softening point of the flask. In spite of great care, spontaneous decomposition sometimes occurred with concurrent rapid pressure rise which separated the joints in the apparatus. It was therefore found necessary to employ a specially constructed, high velocity hood on the distillation rack to draw off the beryllium oxide smoke formed in such cases. The dialkylberyllium obtained in this way was always accompanied by some solvent and the solution was used directly as obtained. A second distillation was found to be almost impossible to carry out due to uncontrollable foaming and consequent contamination of the distillate.

The procedure for the preparation of diphenylberyllium was essentially the same as that for diethylberyllium except that the vacuum distillation step was omitted, since the product decomposes rather than distills.

It should be noted that the procedure herein described differs from that of Goubeau[9] in that we prepare the Grignard reagent directly in the presence of beryllium chloride tetrahydrofuranate rather than in a separate step. This not only eliminates one time-consuming operation, but also minimizes transfer and consequent risk of exposure to air. The yields by either technique are comparable -- about 70-80% based on the beryllium chloride used.

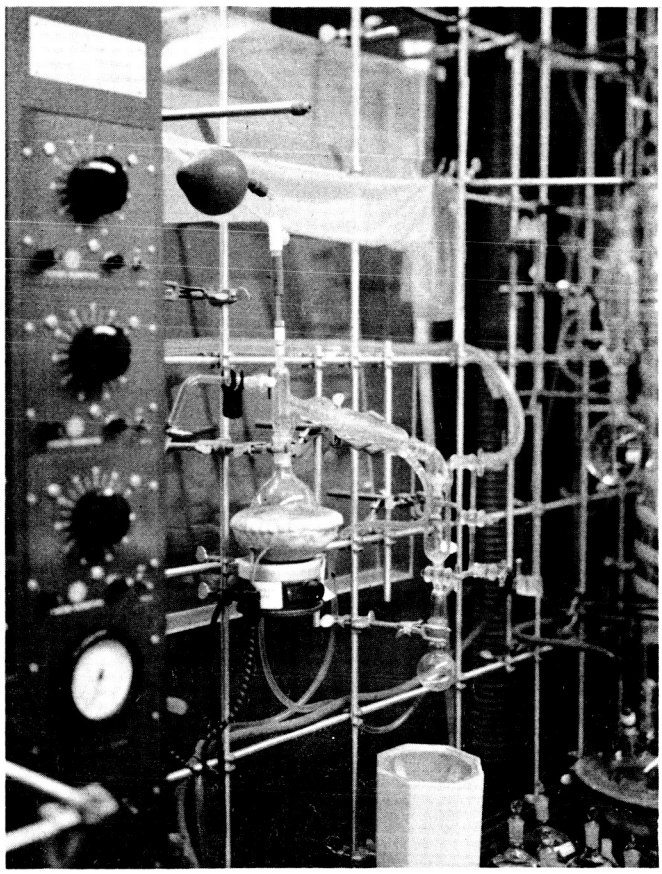

Figure 52: APPARATUS FOR VACUUM DISTILLATION OF DIALKYLBERYLLIUM COMPOUNDS

3. Properties of Dialkylberyllium Compounds.

Dimethylberyllium is obtained as white needles from hot ether and sublimes without melting at 200°C. Diethylberyllium is a colorless liquid boiling at 93° to 95° at 4 mm of mercury and melts at -13° to -11° when pure. Di-n-butylberyllium is a colorless liquid boiling at approximately 170° at 25 mm of mercury. Diphenylberyllium is a white solid which decomposes at 250°C without melting when pure; however, our product was yellow due to the presence of magnesium bromide.

Dimethyl, diethyl, and dipropyl beryllium are spontaneously flammable in air, especially humid air. They burn with luminous flames and give off a dense white smoke of beryllium oxide. Their sensitivity to oxygen is so great that Gilman found it necessary to have an ether solution of phenylmagnesium bromide in the nitrogen gas train to remove traces of oxygen. We did not find this necessary with the commercial nitrogen used in our work. Di-n-butyl and diphenyl beryllium are not spontaneously flammable but oxidize rapidly in air with the evolution of heat.

All of these compounds react violently with water and sometimes ignite. Therefore, all manipulations involving these compounds were carried out in an argon filled dry box using hypodermic techniques where appropriate.

The solvent power of these compounds is considerable. For example, diethylberyllium dissolves the beryllium oxide or ethoxide formed when exposed to traces of water, air, or alcohols. For this reason, solutions rapidly become contaminated with dissolved beryllium oxide during use, even in dry boxes.

The electrolytic conductivity of diethyl and diphenyl compounds of the group II elements were studied in benzene, dioxane, ether, tetrahydrofuran, and triethylamine by Strohmeier and Seifert[10]. They found that the electrolytic conductivity is a function of the dielectric constant of the solvent and increases as the latter increases. The conductivity in a given

solvent decreases in the following order:

$$MgR_2 \quad BeR_2 \quad ZnR_2 \quad CdR_2 \quad HgR_2$$

Tetrahydrofuran gives the highest conductivity (dielectric constant = 7.58) and is, of the ethers, the best ionization promoting solvent. We found the specific conductivity of freshly distilled diethylberyllium dietherate to be 10^{-7} ohm^{-1} cm^{-1}.

C. Synthesis of Organoberyllium Complex Salts.

1. Discussion

The recent work by Strohmeier and Gernert[2], [3] has shown that complex salt formation depends on the ionic radius of the alkali metal and the crystal lattice energy of the alkali halide. The complex forming tendency increases with increasing ionic radius of the alkali metal and with decreasing ionic radius of the anion. The smaller the lattice energy of the alkali halide the greater is the complex forming tendency. The influence of the ionic radius is greater than that of the lattice energy. Thus, potassium, rubidium, cesium, and tetraethylammonium cyanide and fluorides give isolatable complex salts with diethylberyllium whereas the corresponding sodium compounds give complexes which could not be isolated. The only chloride which gave a complex was the tetraethylammonium salt.

Recent work was also carried out by Dessy[11] on the exchange reaction of tagged beryllium bromide. Beryllium bromide was prepared from radioactive beryllium and mixed with diphenylberyllium in ether to study exchange in the system:

$$R_2Be.Be^*X_2 \qquad R_2Be + Be^*X_2 \qquad 2\ RBe^*X$$

No exchange was observed indicating the reaction to be:

$$R_2Be + Be^*Br_2 \qquad R_2Be.Be^*Br_2$$

Although Dessy suggests that the structure of such complexes is probably

$$\begin{matrix} R & & X \\ R & Be & X \end{matrix} Be \qquad \text{or} \qquad \begin{matrix} R \\ R \end{matrix} Be\text{-}X\text{-}Be\text{-}X$$

the ionic conductivity reported by Strohmeier and found in our work indicates that the above structures are in equilibrium with solvated forms of species such as

$$(R_2BeX^-) + (BeX)^+ \qquad \text{or} \qquad (R_2BeX_2)^{--} + Be^{++}$$

In both cases reported above the method of preparing the complex consisted merely of mixing an excess of the etherates of the dialkyl beryllium with the anhydrous metal halide. In some cases heating was necessary to effect a reaction. The ether liberated was pumped off under vacuum and the residual complex washed with heptane to remove unreacted dialkylberyllium. We used the same technique in all cases and only one specific example will be given in the following discussion.

2. Experimental

All preparations of complex salts were carried out in an argon filled dry box equipped with a magnetic stirrer, hot plate, vacuum line to an exterior pump, triple beam balance, and assorted automatic pipets as shown in Figure 53. As an example of the procedure followed, the preparation of a sample of rubidium fluoride - diethylberyllium will be described in detail.

Twenty-five ml. of diethylberyllium tetrahydrofuranate was pipetted into a 100 ml. round bottom flask containing a Teflon covered stirring magnet. Five g. of anhydrous rubidium fluoride was then added in small portions with continuous stirring. Heat was evolved along with some foaming. The mixture was stirred in the stoppered flask overnight after which time all of the salt had dissolved to form a grey, milky solution. The flask was fitted with a vacuum line attachment and the liberated tetrahydrofuran was pumped off with gentle heating. The viscous grey residue was then washed three times

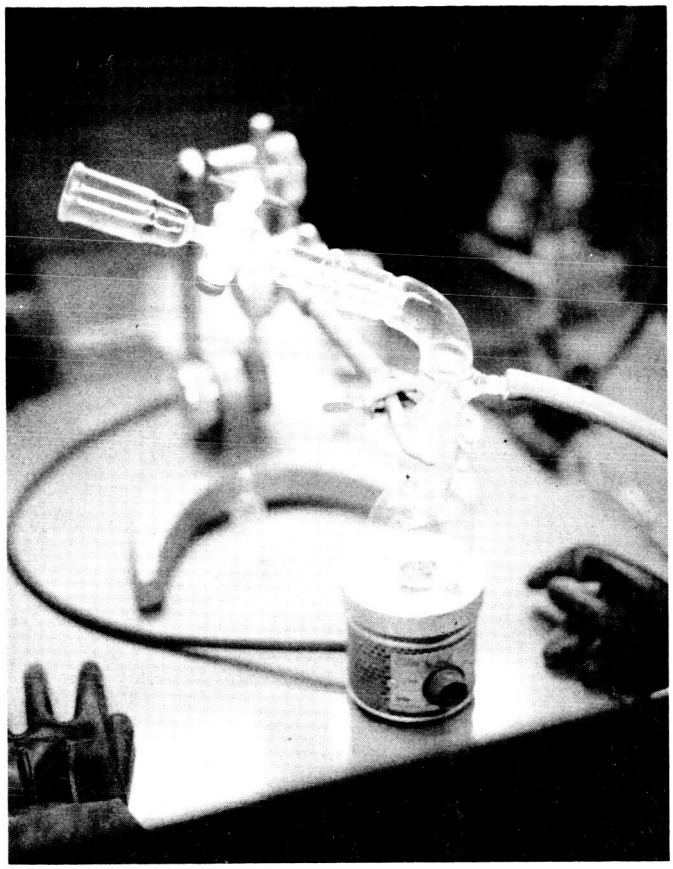

Figure 53: DRY BOX EQUIPMENT FOR SYNTHESIS OF DIALKYLBERYLLIUM COMPLEX SALTS

with fresh portions of heptane by decantation and the washes discarded. The heptane remaining in the sample was removed under higher vacuum with heating. The product, a very viscous grey liquid, was stored in the flask used to prepare it.

In order to measure the specific conductivities of liquid complexes it was necessary to construct special conductivity cells having a small internal volume, a large cell constant, and shape such that it could be filled like a pipet and the contents sealed off from the atmosphere. The requirements were fulfilled by the cells shown in Figure 54, fabricated from capillary tubing and small bore stopcocks. One end of each was ground to accept the fitting of a hypodermic needle for filling purposes and each contained a pair of platinized platinum electrodes. The cells were used with a General Radio type 1650-A impedance bridge, a type 1210-CRC oscillator, a type 1232-A tuned null detector, and a conventional water bath assembly.

3. Results

A total of twenty different combinations of metal halides and dialkylberyllium compounds were prepared with the results shown in Table IV-1. Although five organoberyllium complex salts were found to be liquid at 25°C, their specific conductivities were in the range of only 1×10^{-2} to 6×10^{-5} ohm^{-1} cm^{-1} which is no greater than can be achieved with many nonaqueous salt-solute combinations. In addition, their undiluted viscosities were medium to very high and their solvent power for lithium salts low. Consequently, the original application for which these materials were intended -- battery electrolytes with conductivities similar to fused salts -- does not appear feasible in view of these findings.

D. Electrochemical Studies of Complex Salt Solutions.

A chronopotentiometric study of a tetrahydrofuran solution of the beryllium chloride - diethylberyllium complex was carried out using the H-cells described in Sections II and III of this report. Since 200 ml. of

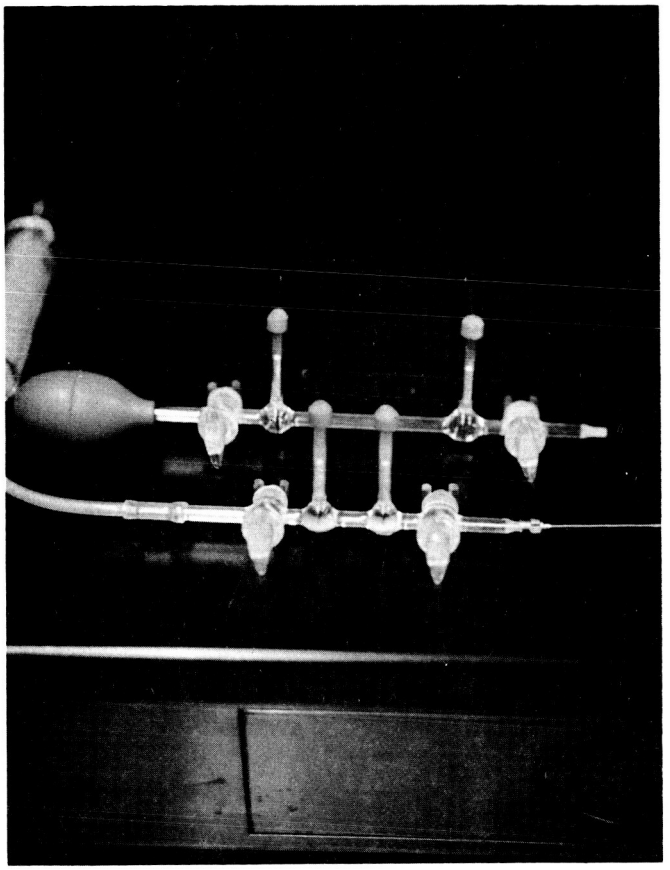

Figure 54 SPECIAL CONDUCTIVITY CELLS FOR DIALKYLBERYLLIUM SALTS

Table 13

PROPERTIES OF ORGANOBERYLLIUM COMPLEX SALTS

Complex Salt	Physical State [1]	Melting Point	Specific Conductivity, $ohm^{-1}\ cm^{-1}$
$KCN.2BeMe_2$	White solid	None	---
$KCN.2BeEt_2$	White solid	None	---
$BeCl_2.2BeMe_2$	N.R.	---	---
$BeCl_2.2BeEt_2$	Yellow liquid	---	2×10^{-4}
$BeCl_2.2BeEt_2.ThF$	Yellow liquid	---	7×10^{-5}
$BeCl_2.2Ben\text{-}Pr_2$	Viscous brown liquid	---	5×10^{-5}
$BeCl_2.2Be\ i\text{-}Pr_2$	White solid	Decomp.	---
$BeCl_2.2BeBu_2$	Tan liquid	---	6×10^{-5}
$BeCl_2.2BePh_2$	Yellow solid	250°C	---
$BeF_2.2BeMe_2$	N.R.	---	---
$NaF.2BeEt_2.ThF$ [2]	Brown solution	---	6×10^{-3}
$NaF.2Be\ n\text{-}Pr_2$	White solid	None	---
$NaF.2BePh_2$	N.R.	---	---
$Et_4NCl.2BeEt_2$	Gummy solid	---	---
$Et_4NCl.2Be\ i\text{-}Pr_2$	White solid	Decomp.	---
$Et_3NCl.2BePh_2$ [3]	N.R.	---	---
$Me_4NBr.2BeMe_2$	White solid	None	---
$Me_4NBr.2BeEt_2$	Yellow solid	Decomp.	---
$Me_4NBr.2Be\ n\text{-}Pr_2$	White solid	None	---
$CsF.2BeEt_2$	Viscous milky liquid	---	4×10^{-4}
$CsF.2BeEt.ThF$	Milky liquid	---	6×10^{-3}
$BeEt_2.Et_2O$ [4]	Colorless liquid	---	10^{-7}
$RbF.2BeEt_2.ThF$	Milky liquid	---	10^{-2}

1 The white solids which decompose were probably the unreacted starting salts

2 Not isolatable as a pure complex

3 The $BePh_2$ could not be isolated pure;by the technique employed--it contained $BeCl_2$

4 For comparative purposes

solution was required to fill these cells, 0.25 moles of complex were prepared and diluted with an equal volume of tetrahydrofuran, giving a total volume of about 200 ml. Copper working electrode discs in the lollipop configuration previously described were used.

It was found that beryllium metal could be reversibly deposited from the solution with the reanodization efficiency behavior shown in Figure 55. Anodic efficiencies were determined in the conventional manner by cathodizing at a given current for a given period of time in stirred solution and anodically recovering the deposited lithium.

It can be seen that the anodic efficiency decreases with increasing cathodic current density, but increases with increasing anodic current density. For small deposits -- less than 100 mC cm^{-2} -- the efficiency approached 100%. Although it was beyond the scope of this work to thoroughly characterize the nature of the deposited beryllium, these results demonstrated such complex solutions could be used for electroplating and electrorefining beryllium.

Metallic looking beryllium deposits could be obtained at all current densities employed; however, in thick layers these deposits became black and amorphous looking. They could be completely removed by reversing the current. No cathodic transition time could be obtained within the current limitation of the apparatus used.

Attempts were made to determine the cathodic efficiency by chemical analysis. Large quantities of beryllium were deposited on the copper electrodes and the deposits dissolved in aqueous HCl and the solution back-titrated. The results were too erratic to be relied on.

In order to determine whether beryllium was deposited from ionic species provided by the beryllium chloride or the diethylberyllium, a second complex salt was prepared from tetraethylammonium chloride and diethylberyllium diluted with tetrahydrofuran. No beryllium could be deposited from this solution under any conditions.

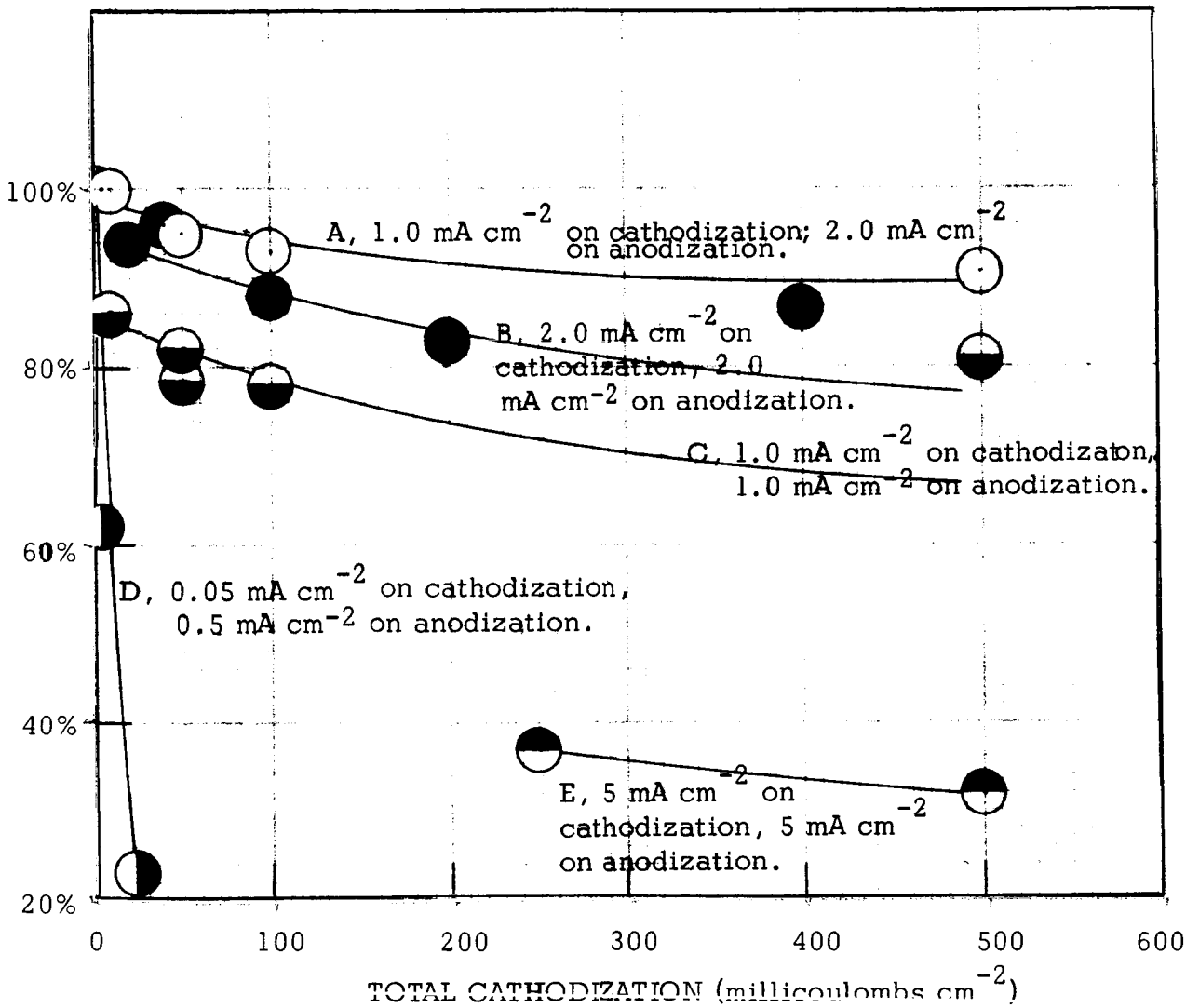

Figure 55 ANODIC RECOVERY OF BERYLLIUM

In beryllium chloride - diethylberyllium - tetrahydrofuran solution (see text). Cathodic-anodic cycling regime as indicated above, performed on polished copper electrodes.

1. The RbF/Et_2Be Tetrahydrofuran System.

A brief chronopotentiometric investigation was carried out on the complex salt prepared from 4 g. of rubidium fluoride and 10 ml. of diethylberyllium diluted to 150 ml. with tetrahydrofuran. Anodizations on copper and silver electrodes were performed to investigate fluoride film formation. Low potential plateaus were observed on both metals but no transition times developed. Current reversal indicates no reversible reduction of the anodically formed products. Cathodization of the polished metal electrodes resulted in the deposition of rubidium with re-anodization efficiencies of 90 to 100% over a current range of 1 to 64 mA cm^{-2} as shown in Table 14. The nature of the deposited metal was verified by using a beryllium electrode which gave the same transition times as copper or silver and by the observation that a drop of water on the bright, silvery rubidium deposit resulted in a burst of blue flame.

It should be noted that the deposition of rubidium from this complex is contrary to the expectation based on the results reported by Hans[12], who claimed that beryllium is deposited from a melt of alkali metal fluoride and diethylberyllium. Apparently the use of a strongly coordinating solvent as tetrahydrofuran in our work is responsible for our results, but this was not further verified by experiment. The open circuit potential of the electrodeposited rubidium in our work was only -1.1 V versus a reference silver disc electrode in the same solution.

Table 14

Reanodization Efficiency of Rubidium

Current Density mA cm^{-2}	Deposition Time, Sec.	Anodic Transition Time, Sec.	Efficiency %	Open Circuit Voltage of Deposit[2]
5	50.0	48.2	96.5	-1.2
10	30.0	29.0	96.7	
20	30.0	30.0	100.0	
40	30.0	28.0	93.5	
80	30.0	28.0	93.5	-1.1
160	30.0	27.0	90.0	
320	30.0	28.0	93.5	
5[1]	30.0	28.0	93.5	

(1) Deposited on silver electrode, all others are on copper.

(2) Open circuit voltages were measured with respect to a silver electrode in the same solution.

E. References Cited

1. Technical Documentary Report No. ASD-TDR-62-1, page 11, April (1962).
2. W. Strohmeier and F. Gernert, Chemische Berichte, 95, 1420-7 (1962).
3. W. Strohmeier and F. Gernert, Z. Naturforsch, 17B, 128 (1962).
4. W. Strohmeier, private communication.
5. Cahours, Ann. Chim. Phys., 58, 22 (1860).
6. H. Gilman and F. Schulze, J. Chem. Soc., 2663 (1927).
7. H. Gilman and F. Schulze, J. Am. Chem. Soc., 49, 2904 (1927).
8. H. E. Ramsden, U. S. Patent 824,944 (1959).
9. J. Goubeau and B. Roodewald, Z. Anorg. allg. Chem., 258, 162 (1948).
10. W. Strohmeier and F. Seifert, Z. Electrochem., 63, 683 (1959).
11. R. E. Dessy, J. Am. Chem. Soc., 82, 1580 (1960).
12. Guenther Hans, German Patent 1,162,576 (Cl, C 22d), February 6, 1964.

V. Appendix: Abbreviations, Potential Measurements

The abbreviations used are listed below:

C = concentration in the units specified. For the expression $iT^{1/2}/C$, when the current is in mA cm^{-2}, T in sec, C is in mM cm^{-3} which is numerically equal to the concentration in moles per liter.

i = current density in mA cm^{-2}

l = liter

M = Molarity (moles per liter)

mA = milliamperes

mC = millicoulombs

mM = millimoles

T = the transition time in seconds. Transitions are normally abbreviated by the Greek letter, tau.

The potential measurements given in this report are normally those of one of the circumferential disc working electrodes with reference to the center silver disc. The potential of the center silver disc has been repeatedly observed to be well-poised and constant during a series of measurements. Invariably the potential of the silver disc, though not thermodynamically well defined, is of such a value that the potential of other reversible couples measured against it is close to the potential of the couple in aqueous solution versus a normal hydrogen electrode. Thus the open circuit potential of a lithium electrode in a solution of a lithium salt is about -3 V versus the disc; the potential of a silver electrode in a solution of a silver salt is about +0.8 V versus the silver disc in a solution not containing silver ions.

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