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TECHNICAL REPORT NO. 2

**EVALUATION OF RECHARGEABLE
LITHIUM-COPPER CHLORIDE
ORGANIC ELECTROLYTE BATTERY SYSTEM**

By

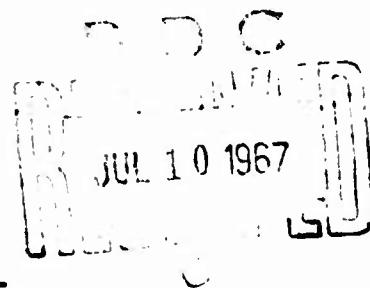
M. L. B. Rao and K. R. Hill

20 March 1967

Prepared for
**U.S. ARMY ENGINEER
RESEARCH AND DEVELOPMENT LABORATORIES
FORT BELVOIR, VIRGINIA**

Contract No. DA-44-009-AMC-1537(T)

Submitted by:
**P. R. MALLORY & CO. INC.
LABORATORY FOR PHYSICAL SCIENCE
NORTHWEST INDUSTRIAL PARK
BURLINGTON, MASSACHUSETTS 01803**



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FORWARD

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ABSTRACT

The electroformation and discharge of lithium and copper chloride was investigated in half cell and cell configurations in 1M LiAlCl_4 -P.C. The utilization efficiency of lithium in a half-cell depended on the substrate, current density and the loading. In the operation of rechargeable cupric chloride electrodes the tendency of copper salt to form highly soluble chloro cuprate complexes was observed. Impurities present in the solution caused significant self-discharge of the lithium electrode and increased the copper salt solubility. The formation of highly soluble chloro-complexes was a general phenomenon found for other cathode salts also such as AgCl and PbCl_2 in chloride containing electrolytes. This problem significantly affected the Li-CuCl_2 cell performance. The transfer of dissolved copper species to the lithium anode by diffusion or migration resulted in the deposition of a copper film on the anode. It was possible to retard the rate of transfer and consequently to improve the 1st discharge of the cell by employing thick separators. At higher current densities passivation of the lithium anode occurred in the cell. The cells were rechargeable but the cycle life was limited due to loss of cathode active material. A course of investigation to effect possible improvements in the cell performance is suggested.

SUMMARY

The reversibility and rechargeability of lithium and copper chloride electrodes were demonstrated in half-cell and full-cell configurations in the presence of a 1M LiAlCl_4 propylene carbonate electrolyte. The operating characteristics of the system were evaluated.

In excess electrolyte the coulombic efficiency of the lithium anodes depended on the substrate, the current density, and the loading. No lithium deposition was observed on graphite in the presence of LiAlCl_4 -P.C electrolyte while the electroformation and discharge of lithium occurred with an efficiency of 80-90 percent at $5\text{-}10\text{ mA/cm}^2$ and with a 1 to 2 mA hr/cm^2 loading on lithium, aluminum and copper substrates. An increase of the current density to 20 mA/cm^2 and of the loading to 10 mA-hr/cm^2 reduced the efficiency to 20 percent. No significant change was observed in the efficiency during the cycling of the lithium electrodes. Porous copper substrates exhibited higher efficiencies than did solid copper substrates. The behavior of lithium electrodes in limited electrolyte was similar to that observed in excess electrolyte. However, a complication due to filamental growth of lithium through the separator was noticed.

Self-discharge studies indicated that lithium deposited on aluminum substrates possessed good charge retention on open circuit. However, corrosion rates of approximately one microampere per square centimeter were observed on copper substrates. The addition of impurities which arose from the cathode and the electrolyte increased the self-discharge rate.

The charging of the copper cathodes in the LiAlCl_4 -P.C electrolyte generated a partially soluble CuCl salt the coulombic efficiency of which

varied with the discharge current density from 50 percent at 0.5 mA/cm^2 to 70 percent at 10 mA/cm^2 . A discharge mechanism involving the formation of a highly soluble chlorocuprate complex accounted for the low efficiency.

It was possible to increase the charge acceptance of the cathode by employing a mixture of CuCl and graphite. The discharge to Cu^0 of the CuCl_2 thus formed occurred stepwise with the intermediate formation of CuCl . The coulombic efficiency of the discharge was limited to 50-70 percent at 1 to 5 mA/cm^2 . The electrodes were rechargeable with a current efficiency of 90-95 percent, but the active material utilization decreased with the number of cycles. The tendency of CuCl towards complexation could be partially suppressed by the addition of an excess of AlCl_3 , and a coulombic efficiency greater than 95 percent was obtained under suitable conditions of current density and electrode porosity. However, the addition of AlCl_3 was found to be incompatible with the electrodeposition of lithium.

Experiments based on the salt transformation cycle in LiBF_4 , LiClO_4 , and MgClO_4 electrolytes in P.C were tried to effect the formation of CuCl from copper in the presence of insoluble LiCl . Anodization experiments indicated that CuCl was formed. However, the discharge efficiencies were similar to those observed in 1M LiAlCl_4 -P.C. Mixed solvent electrolytes comprised of 1M LiAlCl_4 in P.C and xylene gave no improvement in the cathode performance. It was not possible to suppress the tendency of the copper salt to form soluble chlorocomplex during the discharge by these methods.

Studies on the 1M LiAlCl_4 -propylene carbonate and 1M AlCl_3 -propylene carbonate electrolytes prepared from initially purified reagents

indicated that they contained approximately 5% wt of volatile impurities such as CO_2 , allyl alcohol, propionaldehyde, and propylene glycol. The total amount of impurities generated increased linearly with an increasing concentration of the electrolyte salt. It was possible to purify 0.1M solutions of the electrolyte by pre-electrolysis. However, attempts to purify 1 Molar solutions were unsuccessful. An increase in the concentration of the organic impurities by 5 percent increased the cathode salt solubility from 5×10^{-3} M/l to 1×10^{-2} M/l. An increase of 0.5 percent in the concentration of inorganic impurities increased the solubility of CuCl_2 similarly.

Studies on prototype cells also indicated the existence of problems arising from the tendency of the cathode salt to form soluble complexes during discharge. The diffusion and migration of the cathode species to the anode resulted in copper deposition at the lithium electrode. The rate of transfer of the dissolved copper salt to the cathode was decreased by varying the thickness of the separators. This was evident from the fact that the utilization efficiency gradually increased from 30 to 85% when the thickness of the separator increased. Under a given condition of separator thickness, the efficiency decreased with increasing current density. At 0.31 mA cm^{-2} the utilization efficiency was close to 90% and this decreased to 40% at 3.1 mA cm^{-2} . The high polarization of the lithium electrode was responsible for the observed results. The formation of a compact layer of LiCl or of Cu^0 metal originating from the discharge of the chlorocuprate complex was thought to be responsible for this behavior. The filamental growth of copper from the anode to the cathode and the loss of material from the cathode, both due to the dissolved copper salt affected both the cell life and the cycle life. However, the cells were rechargeable.

An examination of the solubility of other cathodes such as AgCl and PbCl_2 in chloride containing electrolytes indicated that the tendency of chloro-complex formation was not characteristic of CuCl_2 alone but a general phenomenon applicable to other cathodes as well.

Investigations based on active ion-exchange separators to retard the rate of transfer of soluble copper species to the lithium is suggested as a possible method of improving the Li-CuCl_2 cell performance.

The operational advantages that would accrue from electric vehicular propulsion systems have long been recognised. The well known energetic deficiencies of conventional batteries have resulted in extensive investigations leading to significant advances in aqueous media such as the hydrogen-oxygen fuel cells and metal-air breathing systems. The limitations imposed on electrochemical systems in protic solvents have generated considerable interest in high temperature cells operating in molten salts and high pressure cells operating in liquid ammonia or liquid sulfur dioxide. It was recognized early that from a thermodynamic point of view high energy density cells operating at room temperature and atmospheric pressure would most probably be made with first row transition metal cathodes and light metal anodes in aprotic electrolytes such as organic solvents containing inorganic salts. An investigation of a selected cell system utilizing one such organic electrolyte is presented in this report.

A. Objective

Although studies of electrochemical phenomena in organic electrolytes have a long history it has been only in recent years that intensive efforts have been made to investigate the utility of such electrolytes in high energy density batteries. Work on this subject may be traced to Harris¹ who demonstrated that a variety of cyclic esters could support active metal deposition. The electrolytes used by him had sufficient conductivity to allow consideration of their incorporation in primary and secondary batteries. Further work on complete cell assemblies by Chilton, et al² revealed that a number of promising systems existed. Since then, further exploratory work resulted in a considerable body of evidence that suggests that high energy density primary cells in reserve and non-reserve configurations are possible using organic electrolytes. However, the most pressing question in this field today is whether or not practical rechargeable high energy density systems in organic electrolytes are feasible. Since the existing information in

this field is too meager to answer this question, it is essential that investigations on a large number of systems be carried out. Such investigations would consist of the characterization of selected anode-cathode couples in terms of their thermodynamic and kinetic parameters. We have chosen to study the lithium-copper chloride system in the present work.

The objective of the present contract was to establish the state of the art for the lithium-copper chloride system by collecting and evaluating data on its reversibility, reactivity, cyclability and practicability.

B. Basis of Selection of the Lithium-Copper Chloride System.

1. The Lithium Anode.

The choice of lithium for the anode was based on its low equivalent weight, high potential, and most importantly, on the results of extensive investigations^{2,3,4} which have shown that it can be cycled at efficiencies greater than 80 percent in a number of organic electrolytes. This promising performance, which is superior to all other alkali and alkaline earth metals, provided the primary justification for concentrating the present work on this anode to the exclusion of other possible candidates.

2. The Copper Chloride Cathode.

The choice of copper chloride for the cathode was based on a great many considerations which are summarized below.

The fluorides and chlorides of the first row transition metals have received preferred consideration for cathodes because of their high theoretical energy density. In order for the halide salts to be rechargeable an anion supply must be available at the cathode. No organic electrolyte has yet been reported that is capable of providing fluoride ions from solution. The situation regarding chloride salts was more promising as both lithium chloride and lithium tetrachloroaluminate salts were capable of providing chloride ions from solution in organic solvents.

Exploratory investigations^{2,3,4} for the selection of a suitable transition metal chloride indicated that the charge-discharge potentials, utilization efficiencies, and solubilities of nickel, cobalt, iron, and copper chlorides were dependent on the specific electrolyte employed. The major problems associated with their behavior were: (a) high overvoltages for charge-discharge as in the case of nickel chloride, (b) high solubilities as in the case of copper chloride, and (c) both high overvoltages and excessive solubilities as in the case of iron and cobalt salts. High overvoltage cathodes were unsuitable from an energy density point of view although a solution to this problem might be found in the upgrading of the electrode performance by suitable catalysts.⁴ Reversible cathodes involving excessively soluble salts such as copper chloride were undesirable too, and a solution to the problem can be sought in the suppression of their solubility to tolerable limits by applying techniques which may involve the use of mixed solvents and complex salts to change the ionic equilibria. We have operated copper chloride electrodes at 70-75 percent efficiency, by employing complex salt electrolytes. The charge retention of copper electrodes in these electrolytes and their low over-potentials combined with the higher theoretical energy density of lithium cells with this salt in comparison to those with nickel, cobalt and iron chlorides fully justified the selection of copper chloride as a cathode for the present investigation.

3. The Electrolyte (1M LiAlCl₄-P.C).

A variety of organic solvents have been evaluated for non-aqueous cells among which the most frequently employed were: propylene carbonate (P.C), γ -butyrolactone, dimethylformamide, dimethylsulfoxide, acetonitrile, and ethylene diamine. Inorganic lithium salts such as lithium chloride, lithium nitrate, lithium perchlorate, lithium tetrafluoborate, lithium hexafluophosphate, lithium tetrachloroaluminate dissolve in the listed solvents to give low conductivity solutions (maximum specific conductivities of approximately $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$). Though the specific conductivities of these solutions are considerably less than those of aqueous electrolytes, it may be possible to keep IR losses of operating

cells within acceptable bounds by proper cell designs. Hence, these electrolytes were considered sufficiently conducting to be incorporated in cells.

The selection of the electrolyte for the present work was based on the requirement of chloride ions for the operation of copper chloride electrodes. The high efficiency of copper chloride cathodes and their capacity for charge retention reported earlier has been observed in a propylene carbonate solution of lithium tetrachloroaluminate. Hence, a one molar solution of lithium tetrachloroaluminate in propylene carbonate was chosen as the electrolyte for the present investigation.

II. GENERAL APPROACH TO THE INVESTIGATIONS

A. Introduction

The evaluation of the lithium-copper chloride cell in 1M LiAlCl_4 -P.C comprised of two important aspects.

1. The evaluation of the inherent characteristics of the individual active materials and of the electrolyte.

2. The evaluation of the cell behavior.

The former involved the reversibility and rechargability of the electrodes and the stability of the electrolyte. The latter dealt with the practicality of the system in relation to the mutual interactions of the anodic and cathodic reactions, and also pertained to the engineering aspects such as the selection of separators, and the development of suitable electrode structures. The relevance and necessity of this approach is detailed below.

The information available in the literature on the chosen active materials was inadequate to proceed directly to cell construction. Some outstanding problems needed to be understood or solved before cell evaluation could be undertaken.

B. The State of Art at the Inception of the Contract.

1. The problems of lithium anode.

- a. Utilization efficiency.

Though it had been possible to cycle lithium electrodes repeatedly at depths of discharge in excess of 80 percent, the lithium anode was not trouble free. The problem can be stated most simply in terms of the efficiency of utilization of lithium. Whenever the current efficiency is less than 100 percent lithium is either consumed by parasitic reactions or solvent is electrolyzed at the anode. Either of these reactions may affect cell operation and life.

- b. Self-discharge.

A loss of anode capacity may be caused by anode dissolution

due to soluble cathode salts or by electroactive impurities such as water, glycol, dissolved oxygen, hydrogen chloride, carbon dioxide, etc. The severity of these parasitic reactions depends on the nature of the reagents and the operating conditions of the electrodes.

c. The effect of possible solvent decomposition reactions.

Parasitic reactions originating from the inherent instability of the solvent or due to electrochemical decomposition may result in more than one product. If such products contain electroactive functional groups such as aldehydes, alcohols, etc. which can be reduced by lithium then the anode efficiency will be seriously effected. Polymeric products may also arise from electrochemically generated free radicals. These polymers may accumulate on the electrode surface and interfere with the lithium electrode performance. There is evidence from previous work,³ that such interference exists and, hence, it is necessary to understand the role of such parasitic reactions in order to find ways and means to minimize or eliminate them.

d. The substrate effect.

Investigations of lithium anodes^{3,5} have shown that their efficiency and open circuit stability depend on the nature of the supporting conductor. A further evaluation of these effects must be made to assist in the selection of the proper support materials for the cell.

e. The effect of the structure of the lithium deposit.

The texture of the deposit has a large influence on the cycle life of cells. Excessive dendritic growths may result in lithium shedding and the short circuiting of the cells internally. Such effects have to be evaluated in terms of the properties of the system and variables such as the concentration of the electrolyte, addition agents, current density, etc.

2. Problems Relating to the Copper Chloride Cathode.

a. Low efficiency.

As reported earlier, the maximum efficiency of the copper chloride

cathode on charge-discharge cycling in the electrolyte of interest had been limited to 70-75 percent. This may indicate parasitic reactions in the potential region of cathode operation which may be intolerable, or the loss of efficiency may simply be due to the cathode solubility. It was not clear from previous work which of the two causes was responsible for the loss of efficiency. Thus, the first problem requiring experimental solution was the identification of the causes of its inefficiency during charge-discharge cycling.

b. Utilization of the divalent copper state.

Since no information was available on the number of electrons involved in the oxidation-reduction reaction, experiments which could be evaluated in terms of the properties of the system and variables such as the concentration of the electrolyte, addition agents, current density, etc. to reveal the most favorable conditions for the formation and discharge of copper (II) chloride needed to be worked out.

c. The effect of disproportionation reactions.

Ionic equilibria involving the disproportionation reaction between Cu^0/Cu^+ and Cu^{++} , as in aqueous media, needed to be considered. If such disproportionation reactions were to occur in the organic electrolytes, the energy density and performance characteristics of the cells would be adversely affected.

3. Problems Associated with the Electrolyte.

a. The dissociation equilibria of the electrolyte salt.

The dissociation of the tetrachloroaluminate ion in P.C involves the generation of the Lewis acid AlCl_3 as in $\text{AlCl}_4^- = \text{AlCl}_3 + \text{Cl}^-$. It is clear¹ that the presence of a free Lewis acid has an adverse effect on the stability of the solvent and the products of decomposition may have an effect on the anode stability and/or the cathode solubility.

b. Thermal effects.

Internal heating during high current operation may effect the stability of the anode, the cathode, and the electrolyte, e.g. electrolyte

decomposition.

4. Problems Relating to the Cell Evaluation.

a. The formation of suitable electrodes.

The electrodes for rechargeable cells may be obtained either by electroforming the active materials or developing suitable electrodes starting from chemicals obtainable in charged state. At the inception of the contract, some information was available on the lithium anodes, used in lithium-silver and lithium-nickel chloride cells. However, the question of how to make suitable copper chloride electrodes for the cell evaluation was open, and hence investigations were necessary in this area.

b. The selection of suitable separators.

Although separators of different kinds had been tested in earlier investigations, the information available was too meager to predict the suitability of any particular kind of material in the present work. Thus, there was a necessity to evaluate different separators before a selection of a particular separator could be made.

c. The evaluation of the cell performance.

No data were available which allowed a meaningful estimation of the performance of the lithium-copper chloride cells and the work was planned to provide such data.

C. Experimental Techniques.

Information on the various aspects of the problems discussed above may be obtained through half-cell measurements, studies involving chemical and ionic-equilibria in solution, and through limited-electrolyte cell studies.

1. Solvent.

Propylene carbonate (obtained from Matheson, Coleman, and Bell) was passed through a column of Linde 4A molecular sieves to remove part of the

water initially present in the solvent. It was then vacuum distilled at 3-5 mm Hg and the useful fractions collected at 89 - 91°C. The water content of the various fractions was analyzed by gas chromatography and found to be between 0.002 and 0.5 percent by weight, depending on the fraction considered. The solvent fraction containing 0.002 to 0.005 percent water was used in the present experiments.

2. Electrolyte Solutions.

a. 1M LiAlCl_4 -P.C

Various procedures for the preparation of solutions of lithium tetrachloroaluminate have been described^{2,3,4}. The most common method involves the controlled addition of stoichiometric quantities of AlCl_3 and LiCl to propylene carbonate. Such solutions become discolored and give evidence of extensive side reactions, probably the decomposition of solvent catalyzed by AlCl_3 . We have adopted the procedure previously reported³ involving the direct formation of LiAlCl_4 through fusion of solid AlCl_3 and LiCl at 200°C. All the operations of pre-mixing the salt, melting, and cooling were carried out in a dry atmosphere to exclude hydrolytic processes. The electrolyte was prepared by dissolving known amounts of this salt in given volumes of distilled solvent. Normally, such electrolytes were more stable than those obtained by other procedures, as evidenced by the very slight discoloration.

b. Other electrolytes

Other solutions were used in the investigations and they were prepared by dissolving the required amounts of the salts in the given solvent or solvent mixtures.

3. The Cells.

The half-cell measurements were carried out in an H-cell of 50 ml capacity with a fine sintered glass frit separating the two compartments. The cell had a suitable lid for mounting the electrodes and had provisions for admitting dry argon gas for deaeration and for maintaining a moisture free atmosphere over

the electrolyte.

4. Instrumentation.

The half-cell and cell charge-discharge measurements were carried out under constant current conditions provided by a constant current power supply: Electronic Measurements Inc., Model 620. The half-cell and cell potentials were measured with an electrometer, E-H-Research Labs. Model 230 whose output was recorded on a potentiometric recorder, Mosley Autograph 680.

The potential of the half-cell during the measurement was measured against a silver wire reference electrode in the same solution. The potential of this reference electrode was found to be well poised.³

The counter electrode for the half-cell measurement was a strip of lithium metal situated in the counter electrode compartment of the H-cell.

The solubility measurements were made employing polarographic techniques using a Metrohn Polarecord Model E-261.

The x-ray diffraction studies were made with a Phillips Type 422730 unit.

Gas chromatographic techniques were employed to evaluate the properties of the solvent and electrolyte solutions by means of a Perkin-Elmer Model 801 chromatograph with a hot wire detector.

5. Procedures.

The detailed procedures of the individual experiments will be reported in subsequent sections of the report.

III. HALF-CELL STUDIES.

In this section we deal with the experimental results and a discussion of the electroformation and discharge of lithium and copper chloride half-cells. The section also covers our attempts to develop suitable electrode structures, the electrochemical behavior of the prepared electrodes, and the investigations pertaining to the improvement of the anode and cathode behavior. Part A of the section deals with lithium half-cell investigations and Part B with the copper chloride cathode studies.

A. Lithium Anode Investigations.

1. The problem: In Section II we dealt with the outstanding problems of the lithium anode at the inception of the contract. These related to its utilization inefficiency, self-discharge rate, the substrate effect, and the structure of the lithium deposit. In this section we present the results pertaining to these aspects of the problem.

2. Experimental methods.

a. Charge-discharge studies in excess electrolyte: The electrodeposition and dissolution experiments on different substrates in excess electrolyte were carried out using 2 sq cm (apparent) area square electrodes made of 10 mil copper foil, Clevite porous copper plaque, 10 mil pure aluminum foil, 15 mil lithium ribbon, and graphite cloth. Small tabs were left on one side of the electrodes for making electrical connections with an alligator clip. The tabs were wrapped with 3/16" wide strips of teflon tape. The electrodes were immersed in 1M LiAlCl_4 -P.C or other electrolytes and cathodic charge-anodic discharge experiments were carried out employing the previously described experimental conditions. Unless otherwise mentioned, the discharge of the electrodes was begun at the completion of the charging process and the discharge was discontinued when the working electrode potentials reached zero volts vs. the Ag reference

electrode. From the observed charge and discharge capacities the utilization efficiency of the process was calculated.

Charge and discharge experiments of lithium half-cells were also carried out in other electrolytes such as 1M LiAlCl_4 -P.C containing xylene, excess aluminum chloride, and also in 1M LiAlCl_4 in nitrotoulene. These experiments were similar to the ones described above. The results will be discussed in later sections of this report.

b. Charge-discharge experiments in limited electrolyte cells.

The working electrodes were made of 12.9 cm² copper or aluminum electrodes, 15-30 mil thick and were used as substrates for lithium deposition and dissolution studies. Two lithium metal foils surrounding the working electrodes in parallel plate configurations comprised the counter electrodes. These were kept separated from the working electrodes by means of separators. The electrode assembly was placed in cubic pyrex glass containers of approximately 1" x 1" x 1" dimension. Polytetrafluoroethylene inserts of suitable dimensions were packed in the cell container to fill the space between the electrode assembly and the cell walls. The amount of electrolyte in the cells was limited to the volume of the separator. A silver wire positioned suitably in the cell served as a reference electrode to monitor the charge and discharge of the lithium. The operation of the cell assembly, the wetting of the cell with electrolyte and the charge-discharge experiments were carried out in a polyethylene glove bag in an argon atmosphere.

c. Self-discharge of electrodeposited lithium.

Self-discharge experiments were conducted by keeping electro-deposited lithium electrodes immersed in the electrolyte for different intervals of time and measuring the utilization efficiency by discharging the electrodes after the said interval of time. Any difference in the utilization efficiency of a discharge immediately after charge and after a lapse of known interval indicated the extent of any self-discharge.

3. Results and discussion.

a. Nature of lithium charge-discharge curves.

Typical polarization curves obtained during the formation and discharge of lithium in 1M LiAlCl_4 -P.C on different substrates are presented in Figure 1. The curves in Figure 1 which are characteristic of the substrates involved were obtained under approximately the same experimental conditions.

The following information may be derived from the curves in Figure 1.

(i) Lithium deposition did not occur on graphite under the experimental conditions.

(ii) The open circuit and charge-discharge potentials of lithium on lithium and on copper substrates were 150 to 200 mv more cathodic than lithium deposited on aluminum substrate.

(iii) The discharge potentials of Li° on Cu° and of Li° on Li° were fairly steady. In the case of the discharge curve of Li° on Al a decrease of the potential with an increasing depth of discharge was observed.

A quantitative discussion of the charge-discharge behavior of Li° on Li° was possible by virtue of the following observations: In the discharge curve of electrodeposited Li° on Li° from 1M LiAlCl_4 -P.C, a point of inflexion, designated (A) in Curve 3, Figure 1, was observed. The magnitude of this point of inflexion depended on the pretreatment of the substrate. It is suggested that it is related to the IR due to some impurity film present on the lithium substrate. Considering the point of inflexion as the end point for the anodic stripping of electrodeposited lithium metal, the utilization efficiencies were calculated. For experiments involving 1 mA hr/cm^2 loading and 10 mA/cm^2 current density, the observed utilization efficiency was about 75 percent for electro-deposition-dissolution of lithium on lithium. The lithium substrates used in these experiments were cleaned by scraping the surface under P. C.

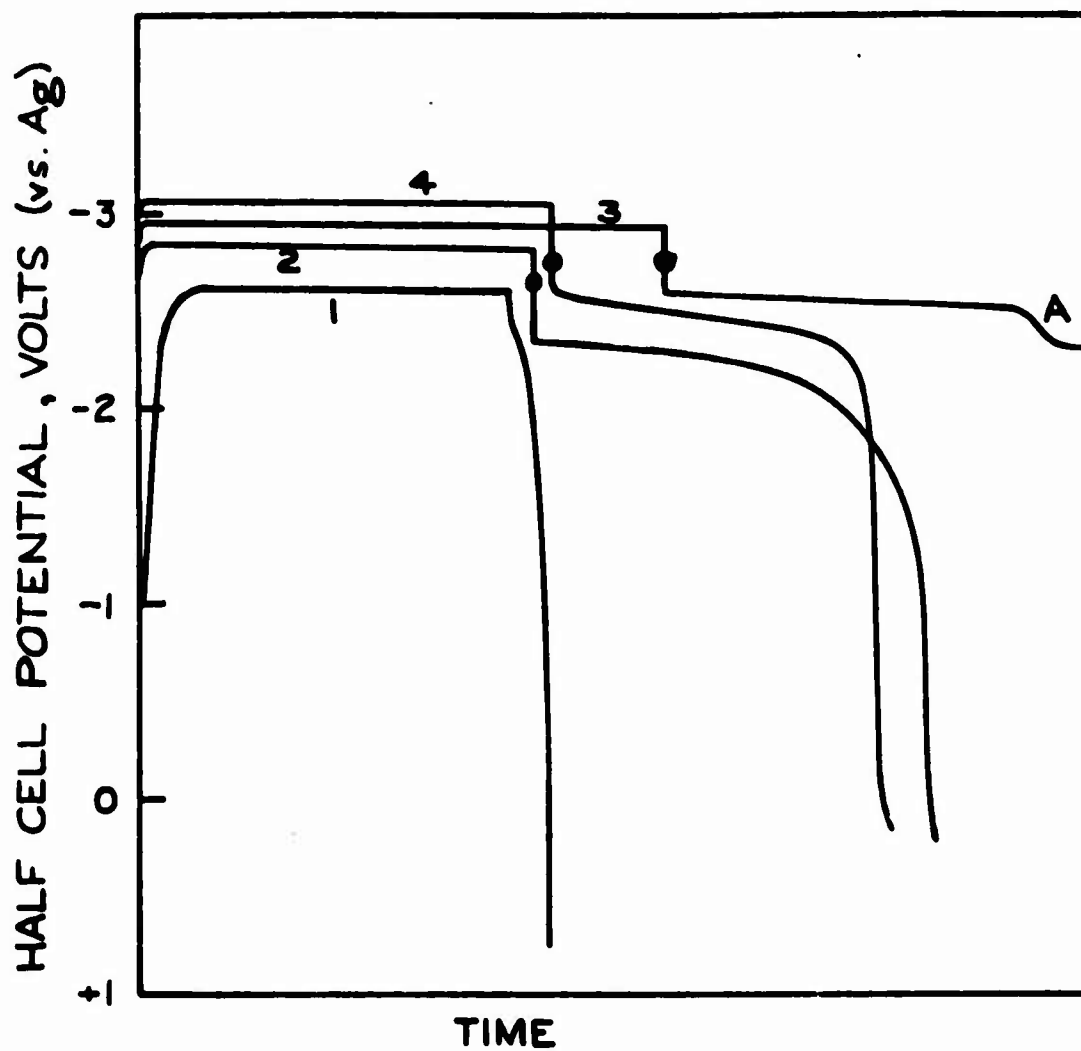


Figure 1. Polarization curves for the formation and discharge of lithium on different substrates in 1M LiAlCl_4 - P. C.

- (1) Porous graphite
- (2) Aluminum
- (3) Lithium
- (4) Copper

b. The polarization of lithium on graphite substrates.

Table 1 gives the data on the cathodic and anodic efficiency of Li^0 on porous graphite.

TABLE 1

The performance of porous graphite as substrate for the formation and discharge of lithium in 1M LiAlCl_4 - P. C.

Cycle No.	Loading mA-hr/cm^2	Current density mA/cm^2	Anodic efficiency
1	1	20	11
2	1	20	30
3	1	20	17
4	1	40	27
5	1	80	26

Under the conditions given in Table 1, the electrode potential did not reach -2.80V vs. Ag and no visible deposit of lithium was observed. The observed discharge efficiencies were therefore not related to lithium dissolution. At this stage it was necessary to understand whether the non-occurrence of lithium deposition on graphite was common to other propylene carbonate containing electrolytes, or whether it was a particular phenomenon in 1M LiAlCl_4 - P. C. To answer this question, similar charge-discharge experiments were carried out in 1M LiClO_4 - P. C. The results of these experiments are presented in Figure 2. They indicated that lithium deposition was possible on graphite substrates in 1M LiClO_4 - P. C. Hence, it appeared that the reason for not obtaining Li^0 deposition from 1M LiAlCl_4 - P. C. may have been due to the sensitivity of the graphite substrate to alternate electrode processes related to lithium aluminum chloride.

c. Electrodeposition and dissolution of lithium on aluminum and copper substrates.

Figures 3, 4 and 5 illustrate the utilization efficiency of lithium on aluminum, copper and porous copper substrates, respectively, as a function of current density, loading and cycling. It was observed that at a loading of 1 mA-hr/cm^2 on an aluminum substrate, the utilization efficiency was close to

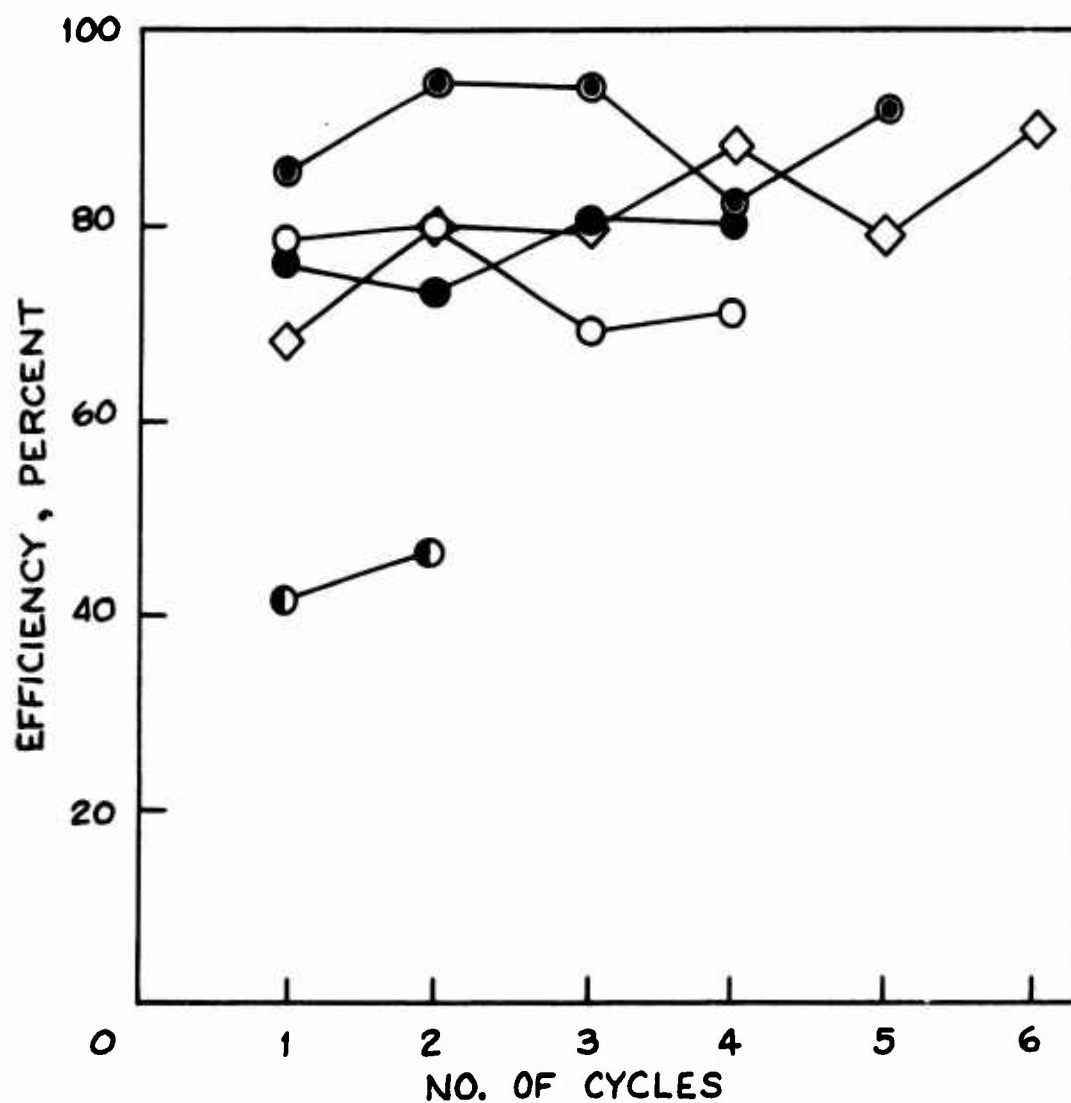


Figure 2. Utilization efficiency of lithium during charge-discharge in 1M LiClO₄-P.C on Graphite Substrate.

Current density- Charge capacity

- 5 mA cm⁻², 1 mA-hr cm⁻²
- 10 mA cm⁻², 2 mA-hr cm⁻²
- 20 mA cm⁻², 2 mA-hr cm⁻²
- ◇ 10 mA cm⁻², 1 mA-hr cm⁻²
- 20 mA cm⁻², 10 mA-hr cm⁻²

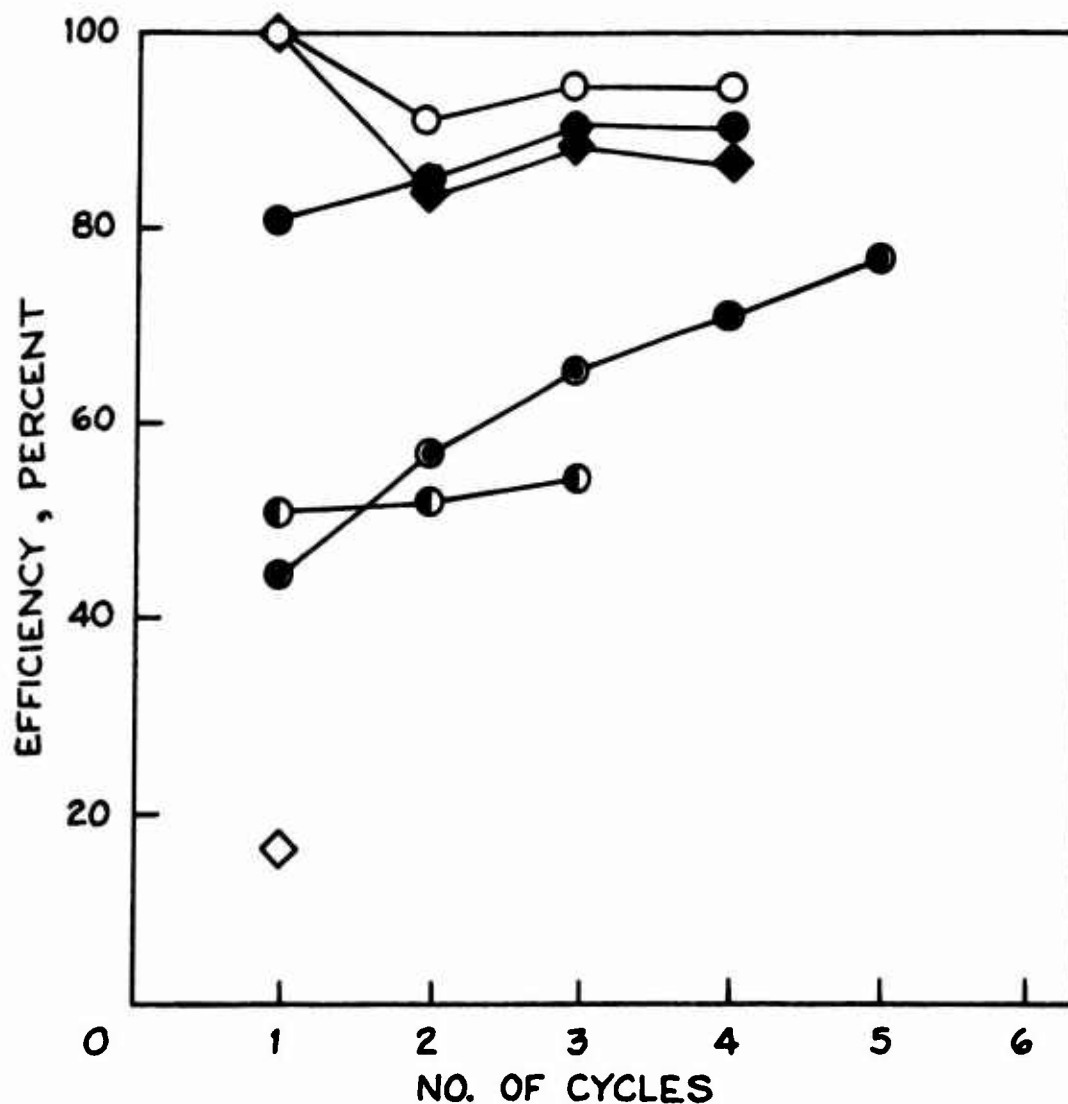


Figure 3. Variation of utilization efficiency of lithium during charge-discharge on aluminum substrate with current density, loading and cycling in 1M LiAlCl₄-P.C.

Current density-Charge capacity

- 5 mA cm⁻², 1 mA-hr cm⁻²
- ◆ 10 mA cm⁻², 1 mA-hr cm⁻²
- 5 mA cm⁻², 2 mA-hr cm⁻²
- ◐ 20 mA cm⁻², 2 mA-hr cm⁻²
- ◑ 20 mA cm⁻², 1 mA-hr cm⁻²
- ◇ 20 mA cm⁻², 10 mA-hr cm⁻²

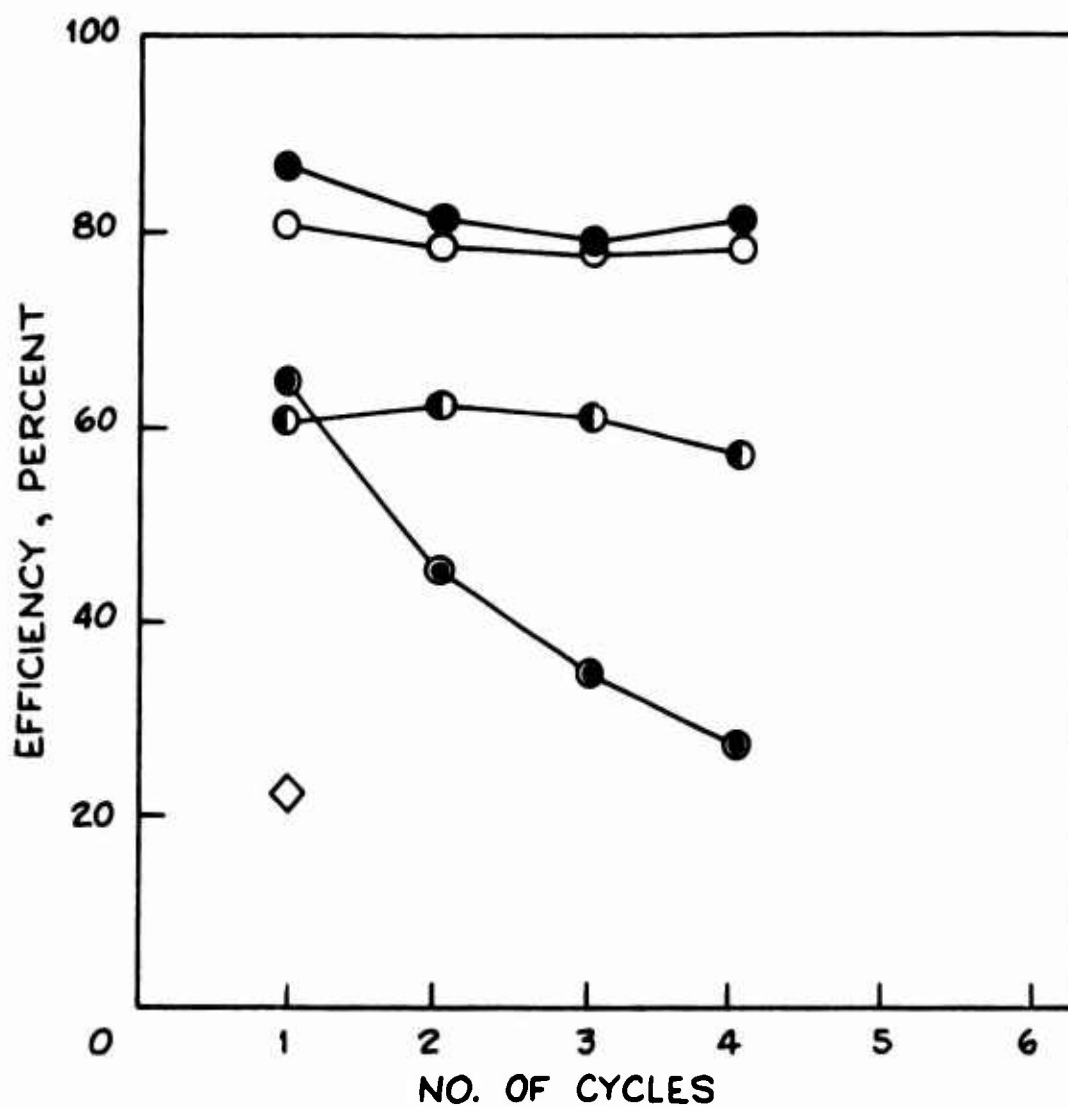


Figure 4. Variation of utilization efficiency of lithium during charge-discharge on copper substrate with current density, loading and cycling in $1M LiAlCl_4$ -P.C.

Current density-Charge capacity

- 5 mA cm⁻², 1 mA-hr cm⁻²
- 10 mA cm⁻², 1 mA-hr cm⁻²
- ◐ 20 mA cm⁻², 2 mA-hr cm⁻²
- ◑ 20 mA cm⁻², 1 mA-hr cm⁻²
- ◊ 20 mA cm⁻², 10 mA-hr cm⁻²

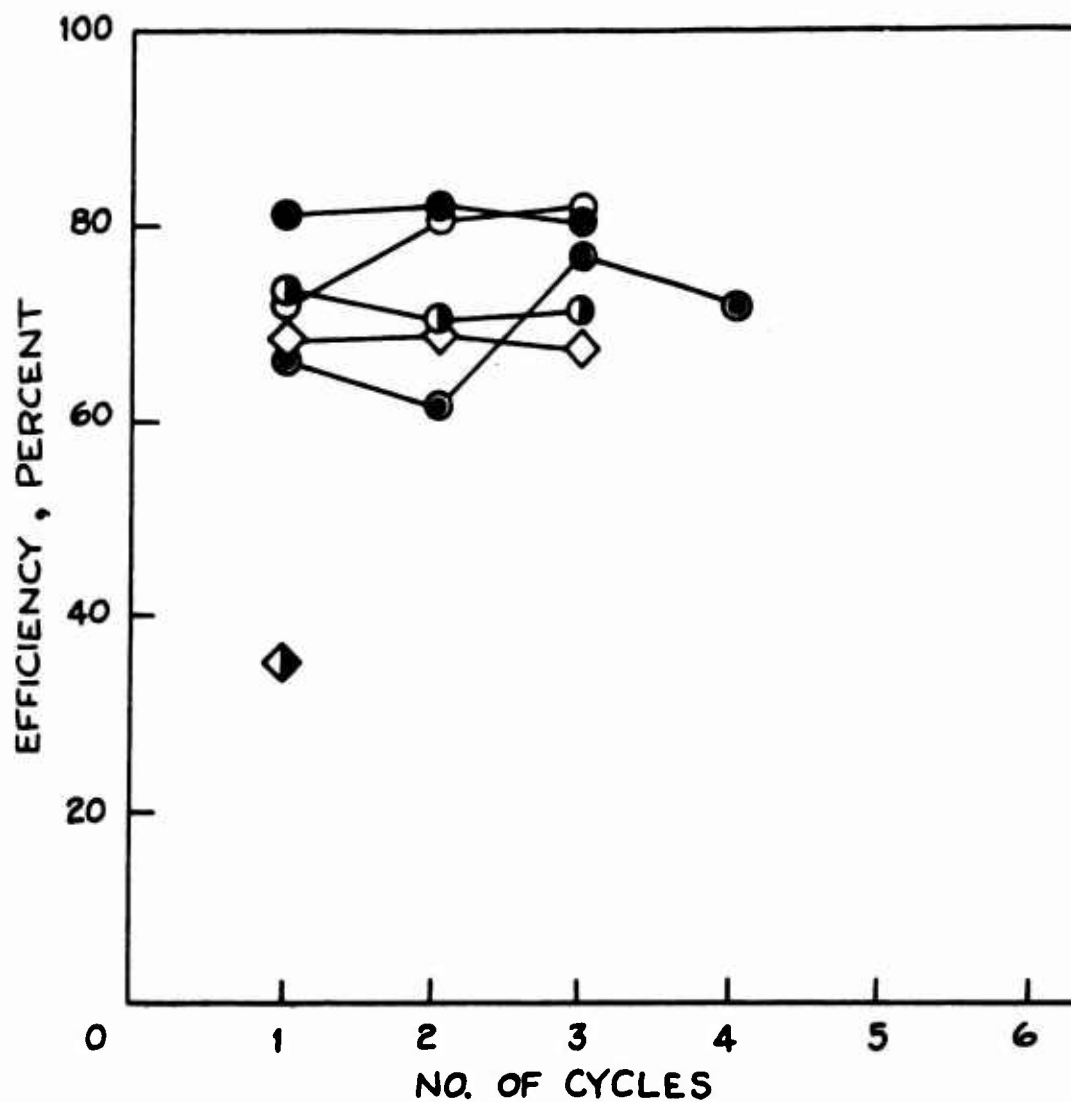


Figure 5. Variation of utilization efficiency of lithium during charge-discharge on porous copper with current density, loading and cycling in 1M LiAlCl₄-P.C.

Current density-Charge capacity

- 5 mA cm⁻², 1 mA-hr cm⁻²
- 20 mA cm⁻², 1 mA-hr cm⁻²
- 10 mA cm⁻², 1 mA-hr cm⁻²
- ◇ 20 mA cm⁻², 2 mA-hr cm⁻²
- 5 mA cm⁻², 2 mA-hr cm⁻²
- ◆ 20 mA cm⁻², 10 mA-hr cm⁻²

90 percent at 5 to 10 mA/cm². The efficiency decreased as the current density increased. An increase of the charge density, i.e. loading, also decreased the utilization efficiency, but the lowering of the efficiency may be due largely to mechanical losses caused by the observed poor adhesion of the deposit.

The behavior of lithium on copper substrates was similar to that of lithium or aluminum at 1 mA-hr/cm² and 5 to 10 mA/cm². As the current density increased to 20 mA/cm², the efficiency decreased to 60 percent on non-porous copper and to 70 percent on porous copper substrates, as may be seen in Figures 4 and 5. Considering the variation of the efficiency with cycling at 2 mA-hr/cm² and 20 mA/cm² on porous and non-porous copper, it appeared that porous structures were more suitable than solid foils.

d. Charge and discharge of lithium in limited electrolyte.

The lithium electrode efficiency was studied in the limited electrolyte cells. The effect of varying the thickness of the separator (Reeve Angel 934-AH glass fiber filter paper) is shown in Figure 6 for a copper working electrode at a loading of 1 mA-hr/cm². An increase of the loading to 2 mA-hr/cm² gave the results shown in Figure 7. Although the data seem to indicate that 3 layers of separator are slightly better than either 2 or 4 layers the observed variations are not large enough to be conclusive for this type of cell.

A cell with 3 layers of Millipore filter paper gave essentially the same results as did the Reeve Angel filter paper, Figure 8.

The use of an aluminum working electrode with 3 layers of Reeve Angel 934-AH paper gave the interesting result shown in Figure 9. The efficiency at 5 mA/cm² increased with the cycle number reflecting the changes in the surface conditions brought about by lithium deposition. A final check run at 5 mA/cm² gave a maximum efficiency of 85%. The aluminum substrate also gave a higher efficiency at a current density of 20 mA/cm².

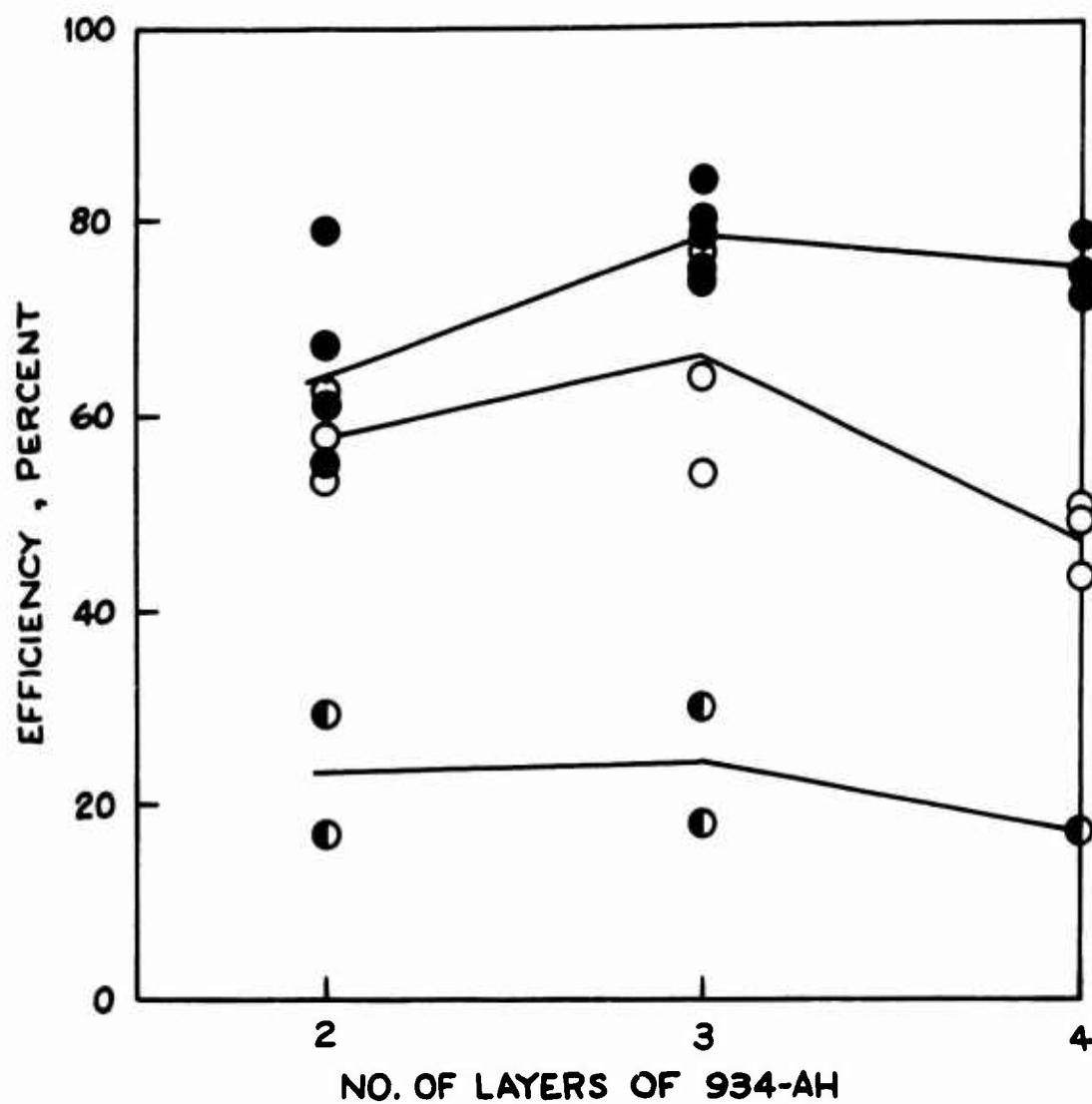


Figure 6. Variation of lithium efficiency on copper substrate with the thickness of separator at 1 mA-hr cm⁻².

Current density-Charge capacity

- 5 mA cm⁻², 1 mA-hr cm⁻²
- 10 mA cm⁻², 1 mA-hr cm⁻²
- 20 mA cm⁻², 1 mA-hr cm⁻²

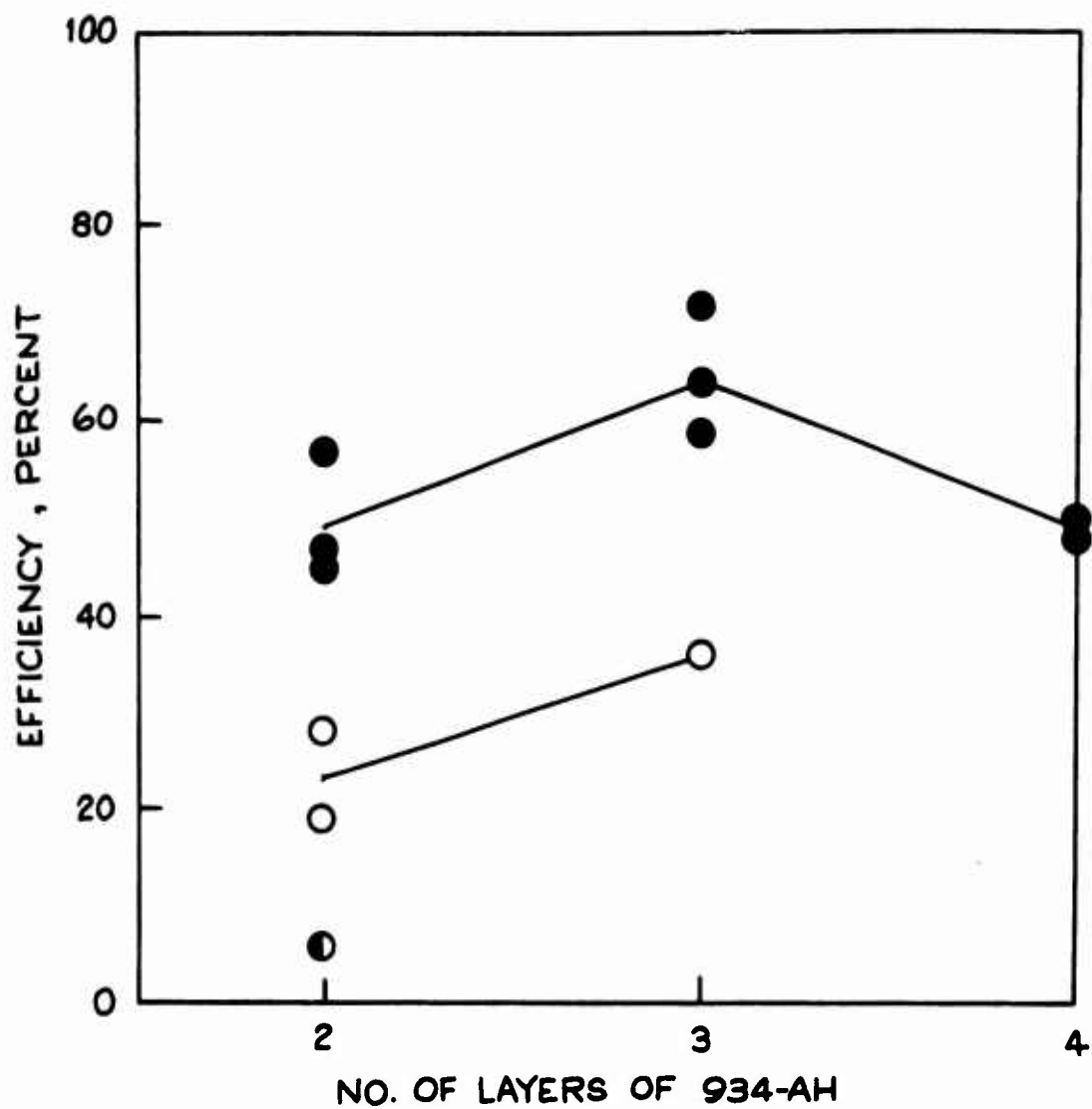


Figure 7. Variation of lithium efficiency on copper substrate with thickness of separator at 2 mA-hr cm⁻².

Current density

- 5 mA cm⁻²
- 10 mA cm⁻²
- 20 mA cm⁻²

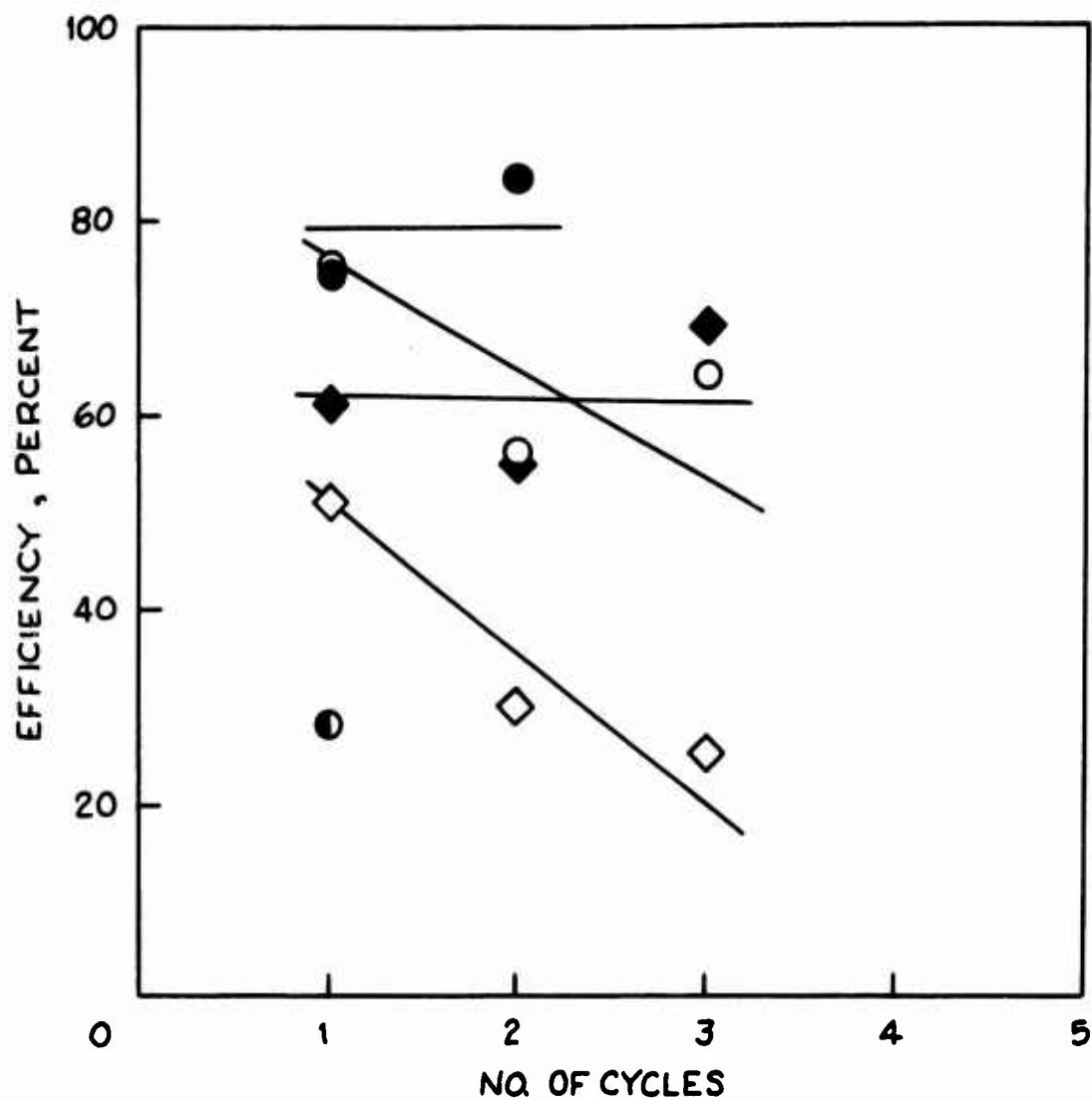


Figure 8. Variation of lithium efficiency on copper substrate using 3 layers of Millipore AP20 glass paper separator.

Current density-Charge capacity

- 5 mA cm⁻², 1 mA-hr cm⁻²
- 10 mA cm⁻², 1 mA-hr cm⁻²
- 20 mA cm⁻², 1 mA-hr cm⁻²
- ◆ 5 mA cm⁻², 2 mA-hr cm⁻²
- ◇ 10 mA cm⁻², 2 mA-hr cm⁻²

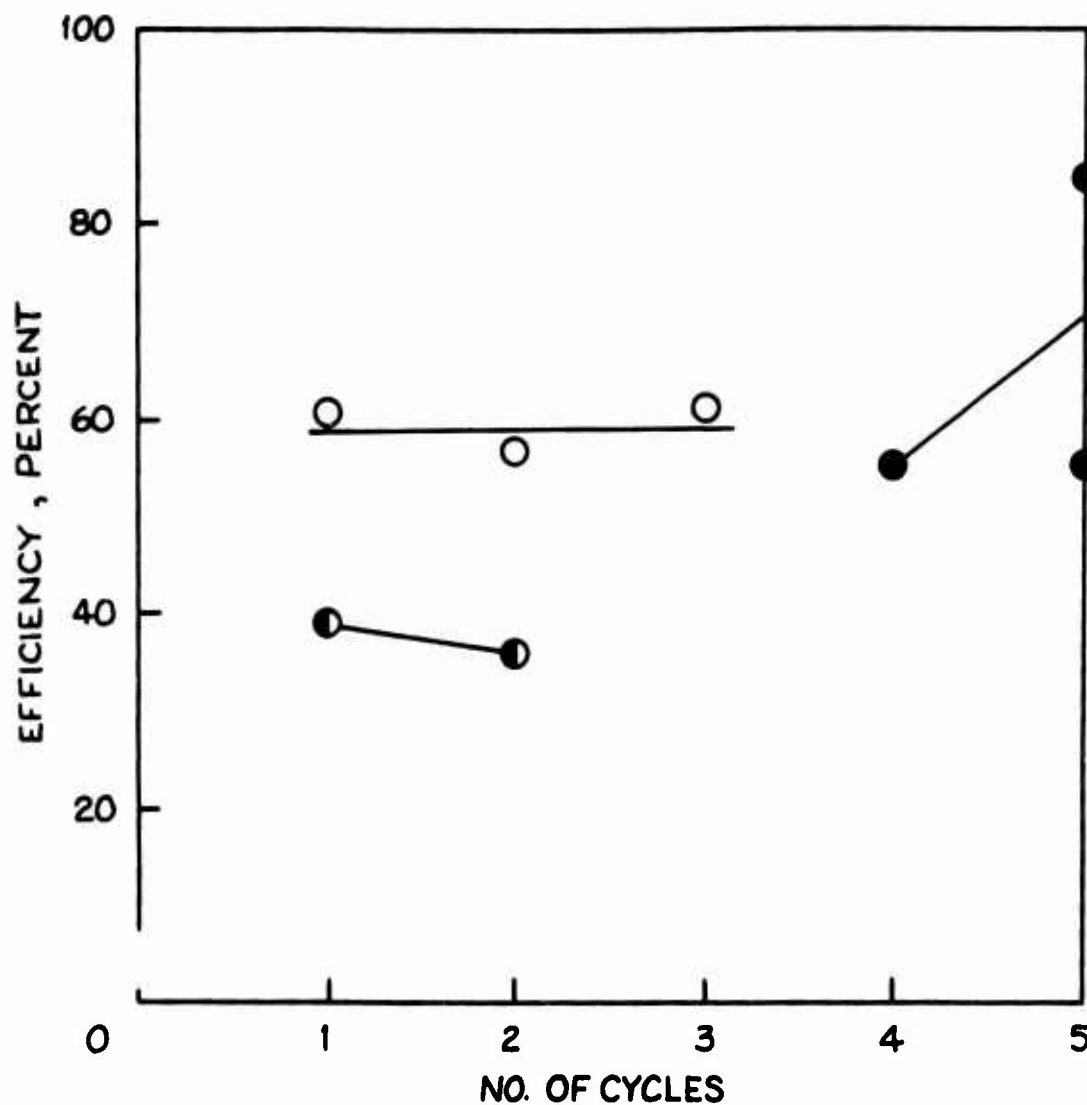


Figure 9. Lithium efficiency on aluminum substrate with Reve-Angel 934-AH glass paper separator.

Current density-Charge capacity

- 5 mA cm⁻², 1 mA-hr cm⁻²
- 10 mA cm⁻², 1 mA-hr cm⁻²
- ◐ 20 mA cm⁻², 1 mA-hr cm⁻²

In general, it was observed that current densities of 10 and 20 mA/cm² or a loading of 2 mA-hr/cm² resulted in concentration polarization of the lithium electrode on repeated cycling. The dismantling of the used cell revealed the presence of considerable dendritic lithium in the first two separator layers next to the working electrode.

e. The self-discharge of the lithium anode.

Figure 10 gives the charge retention under open circuit of electrochemically formed lithium electrodes. It may be seen from Figure 10 that the utilization efficiency of lithium on aluminum was not affected by open circuit standing. However, lithium deposited on copper underwent self-discharge. During the course of four hours, the efficiency decreased from 80 percent at zero hour to 40 percent after four hours.

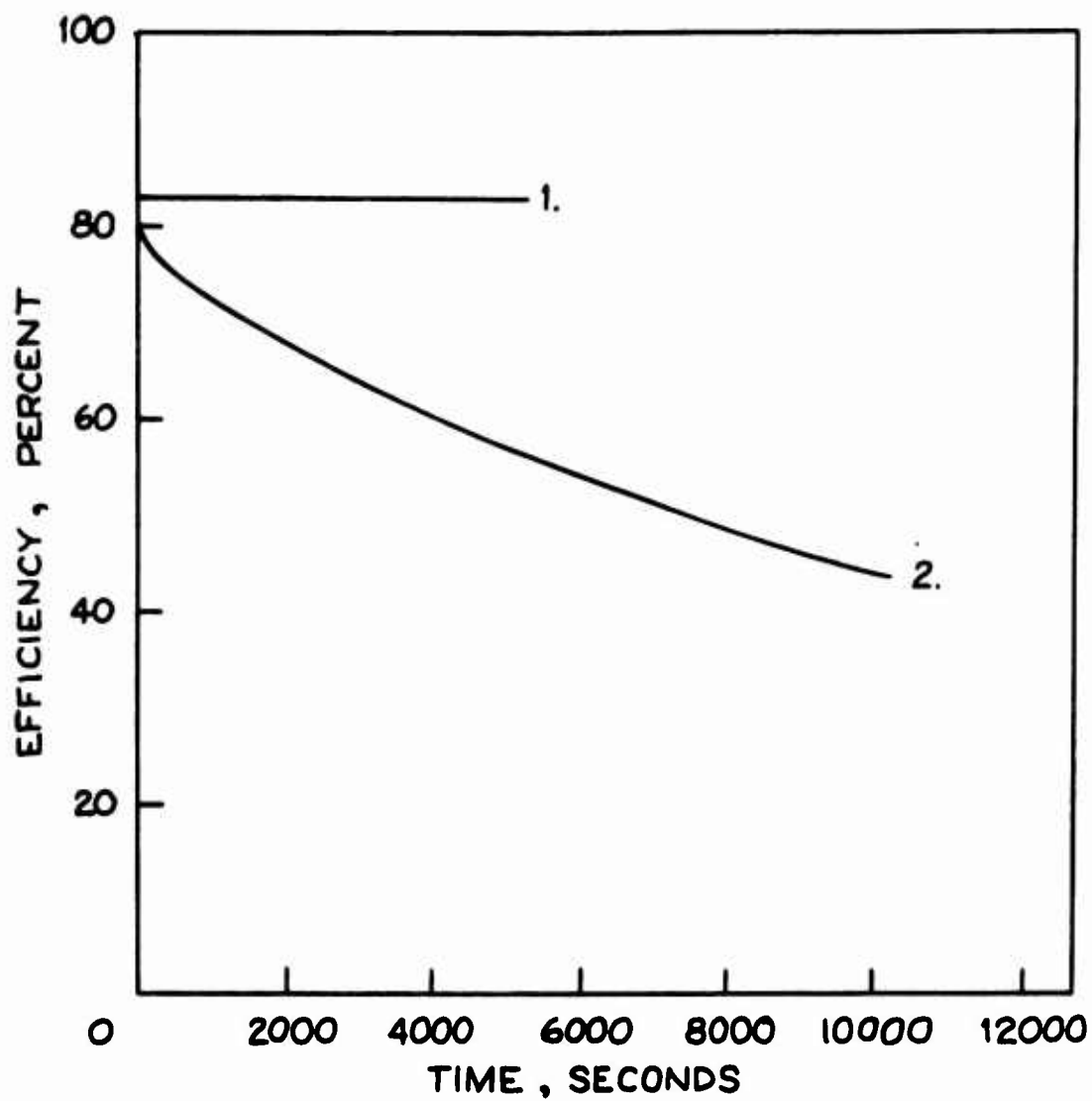


Figure 10. Self-discharge of lithium in 1M LiAlCuCl_4 -P.C.

1. Lithium on aluminum substrate.
2. Lithium on copper substrate.

III-B.

COPPER CHLORIDE CATHODE

1. The Problem: In Section II, some of the outstanding problems of the copper chloride cathode have been discussed. These may be reiterated as follows.

- (i) The problem of low efficiency of copper chloride electrode.
 - (ii) The necessity of utilizing the divalent copper state.
 - (iii) The interference of disproportionation reactions between Cu^{++} , Cu^+ and Cu^0 .
- and (iv) The problem of developing suitable electrode structures for cell studies.

These aspects have been examined during the course of the present work and the results will be reported in this section.

2. The Method of Approach:

The problem relating to the low efficiency of utilization of copper chloride is connected with the mechanism of formation and discharge. This has been examined by carrying out charge-discharge experiments on copper in half-cell configurations. The state of oxidation of the anodic product has been analysed by x-ray diffraction techniques. The problem of interference due to disproportionation reactions have been investigated by analysing the chemical composition of the salts in equilibrium. For the development of suitable electrode structures, pasted plate technique have been employed. These approaches have resulted in an understanding the inherent limitations of the system. In addition, experiments have been carried out to improve the performance of the cathode. The details the experimental approaches are discussed in context with the individual experiments.

3. Experimental, Results and Discussion:

- a. On the mechanism of charge-discharge.
 - (1) Experimental

(a) Electrodes

Solid copper foils of 99.99 percent purity and thickness between 2 and 30 mils were employed to make working electrodes with superficial areas of 2 to 20 square centimeters. Porous copper electrodes were also used in the experiments. They were 2 square centimeters in projected area, 0.076 cm thick and were designated by the manufacturer (Clevite Corp.) to have a porosity of 62 percent. After the electrodes were cut to the required size, copper leads were attached by spot welding. Solid copper electrodes were cleaned in dilute nitric acid followed by rinsing in distilled water and acetone. Porous copper electrodes were used without any pretreatment. In order to prevent the shedding of products formed during anodization, a layer of Whatman No. 40 filter paper was wrapped around the working electrode.

(b) Analytical Techniques

Polarography was used to identify and to estimate the dissolved copper ion species formed in solution during electrolysis. For this purpose, 1-ml aliquots of the electrolyte from the working electrode compartment were added to a thoroughly deaerated, known volume of aqueous 1 M HCl contained in the polarographic cell. Such a medium preserves the ratio of copper (I) and copper (II), since copper (I) will not disproportionate⁶, and no copper metal is present to reduce copper (II) to copper (I). This procedure for analysis allowed the unequivocal identification and estimation of the copper ion species initially present in the working electrode compartment. In other respects the polarographic measurements were conventional and the results were compared against known solutions of copper (I) and copper (II) in aqueous 1M HCl. A Metrohm Polarecord Model E-261 was used in this work.

(c) Specific Experiments

The following experiments were done.

(i) Charge-discharge behavior of solid copper electrodes.

Solid copper electrodes of known dimensions were submerged in a solution of 1 M LiAlCl_4 in propylene carbonate in the working electrode compartment of the cell. The electrodes were anodically charged to capacities of 2.5

to 10 mA-hr cm⁻² at 0.5 to 10 mA cm⁻². The charged electrodes were subsequently discharged at various current densities. Both the variation of electrode potential with time and the utilization efficiency were investigated. The utilization efficiency was calculated by dividing the coulombs recovered on cathodization by the coulombs passed during the preceding anodization.

(ii) Composition of Electroformed Salt

A 20 cm² area electrode was anodized at 10 mA for 15 hours. A large amount of insoluble salt formed on the electrode. The electrode and the adhering salt were repeatedly rinsed in propylene carbonate and then dried. The composition of the salt was determined by x-ray diffraction, using a Phillips Type 422730 x-ray diffraction unit. For the cell constants, copper radiation (no filter) was employed.

(iii) Maximum possible loading.

The maximum anodization that an electrode could sustain was determined by charging anodically a 2 mil thick copper foil of approximately 20 mA-hr theoretical capacity (based on a one-electron oxidation). This electrode could be smoothly charged to a capacity greater than 18 mA-hr. Further charging was limited by the physical discontinuity of the metal due to the exhaustion of the metal rather than to passivation problems.

(iv) Solubility Measurements

At various intervals of time during the charging and discharging of the electrode, 1 ml aliquots were taken from the working electrode compartment and analyzed to determine the nature and concentration of the dissolved copper species.

(v) Open circuit stability of the charged electrodes.

Solid copper electrodes were anodized at 5 mA cm⁻² in 30 ml of solution to a capacity of 3.25 mA-hr cm⁻², and were allowed to stand on open circuit in stirred solution for 5-1/2 hrs. The solutions were analyzed for dissolved copper species before and after the open circuit stand.

(vi) Effect of electrolyte composition on charge-discharge efficiency of electrodes was studied similarly in an electrolyte of composition: 1 M in LiAlCl₄ and 0.5 M in AlCl₃.

(2) Results and Discussion

(a) The Charging Process

The anodic charging of copper metal electrodes in a propylene carbonate solution, 1M in LiAlCl_4 , produced a partially soluble greenish white salt on the electrode. No change in the color of the solution was observed due to the dissolution of the salt. The charging curves, shown as curves (1) and (2) in Figure 11, exhibited a single plateau. The salt remaining on the electrode was analyzed by x-ray diffraction as described above. The results are shown in Table 2. Only three lines were observed and these are compared with the ASTM data for CuCl .

TABLE 2

Chrystallographic Examination of Electro-oxidized
Product of Copper in 1M LiAlCl_4 - P.C

2 θ (Literature, Cu radiation)	I/I ⁰ (Literature)	2 θ (observed)	I/I ⁰ (observed)
28.52	100	28.25	100
47.44	55	47.15	54
56.28	32	56.00	29

The data in Table 2 provide conclusive proof that the bulk of the salt produced on anodic charging was CuCl .

The electrolyte composition was analyzed during anodic charging. The results are shown as Curve (A) of Figure 12. Only copper (I) was found in solution. The concentration of copper (I) increased initially and then leveled off at a value which is assumed to be the point of saturation. This conclusion is supported by the observation that when an anodically charged copper electrode was allowed to stand on open circuit for as long as 5-1/2 hrs. there was no further significant change in the concentration of copper (I) in solution. From these data we may calculate the solubility of copper (I) in this electrolyte to be $4.64 \times 10^{-3} \text{ M l}^{-1}$ at 25°C.

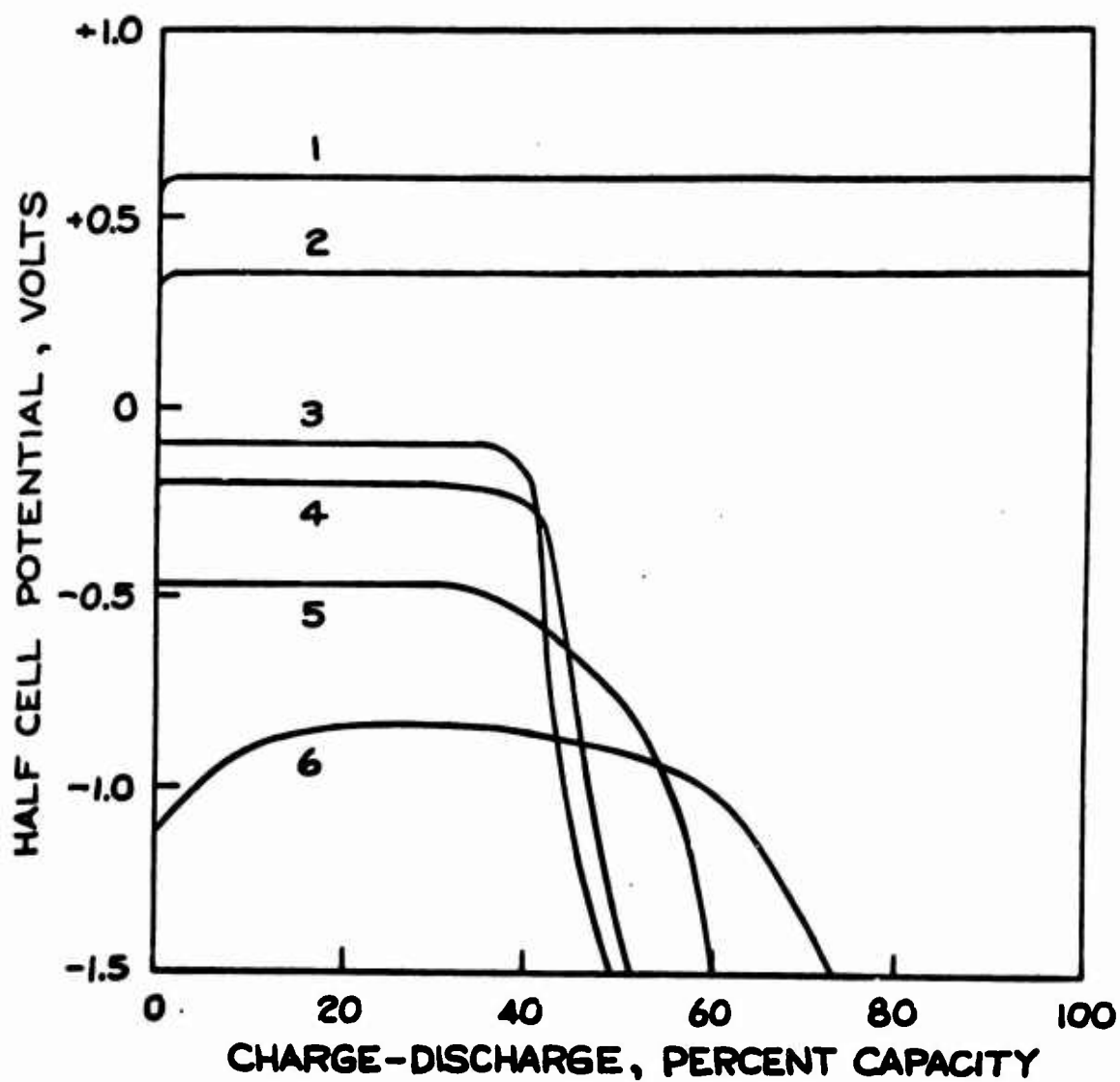


Figure 11. Charge-discharge behavior of copper electrodes in 1M LiAlCl_4 -P.C
Capacity of charging: $2.5 \text{ mA-hr cm}^{-2}$
Curves (1) and (2) refer to anodic charging at 2.5 and 0.5 mA cm^{-2}
Curves (3) to (6) are for discharge at 0.5 , 2.5 , 5 and 10 mA cm^{-2} respectively

(b) The Discharge Process

Cathodic discharge curves for the product formed during anodic charging are shown as Curves 3 to 6, Figure 11. These discharge curves were obtained on copper foil electrodes which had been anodically charged to a capacity of $2.5 \text{ mA-Hr cm}^{-2}$. A single discharge plateau was observed. The utilization efficiencies, calculated as described above, varied with the discharge current density from approximately 50 percent at 0.5 to 2.5 mA cm^{-2} to 70 percent at 10 mA cm^{-2} . It was also observed that the color of the solution in contact with the working electrode changed from a light to deeper yellow upon discharge.

Since the utilization efficiencies observed were rather less than 100 percent it was necessary to analyze the probable causes of the observed inefficiencies. The following phenomena and properties may cause a low efficiency. (a) Parasitic oxidation and reduction reactions, (b) trapping of electroactive material in electrode region not accessible to electron transfer due to shedding or irregular current density distribution, and (c) solubilization of active material in the electrolyte and the diffusion of solubilized species away from the electrode. During the investigations, the variation of the copper (I) concentration in the solution was also measured as a function of the depth of discharge. Surprisingly, the copper (I) concentration increased during the discharge cycle. The observed buildup is presented in Figure 12, Curve (B). It may be seen that the Cu^+ ion concentration increased sharply from 4.64×10^{-3} moles/l at the end of the charge cycle to 2.72×10^{-2} moles/l at the end of the discharge cycle. The observed result was unexpected and seems to have no parallel in electrode processes occurring in aqueous systems.

It was possible to fully account for the loss of efficiency from the magnitude of estimated concentrations of the dissolved copper (I) species. In a typical experiment, an equivalent of 4.1×10^{-3} moles of electricity were used for the charging of the electrode, and an equivalent of 2.46×10^{-3} moles were recovered upon discharge. The analysis of the solution for the Cu^+ ion concentration after the discharge cycle indicated the presence of 1.68×10^{-3} moles of Cu^+ ions in the solution which accounted for the low efficiency on discharge. It was

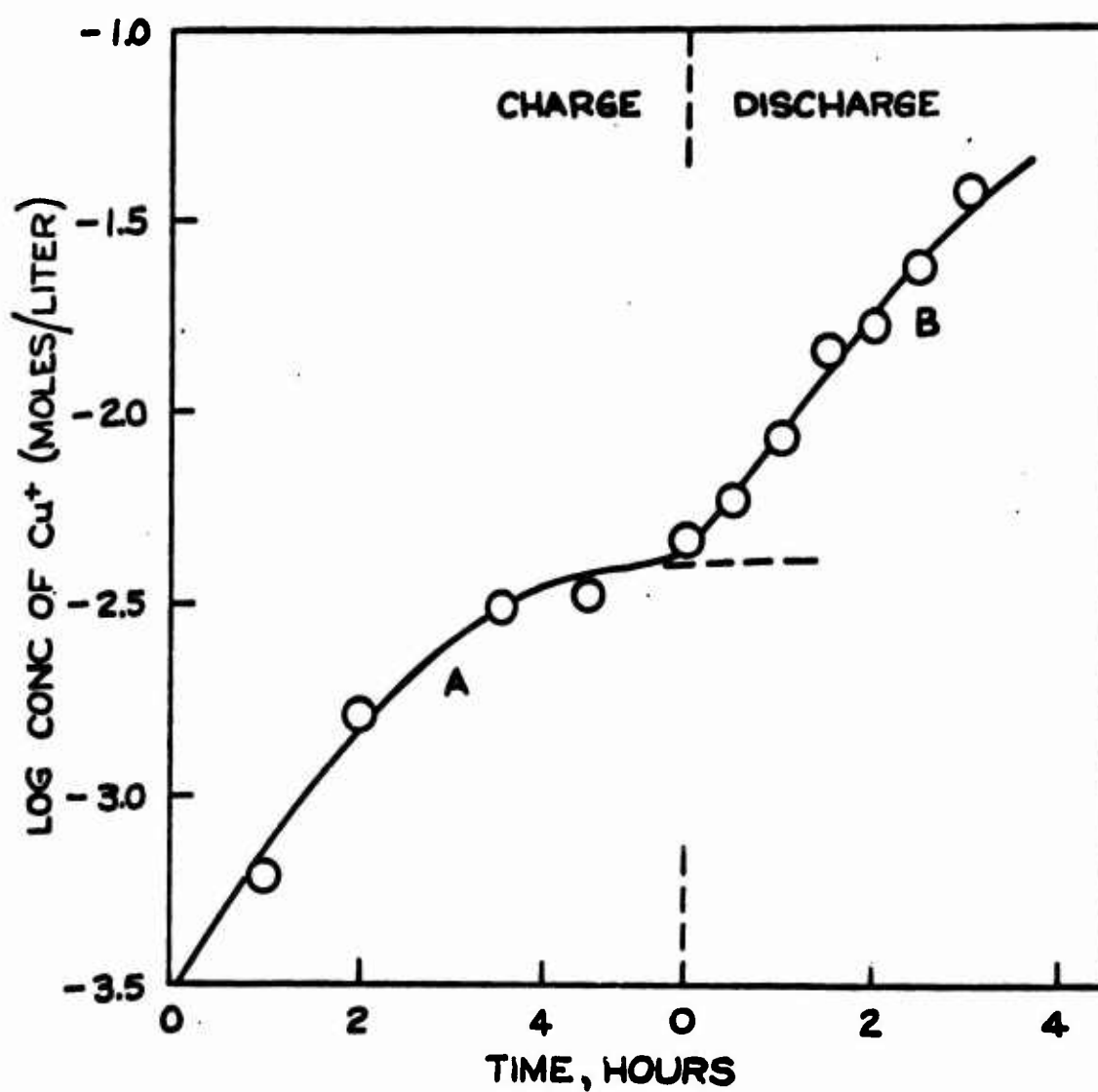
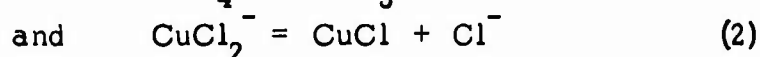
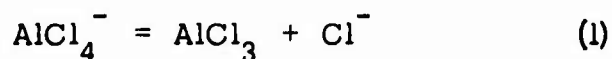


Figure 12. Buildup of copper (I) concentration in the working solution during charge and discharge of copper electrodes in 1M LiAlCl₄-P.C

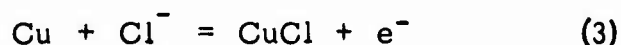
interesting to note that the data indicated a current efficiency of a hundred percent for the cathode salt formation process. Obviously, some ionic process occurred during the discharge that resulted in the production of a copper species more soluble than CuCl. The following explanation may be offered at this time to explain the observed behavior.

Earlier investigations of copper salt systems in organic electrolyte media had led to the suggestion that there is a strong tendency for copper chloride to form more soluble CuCl_2^- ions in the presence of free chloride ions. The exact experiments in this regard concerned measurement of the conductivity of propylene carbonate suspensions of insoluble CuCl and insoluble LiCl. The conductivity of the equilibrium solution in contact with different proportions of CuCl and LiCl increased linearly till equimolar amounts of CuCl and LiCl were present. Thereafter the conductivity did not increase appreciably with further addition of LiCl. The observed increase in conductivity up to 1:1 mole ratio has been explained on the basis of formation of a more soluble CuCl_2^- complex. This led to the formulation of a reaction mechanism involving the cathodic generation of this complex to account for the increased solubility observed in the present experiments.

To examine why more copper (I) goes into solution on cathodic discharge than on anodic charge, it is convenient to consider the following equilibria



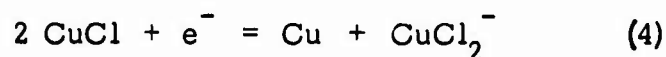
and the reversible electrode reaction



The equilibrium for reaction (1) lies predominately to the left, as is known from the fact that LiCl, which is relatively insoluble in propylene carbonate, does not precipitate in 1M LiAlCl_4 solution in propylene carbonate. The equilibrium for reaction (2) lies predominately to the left also, in the presence of a sufficiently large chloride concentration. This is not the case for the LiAlCl_4 solution, and there is little tendency for the CuCl to go into

solution, as attested by the solubility for copper (I) in this solution of $4.64 \times 10^{-3} \text{ M l}^{-1}$.

At the electrode/solution interface the net reaction during anodization involves the consumption of chloride ions (reaction (3) from left to right); and, hence, there is even less tendency for the dissolution of copper (I) through formation of CuCl_2^- . It is reasonable to assume that the aluminum chloride generated in the above reaction may diffuse away from the electrode. Consequently, at the beginning of discharge the concentration of AlCl_3 at the electrode/solution interface would be less than needed for reversing the quasi-equilibrium steps involved during charging. As such, part of the Cl^- ions released during discharge (reaction (3) from right to left) become available for combination with undischarged CuCl to form the soluble CuCl_2^- species as in



Thus, the formation and diffusion of CuCl_2^- away from the electrode would account for the observed increase in the Cu^+ ion concentration in solution and the low efficiency upon discharge.

(c) The following experiments were designed to take advantage of this postulated mechanism to improve the utilization efficiency of the copper electrode.

(i) Increasing the current density of discharge should increase the utilization efficiency since a large fraction of the soluble CuCl_2^- species would be reduced before they can leave the domain of reduction, the electrode. The results shown by Curves (5) and (6), Figure 11, demonstrate that this did, indeed, occur.

(ii) Increasing the porosity of the electrode should increase the utilization efficiency since the tortuous channels of the porous electrode would impede the diffusion of the CuCl_2^- species into the solution, and a larger fraction of the salt should be reduced. This did occur, as is demonstrated by Curve 3, Figure 13, where a cathodic utilization of 85 percent

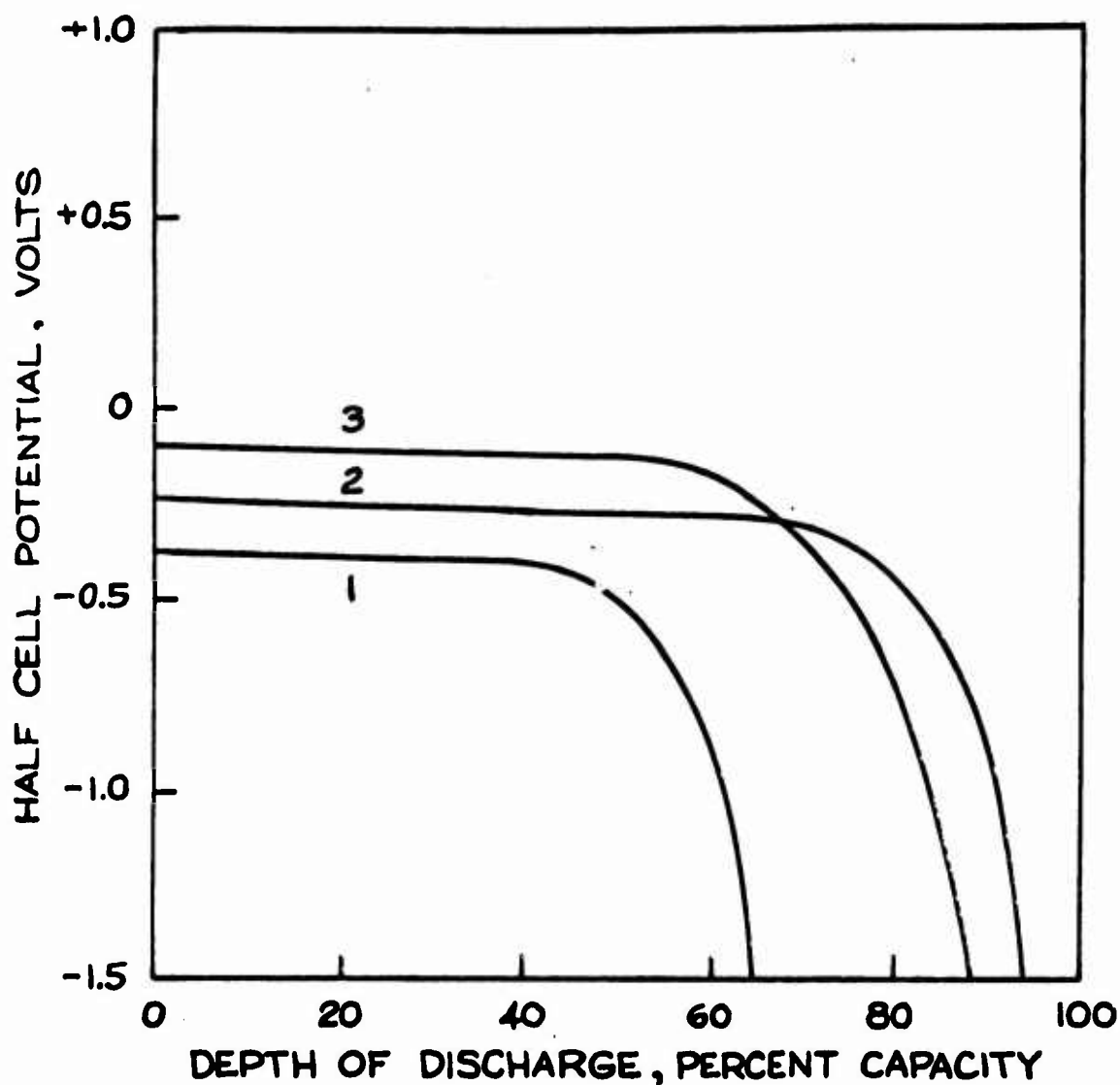


Figure 13. Discharge behavior of charged solid and porous copper electrodes.

Initial charge capacity: $2.5 \text{ mA-hr cm}^{-2}$

Discharge current density: 2.5 mA cm^{-2}

Curve (1) and (2) discharge of electroformed CuCl on solid and porous copper electrode in 1M LiAlCl_4 containing 0.5 M AlCl_3 in propylene carbonate

Curve (3) discharge of electroformed CuCl on porous copper electrode in 1M LiAlCl_4 in propylene carbonate.

was realized with the porous electrode under conditions where the solid electrode would have only yielded a utilization efficiency of 50 percent.

(iii) Increasing the concentration of AlCl_3 should increase the utilization efficiency. This may be seen from an examination of reactions (1) and (3). The larger the concentration of AlCl_3 , the more effective will be the competition of AlCl_3 for chloride ions, and the smaller will be the degree of complexation of CuCl with chloride ions. This was demonstrated to occur as shown by Curves (1) and (2), Figure 13, and Curve (4), Figure 11, in the 1M LiAlCl_4 solution containing 0.5 M AlCl_3 the utilization efficiency was greater than 90 percent, whereas, under similar conditions, the utilization efficiency was only 50 percent when additional AlCl_3 was not present.

b. The Utilization of Divalent Copper State

(1) The Problem: Since the formation of CuCl_2 is desirable from an energy density point of view, the most important question that had to be answered was whether or not it is possible to oxidize copper completely to cupric chloride. The investigations relating to that aspect of the problem are dealt with in this section of the report.

(2) Method of approach.

It was suggested in the previous section that the limitation on the oxidation of copper to CuCl only may be due to the formation of non-conducting cuprous chloride.

It was also suggested that it may be necessary to develop conducting electrode substrates in which the initial oxidation product, CuCl , can be trapped and subsequently oxidized to CuCl_2 . During the studies emphasis was placed upon the possibility of obtaining CuCl_2 , rather than on the optimization of the electrode structure. Electrodes were used which consisted of a mix of carbon with cuprous chloride, and a suitable binder in the form of pressed pellets or pasted plates.

(3) Electrode Preparation

(a) Pressed pellet electrodes.

Dry pressed pellet type electrodes were prepared from a dry mix of 6:1 (wt) of CuCl and graphite with a 10 percent (wt) mix of gum arabic added as binder. The pellets were made by pressure densifying 0.2 to 0.5g of the mix in a stainless steel die of 1 square centimeter area piston. The die had provisions for embedding one end of a stainless steel wire in the mix. The wire was inserted to make an external connection to the active mass. The mix with the wire was pressed at 64,500 pounds for pelleting.

(i) Results and Discussion

The dry pressed pellets possessed good mechanical strength. However, the wet strength in 1M LiAlCl_4 - P.C was very poor. Complete disintegration of the pellet occurred upon passage of current. Increasing the ratio of graphite to cuprous chloride to 1:1, or doubling the ram pressure or changing the binder concentration did not indicate any improvement in the wet strength of the pellets, hence, the dry powder pressing technique was abandoned.

(b) Pasted plate electrodes.

To a 6:1 (wt) mix of cuprous chloride and carbon (graphite or acetylene black in powder form) 4 to 6 cc of different solvents containing 2 to 5 percent (wt) of binder was added and a wet paste prepared. The paste was spread uniformly over a 3" x 3" substrate in the form of a foil or a woven graphite cloth and dried. Both aqueous and non-aqueous binders were tried.

(i) Investigations employing aqueous binders.

Aqueous solutions of polymers such as gelatin, gum arabic, gum tragacanth, gum karaya were used as binders. The pastes were spread on 1 mil stainless steel foil and also on 200 mesh stainless steel wire cloth. The pastes were air dried for 15 to 26 hours.

(ii) Results and Discussion

The air dried pasted plate electrodes with graphite had multiple cracks indicating discontinuities and poor adhesion. Because of this problem, it was not possible to make any satisfactory electrochemical measurements on these electrodes. Acetylene black was substituted for graphite in a

second series of electrodes. The dried pastes showed fewer cracks which indicated a better adhesion. Upon subjecting the electrodes to electrochemical measurements, shedding of the active material was noticed. Thus, the experiments indicated the necessity of changing to steels of more inert composition or to alternate materials such as tantalum or graphite or carbon plates or woven carbon cloth. Because of the shedding problems encountered in the case of aqueous binders further experiments were abandoned.

(c) Investigations employing non-aqueous binders.

A problem encountered with binders soluble in organic solvents was the limited choice of materials. Even binders such as acrylics showed solubility in propylene carbonate and, hence, could not be used. Based on the insolubility of ethyl cellulose in propylene carbonate, this material was chosen as a binder. The solvents employed to make the paste consisted of benzene, toluene, and xylene. In the case of pastes made with benzene and toluene, drying of the paste was experienced while spreading it on graphite cloth, hence, a xylene solution of ethyl cellulose was preferred. The cuprous chloride pasted plate electrodes were made as described earlier. They had capacities of 5-10 mA-hr/cm² depending upon the quantity of material used and the thickness of spreading. The wet strength of these electrodes was good.

(4) Examination of the electrochemical behavior of pasted plate cuprous chloride electrodes.

For the purpose of electrochemical examination, samples of 1 to 5 sq cm area were cut from the 3" x 3" batch, and the active material was removed from part of the electrode by using a sharp knife to expose the graphite cloth for making electrical connections to the electrodes. The electrodes were weighed to obtain the amount of active material present. Suitable clips with lead wires attached were used to make electrical contacts. The electrodes were immersed in 1M LiAlCl₄ - P.C without dipping the contact or lead wires into the solution and charge-discharge experiments were carried out at current densities of 1 to 10 mA cm⁻².

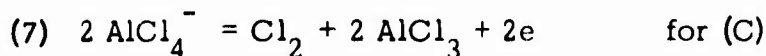
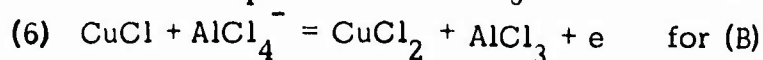
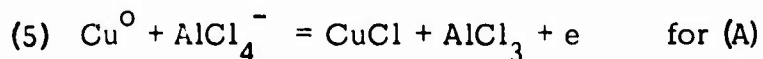
(5) Results and Discussion

(a) The Discharge Behavior of pasted plate CuCl electrodes.

A typical discharge curve at 5 mA cm^{-2} for a 1 cm^2 area pasted plate electrode of capacity 5.5 mA-hr is presented in Figure 14. The open circuit voltage was 0.8V vs. Ag which did not correspond to the thermodynamic value of $+0.124\text{V}$ vs. NHE for the couple $\text{Cu}^0/\text{CuCl}/\text{Cl}^-$. This may be due to air oxidation of CuCl at the surface. The discharge plateau was in the range of -0.3 volts and was comparable to the voltages observed on CuCl electrodes formed on copper (c.f. figure 11, curve 3). From the capacity of the electrode, discharge current and time, the utilization efficiency was calculated to be 52 percent. The behavior of pasted plate electrodes was similar to the CuCl electrodes formed on non-porous copper in all respects, but the reproducibility of the efficiency data was poor because of the shedding of active material. Enclosing the electrodes in layers of filter paper did not improve the reproducibility very much. For different electrodes, the efficiency ranged from 40 to 60 percent under similar conditions.

(b) Charging Behavior of pasted plate CuCl electrodes.

The charging curve of the discharged CuCl electrode used in the previous experiment is given in Figure 15. The curve has three plateaus A, B, and C, which may correspond to the following reactions:



Of these possible reactions, the oxidation of CuCl to CuCl_2 was of utmost interest to us. In order to examine the possibility of the electro-oxidation of CuCl to CuCl_2 in 1M LiAlCl_4 test electrodes were anodised at potentials below 1.2V vs. Ag.

In one set of experiment, the oxidised electrode was transferred into a known volume of 1M aqueous HCl in the polarographic cell, and the dissolved copper salt was analyzed for its Cu^+ and Cu^{++} content. Upon comparing

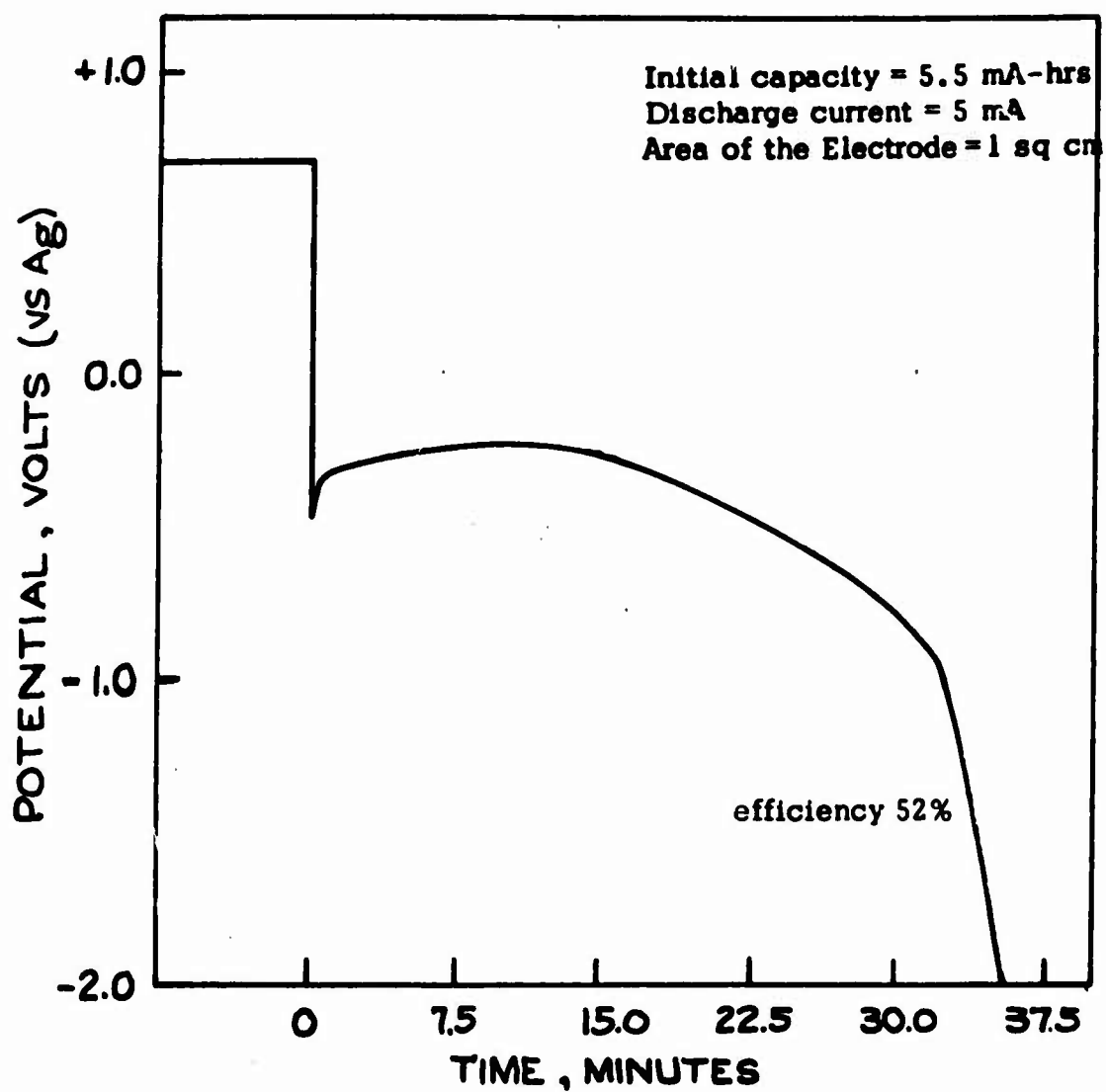


Figure 14. Discharge of pasted plate CuCl electrode in 1M LiAlCl₄ - P. C.

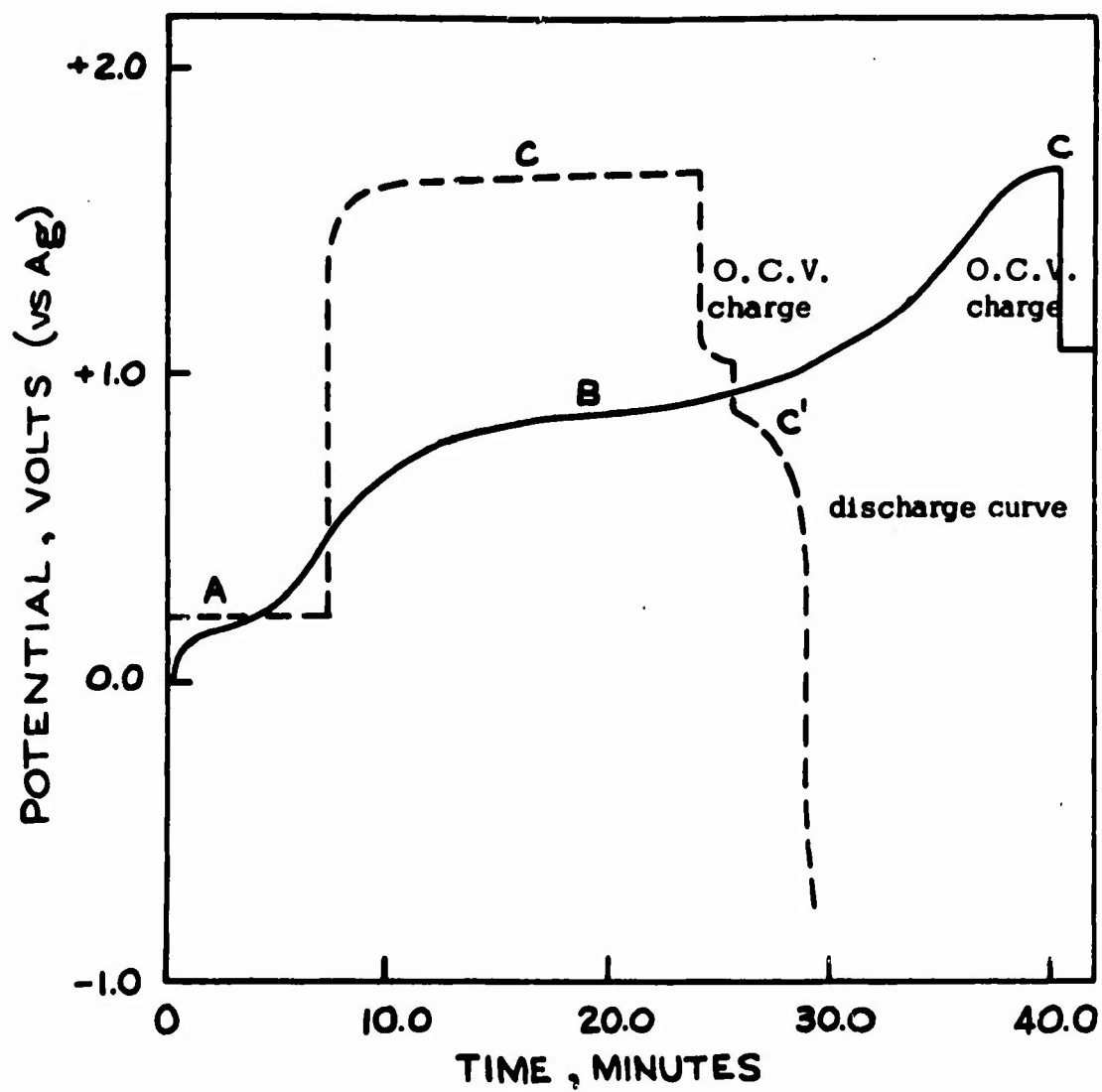


Figure 15. Nature of anodic charging curve for discharged CuCl electrode in 1M LiAlCl₄ - P. C.

the data on non-oxidised electrodes of similar capacity, it was noticed that the solution from the oxidised electrode samples had a larger Cu^{++} concentration. Thus, the first indication of the possibility of the oxidation of Cu^+ to Cu^{++} was obtained. Attempts were then made to relate the anodic charge to the amount of Cu^{++} obtained. The reproducibility of the data in this regard was poor and may be traced primarily to the shedding of the active material during anodization.

A direct proof for the formation of CuCl_2 from CuCl during the electro-oxidation of pasted plate CuCl electrodes in 1M LiAlCl_4 - P.C was obtained from x-ray diffraction measurements. 2 cm^2 area pasted plate CuCl electrodes that had been subjected to anodic oxidation in 1M LiAlCl_4 - P.C, were removed from the test cell, rinsed in deaerated propylene carbonate, and dried by pressing them under filter paper. The active material was removed from the electrode and transferred to the sample holder for x-ray diffraction analysis. The data indicated the presence of (1) CuCl , (2) anhydrous CuCl_2 , and (3) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Table 3.

TABLE 3

X-ray Diffraction Data for Anodized Pasted Plate CuCl
Electrode (Cu K α radiation, 35 kv, 15 mA)

Possible Compounds Present					
Compound (I) CuCl		Compound (II) CuCl_2		Compound (III) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	
2 θ Observed	2 θ Reported	2 θ Observed	2 θ Reported	2 θ Observed	2 θ Reported
28.54	28.52	26.5	26.02	16.1	16.4
47.4	47.44	38.0	38.1	21.8	22.04
56.2	56.28			28.7	28.96
				33.9	36.04
				40.8	41.00
				44.7	45.06
				49.0	49.2
				57.3	57.6

The presence of CuCl in the anodised sample was due to unreacted cuprous salt. The intensity distribution of the three lines observed in the x-ray spectra for this compound followed the ASTM data. It is to be noted that only two lines were identified corresponding to anhydrous CuCl_2 , while a large number of lines corresponded to the data for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Since anhydrous CuCl_2 is very hygroscopic, the hydration of the sample may have occurred during the transfer, or possibly during the x-ray measurements changing any anhydrous CuCl_2 formed to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The data, however, confirmed the formation of divalent copper chloride during the electro-oxidation of CuCl in the presence of an inert substrate.

(c) Electro-formation of CuCl from pasted plate Cu^0 electrodes.

For purposes of identifying the possible reaction in plateau region (A), Figure 15, pasted plate electrodes were prepared from copper-acetylene black mix. The electrodes were oxidised in 1M LiAlCl_4 - P.C till plateau (B) was reached, and the oxidation product was analysed crystallographically. The analysis revealed the oxidation product as cuprous chloride. Hence, it was confirmed that plateau (A) corresponded to the formation of cuprous chloride, probably according to the overall reaction represented in eq. (5).

(d) Chlorine evolution reaction.

On the continued anodic polarization of the electrode beyond region (B), in curve (1), figure 15, another potential plateau was observed in region (C). The plateau region (C) did not involve reactions of copper salts. This was indicated by the fact that the polarization of graphite cloth alone gave rise to the potential plateau (C) as observed in curve (2) figure 15. Upon interruption of the polarization current, the open circuit potential was established at 1.1 to 1.25V vs. Ag. Further observation of the system indicated that gas evolution occurred during the passage of the current. Because of the magnitude of open circuit potential and the pungent odor of the gas, the evolved gas was swept by a stream of argon through a solution of potassium iodide. Liberation of iodine was noticed during the process which indicated the oxidising nature of the gas. Further, another sample of gas was collected in a dilute

solution of sodium hydroxide. The alkali was acidified with dilute nitric acid and a few drops of silver nitrate was added. The precipitation of silver chloride was found to occur. In another test, chlorine was bubbled alongside a graphite electrode immersed in 1M LiAlCl₄ - P.C and the open circuit potential was determined. The magnitude of the measured potential was 1.2V vs. Ag. The above tests identified the reaction occurring in region (C) as a chlorine evolution reaction.

(e) The discharge behavior of charged pasted plate CuCl electrodes.

Figure 16, curve (1), gives the discharge behavior of an over-charged electrode. In the particular illustration, the pasted plate cuprous chloride electrode had received an overcharge for one-half hour at 5 mA; consequently, it was expected to have some accumulated chlorine in the vicinity of the electrode. This was confirmed by the observed open circuit voltage of 1.2V vs. Ag. Upon discharge at 5 mA a distinct plateau region (C) was observed, and the electrode returned to an open circuit voltage of 1.2V upon interrupting the discharge. Thus, the region (C) was attributed to the chlorine reduction reaction. The region (B) probably corresponded to the reverse reaction of (B) of the charging curve, viz. the reduction of cupric chloride to cuprous chloride. This was confirmed by interrupting the current when the open circuit voltage was observed to be 0.8V. Upon the discharge of a pasted plate cupric chloride electrode, plateau (B) was also observed and is represented by curve (2) in Figure 16. Alternate mechanisms involving the formation of CuCl_3^- , CuCl_2 , $\text{CuCl}_4^{=}$ are also possible for the reduction reaction in region (B), and this part needs further investigation. Upon consumption of the available CuCl_2 , the discharge curve assumed plateau (A) which is 500 to 800 mv cathodic to plateau (B). The plateau (A) was similar to the discharge of CuCl represented in figure 14, and hence may be related to the discharge of CuCl. Metallic copper was noticed on the electrode at the end of the discharge, and this confirmed the CuCl reduction process.

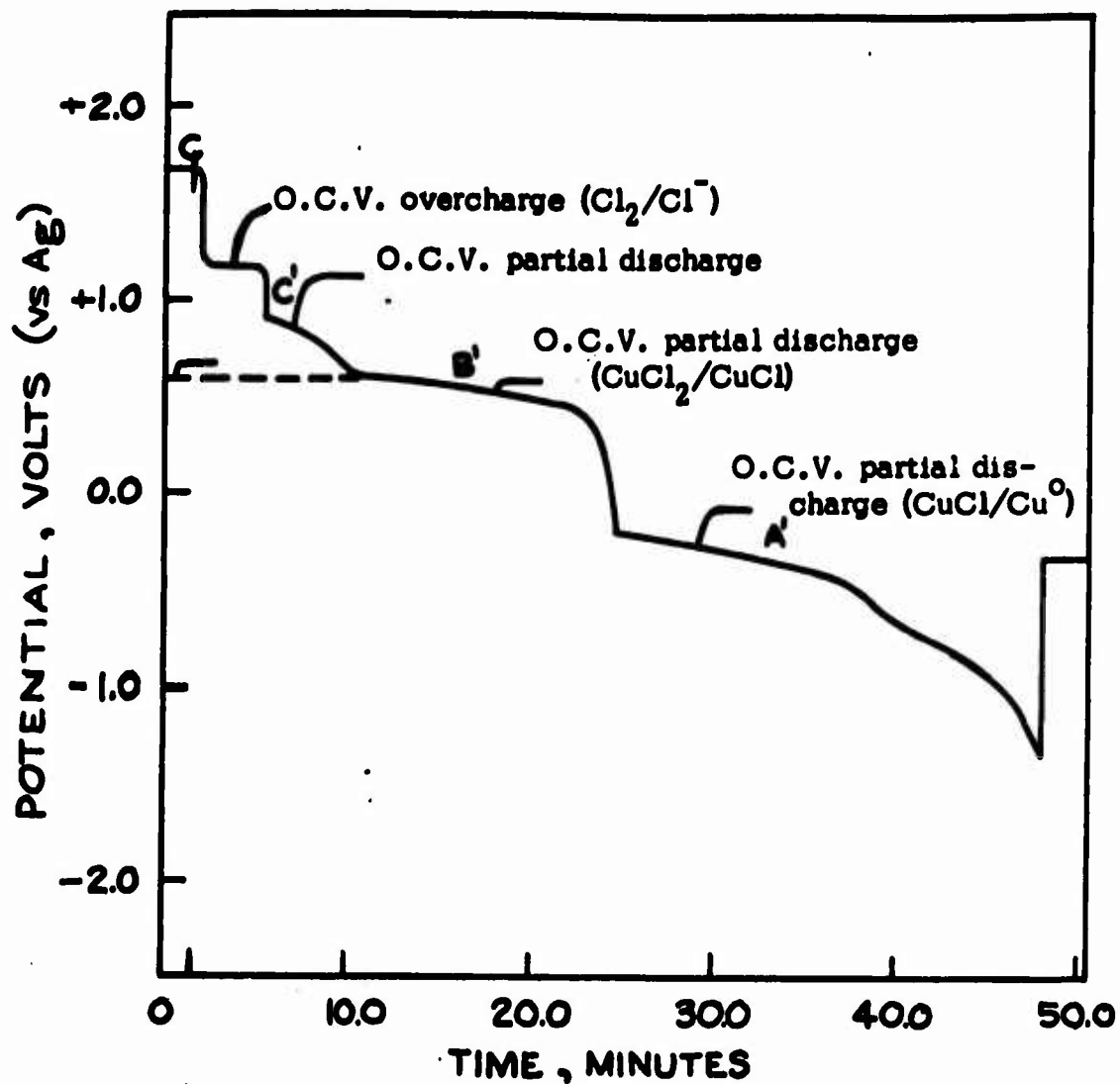


Figure 16. Discharge curve for pasted plate copper chloride electrodes in 1M LiAlCl₄ - P. C.

C. Performance Data on Pasted Plate Electrodes

(1) Electrode Preparation

After confirming that CuCl could be electrochemically anodised in $1\text{M LiAlCl}_4\text{-P.C}$ to form CuCl_2 , investigations were initiated of pasted plate CuCl_2 electrodes. The procedure adopted for the preparation of these electrodes was as follows.

A 7.6:1 weight ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and acetylene black was first treated in water to make a paste and a homogenous mixture of the two components was prepared. The paste was spread on a non-sticking plastic plate (polyethylene or teflon) and air dried. The dried sample was pulverized and sieved to collect the -200 mesh powder. Pasted plate electrodes were prepared from this mixture employing xylene, ethyl cellulose and graphite cloth, according to procedure used for the formulation of CuCl electrodes described earlier (page 38). The electrodes were stored in the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ state when required for use, these were cut to size, and heat treated at 110° to 115°C for 20-30 minutes to dehydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The completion of the dehydration process was confirmed by chemical and x-ray analyses.

(2) Electrochemical Studies

A typical discharge curve for a dehydrated $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ pasted plate electrode is illustrated in Figure 17. The initial open circuit potentials ranged from +0.6 to +0.8V vs. Ag in $1\text{M LiAlCl}_4\text{-P.C}$. The discharge curve had two plateaus, the first one corresponding to the reduction of the divalent copper halide to cuprous salt, and region 2 for the reduction of CuCl to Cu^0 . This behavior is similar to the discharge of preanodised CuCl pasted plate electrodes described earlier. The utilization efficiency ranged from 45-55 percent. Material balance data indicated that the rest of the copper halide, approximately 40-45 percent underwent dissolution, and 5-10 percent of the material remained unreacted. It was evident from the analysis that the tendency of copper halide to form soluble chlorocuprate complex was the cause of low discharge efficiency.

The utilization efficiency obtained during the discharge of electrodes under different conditions of electrode preparation, loading, current density

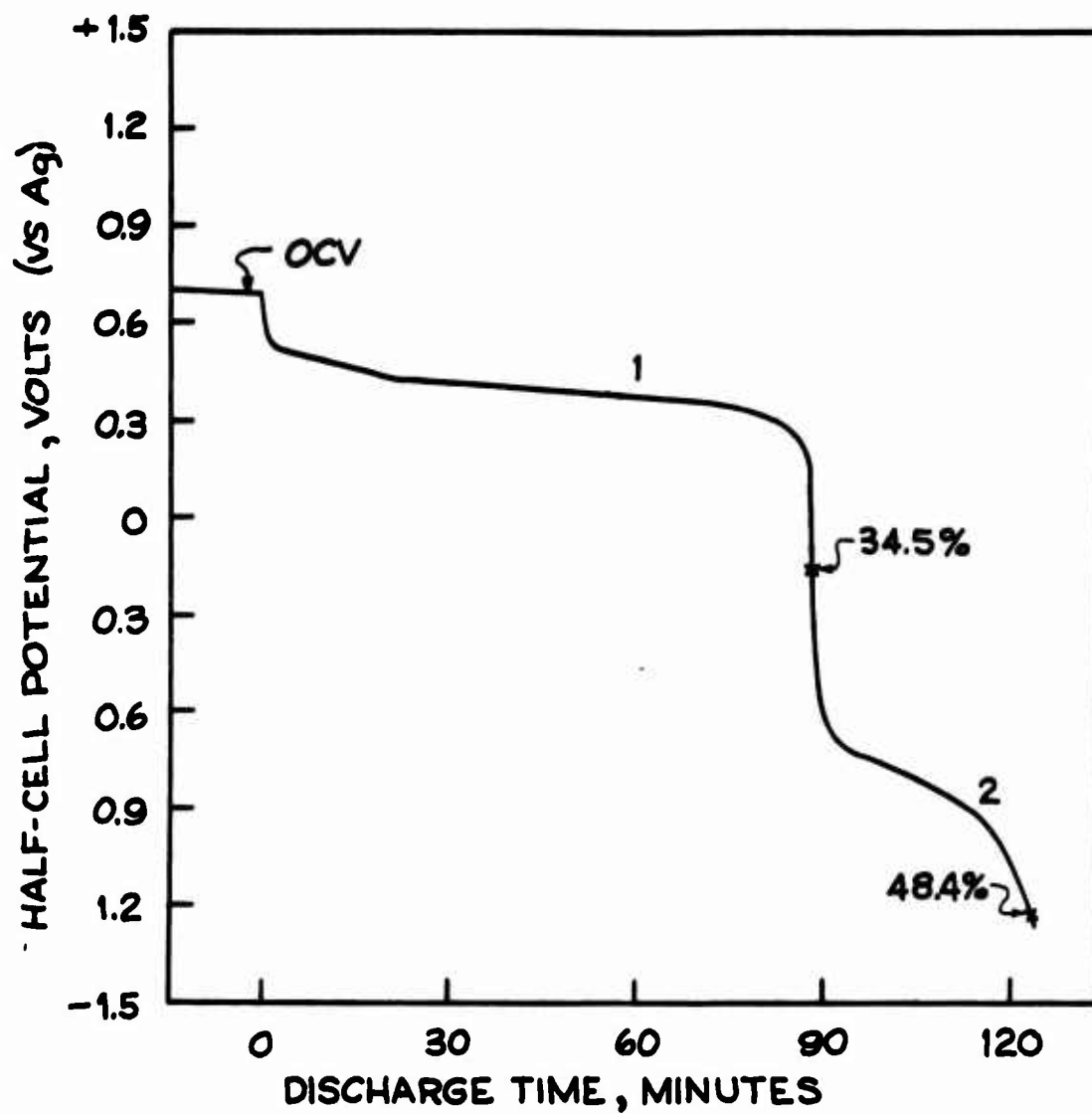


Figure 17. Discharge curve for pasted plate dehydrated $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ electrode. Current 2.0 mA/cm^2 . Capacity $30.6 \text{ coulombs/cm}^2$.

and electrolyte composition is given in Table 4.

TABLE 4

Effect of Electrode Parameter, (Current Density, and the Electrolyte Composition) on the Utilization Efficiency of Pasted Plate Electrodes

Nature of the Electrode	Experimental Conditions			Utilization Efficiency (%) based on Cu ⁺⁺ to Cu ⁰
	Loading Coulombs cm ⁻²	Current mA cm ⁻²	Electrolyte	
A	30.6	2.0	1M LiAlCl ₄ -P.C	48.4
A	28.8	2.5	"	49.9
A	26.1	20.0	"	49.7
A	182.3	2.0	"	49.7
A	192.3	20.0	"	46.2
B	24.4	2.00	"	52.9
A	34.8	2.00	1M LiAlCl ₄ -P.C + 0.5M AlCl ₃	68.0
A	34.4	2.0	1M KPF ₆ -P.C	78.8
A	30.5	2.0	1M LiBF ₄ -P.C	52.0
A	35.0	1.00	1M LiAlCl ₄ -Nitrotoluene	120.0
C	29.2	2.0	1M LiAlCl ₄ -P.C	68.0
D	146.5	7.7	1M LiAlCl ₄ -P.C	49

A = Pasted plate dehydrated CuCl₂·2H₂O electrodes (5% binder)

B = Same as A, but with 10% binder

C = Pocket type pasted plate electrode. The active material was kept in between two layers of graphite cloth.

D = Carbon wafer of 50% porosity impregnated 100% with anhydrous CuCl₂ from methanol solution.

The data in Table 4 indicate that in 1M LiAlCl₄-P.C, a variation in loading, current density, and amount of binder do not have any significant effect on the utilization efficiency. While the sintered plate type structure, as in D, showed no improvement in the utilization efficiency, the pocket type electrodes indicated higher efficiencies. The entrapment and reduction of the chlorocuprate complex at the graphite walls of the sandwich structure may explain the increased efficiency in the latter case. Contrary to the behavior of electroformed CuCl electrodes, the pasted plate CuCl₂ electrodes showed no improvement in the utilization efficiency in the range of 2 to 20 mA cm⁻². However, the addition of excess AlCl₃ to 1M LiAlCl₄-P.C increased the utilization efficiency in agreement with earlier observations (page 37). The effect of the KPF₆ electrolyte in increasing the utilization efficiency may be related to the relatively greater insolubility of K Cl or K CuCl₂ complex in the system. Solvent reduction is an obvious cause of the efficiency in excess of 100 percent observed in the case of the 1M LiAlCl₄-nitrotoluene solution.

The recycling of the discharged pasted plate electrodes is shown in Figures 18 and 19. In these experiments, the anodic and cathodic cutoff points were selected at the sharp changes in half-cell voltage due to chlorine evolution and lithium deposition, respectively. It is seen that the material utilization efficiency decreased sharply with increasing cycle number. It decreased to values below 10 percent after the third cycle. This effect may be related to the increased loss of active material due to solubilization through complexation during each successive discharge. Thus, the inability to retain the reduction product in the structure of the electrode appears to be the major problem. It is interesting to note that the current efficiency during the cycling was greater than 80 percent. This supports the conclusion that if the active materials could somehow be retained in the structure of the electrode, the cycle life of the system could be improved.

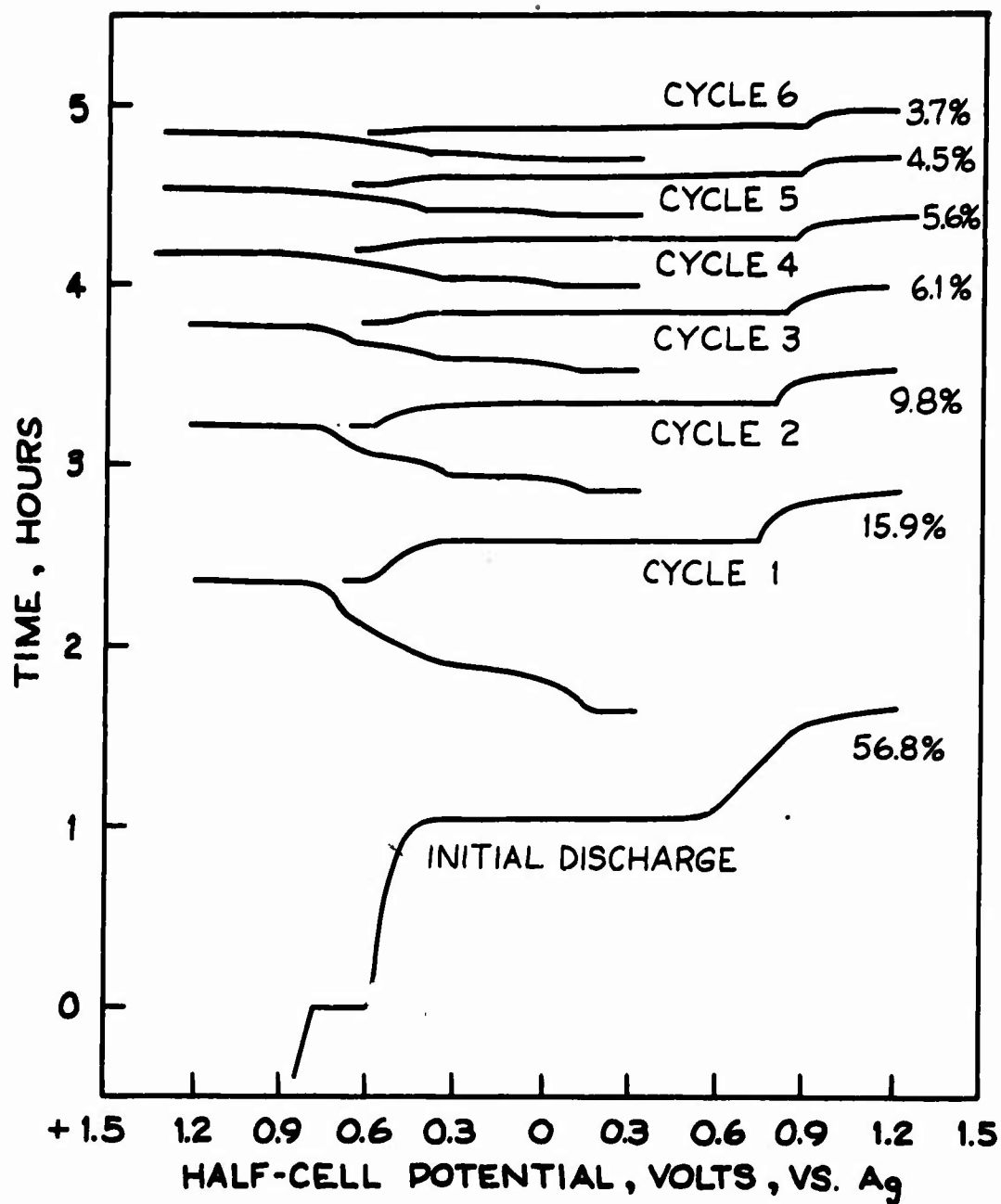


Figure 18. Cycling of pasted plate CuCl_2 electrodes in $1\text{M LiAlCl}_4\text{-P.C.}$.
Current density 2mA cm^{-2} . Initial capacity 22.2C .

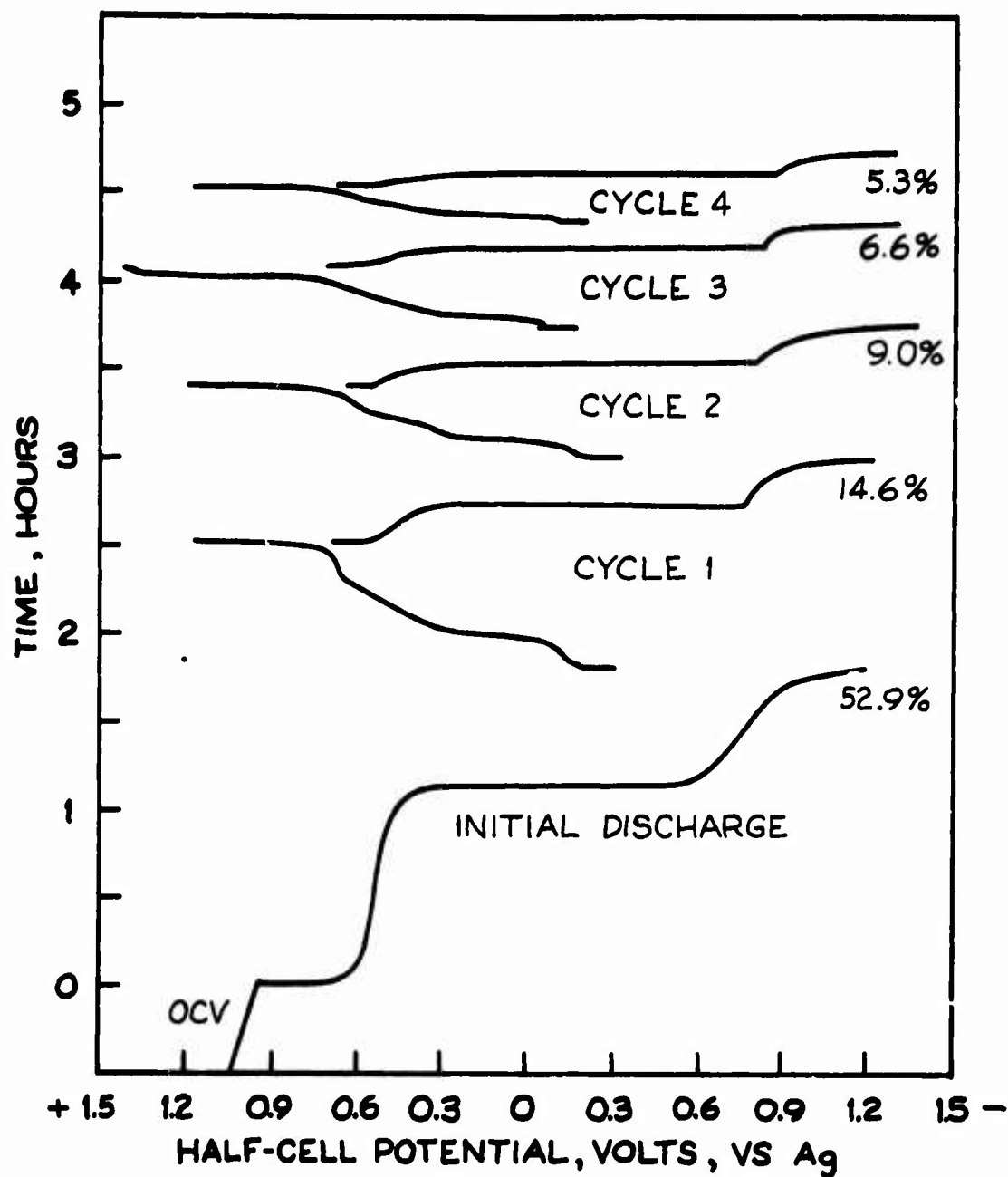


Figure 19. Cycling of pasted plate CuCl_2 electrodes in $1\text{M LiAlCl}_4\text{-P.C}$ current density 2 mA cm^{-2} . Initial capacity 24.2 coulombs.

d. Investigations on the Improvement of the Cathode Performance.

(1) The effect of excess AlCl_3 on lithium and copper chloride half-cells.

(a) The Problem: In the previous sections (c.f.c. iii) it was shown that the addition of excess AlCl_3 to $1\text{M LiAlCl}_4\text{-P.C}$, suppressed the tendency of copper salt to form soluble complexes during discharge, and it increased the utilization efficiency of CuCl_2 . From the point of view of the usefulness of this procedure, in actual cells it is imperative that the following questions be answered.

(i) If the addition of AlCl_3 is useful in improving the efficiency of the cathode, is there an optimum concentration of the AlCl_3 and LiAlCl_4 which gives the best performance of the cathode?

(ii) Is the behavior the Li^0/Li^+ half-cell affected in any way by the presence of excess AlCl_3 in the electrolyte under the optimum electrolyte concentrations, or otherwise?

(b) Method of approach:

In order to answer the above questions, copper chloride and lithium half-cell measurements were made in electrolytes containing various concentrations of LiAlCl_4 and AlCl_3 in propylene carbonate. The experiments concerned mainly the electroformation and discharge of the CuCl and lithium half-cells and were directed towards the evaluation of their rechargeability.

(c) Results and Discussion

Figure 20 gives the variation of the utilization efficiency of electroformed lithium CuCl half-cells in stirred solutions of $\text{LiAlCl}_4\text{-P.C}$ containing AlCl_3 . Stirring was employed to obtain the maximum rate of dissolution of copper salt in the various electrolytes. The results shown in figure 20 indicated that an increase in the AlCl_3 concentration and decrease in the LiAlCl_4 concentration in the electrolyte favoured an increase of utilization efficiency of CuCl discharge. However, the utilization efficiency of electroformation and discharge of lithium under like conditions was adversely affected. Since a high efficiency of both the Li^0 and the CuCl electrodes is

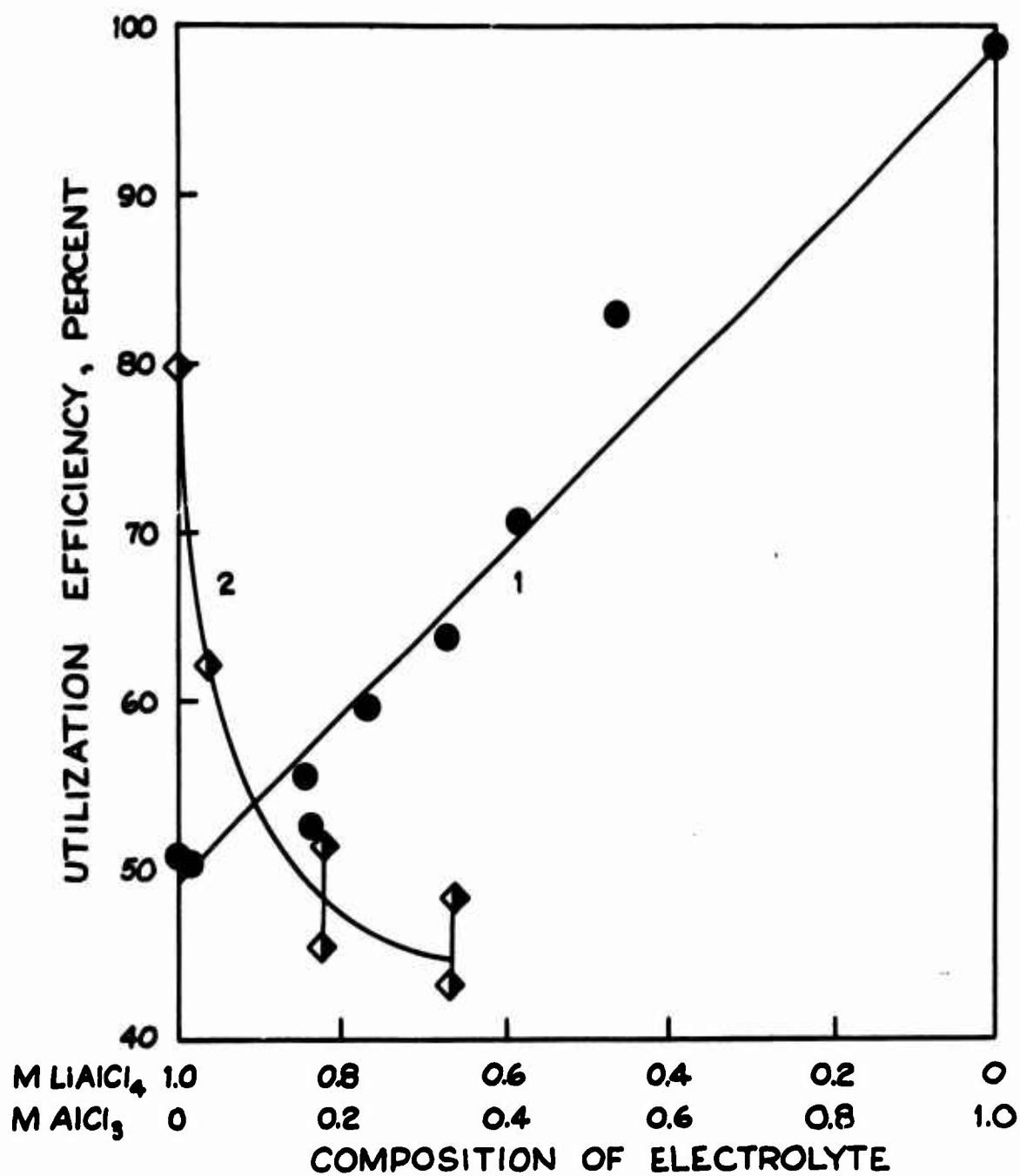


Figure 20. Variation of utilization efficiency of lithium and copper chloride electrodes with electrolyte composition.

1. Performance of copper chloride electrode.
2. Performance of lithium electrode.

necessary to achieve an optimum performance, the addition of excess AlCl_3 to LiAlCl_4 -P.C cannot be considered to be of any practical value for this system.

(2) Investigations in search of means for reducing the copper chloride solubility.

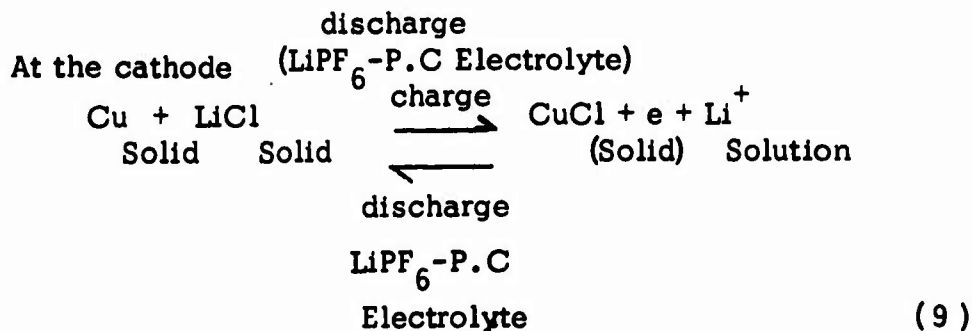
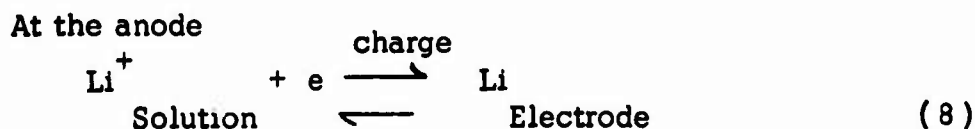
(a) The Problem: In the previous section we indicated that the addition of AlCl_3 to 1M LiAlCl_4 -P.C to reduce the copper chloride solubility was incompatible with the electrodeposition and discharge of lithium. This situation necessitated further investigations in search of alternate methods for reducing the copper salt solubility.

(b) Method of approach.

Since solubilisation depends upon solute-solvent interactions, attempts were made to accomplish the objectives by modifying the electrolyte composition. The modifications chosen for studies were the salt transformation process and the use of mixed solvent electrolytes.

1. The salt transformation cycle.

The salt transformation principle involves the formation of the cathode salt of interest by anodising the metal in question in the presence of an insoluble anion reservoir and supporting electrolyte. For example, the electroformation of CuCl on an electrode containing insoluble LiCl and copper metal in the presence of a supporting electrolyte would constitute a salt transformation cycle:



In order to test this possibility, pasted plate graphite substrate electrodes containing a 1:1 wt mixture of LiCl and Cu^0 were prepared with 5 percent ethyl cellulose as a binder. The electrodes were immersed and anodised in 1.0 M solutions of LiBF_4 , LiClO_4 , MgClO_4 , KPF_6 and LiPF_6 in P.C. The anodic product was rinsed in P.C, air dried, and subjected to x-ray analysis to detect the formation of copper chloride. The data indicated the presence of CuCl and, thus, showed that the salt transformation was possible.

In order to use the salt transformation reaction for the present purpose, the system should satisfy the following conditions.

- (a) The inherent solubility of CuCl_2 in the electrolyte should be low.
- (b) The charge-discharge should involve only the formation of CuCl_2 .
- (c) The supporting electrolyte should be inert and it should prevent the formation of the soluble chlorocuprate complex.

An examination of the inherent solubility of CuCl_2 in the various electrolytes revealed that the solubility of the copper salt was greater than 0.005M except in case of 1M LiBF_4 -P.C. Thus, further experiments on the charge-discharge process were restricted to this electrolyte.

Typical charge-discharge curves for pasted plate $\text{Cu}:\text{LiCl}$ electrode in 1M LiBF_4 -P.C at 5 mA/cm^2 are given in Figure 21. The following features are evident from the figure. (1) The charging curve was unsteady, (2) the discharge curves indicated two plateaus, and (3) the overall current efficiency was 70-90 percent to -1.5 vs. Ag in the same solution.

The double plateau observed during the discharge was probably due to the discharge of both CuCl and CuBF_4 , as only a monovalent copper salt was detected by the x-ray examination of the anodised electrode. The formation of a double salt is undesirable, and the usefulness of the system was clearly in doubt.

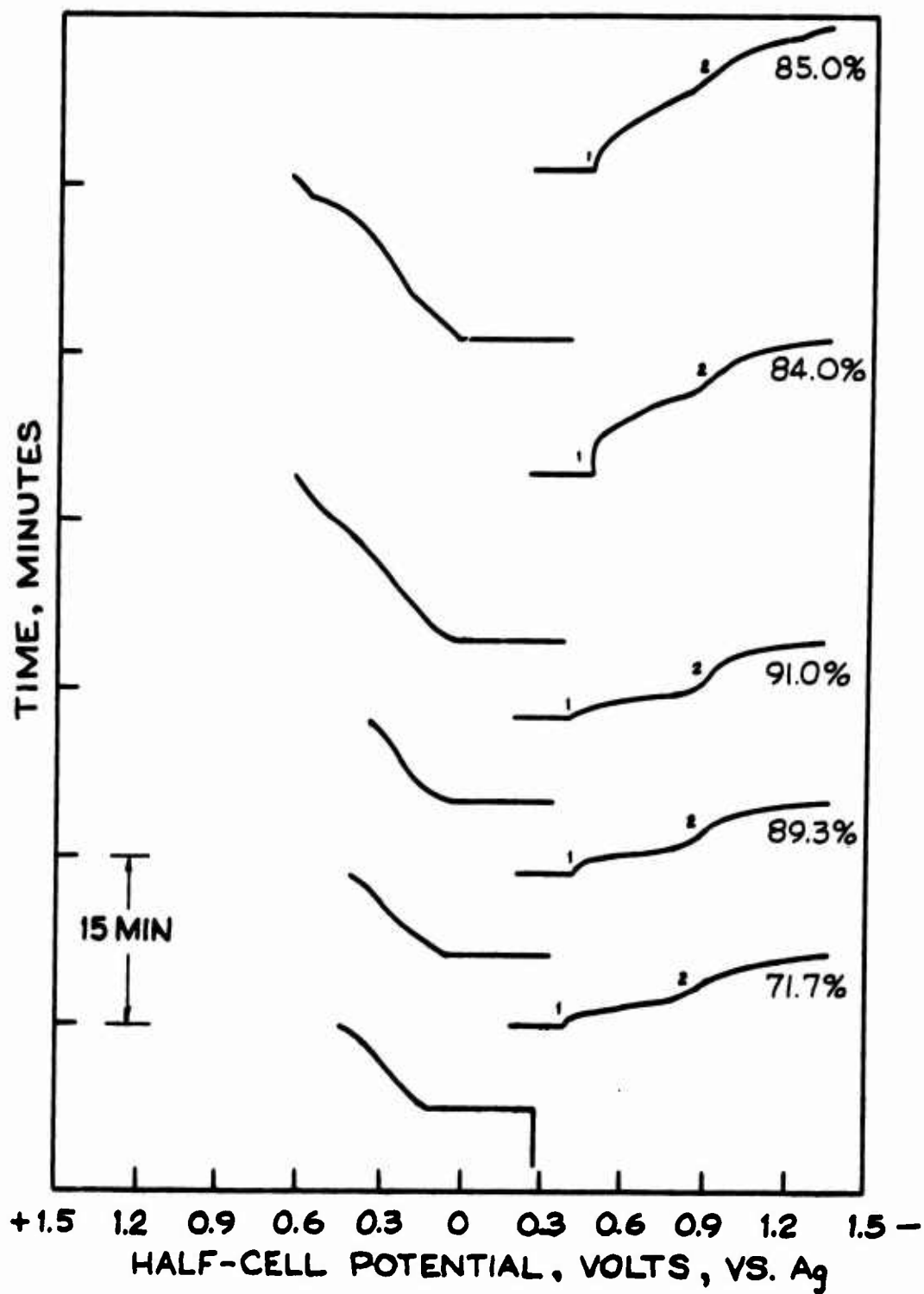


Figure 21. Charge-discharge curve for Cu: LiCl pasted plate electrode in 1M LiBF₄-P.C. Current density 5mA/cm².

The discharge of pasted plate CuCl_2 electrodes in $1\text{M LiBF}_4\text{-P.C}$ revealed that only a 50 percent utilization efficiency was possible, and the electrolyte did not in any way suppress the tendency of the copper salt to form the highly soluble chlorocuprate complex.

It was concluded that a much more comprehensive study would be necessary to achieve control of the ionic equilibria of the system to minimize the copper chloride solubility through the salt transformation process.

2. Mixed solvent electrolytes.

It is known that a given salt may be displaced from a solution by the addition of a suitable "non-solvent" to the system. In the present context we examined whether this principle could be applied to suppress the solubility of the copper chloride.

The following solvents were examined as possible "non-solvents" to be mixed with $\text{LiAlCl}_4\text{-P.C.}$ (1) Dioxane, (2) ether, (3) acetic anhydride, (4) xylene and (5) nitrotoluene. The experiments indicated that the first three solvents were unsuitable as the electrolyte salt itself was salted out upon the addition of these solvents to P.C solutions.

The other mixed solvent electrolytes were prepared by mixing different volumes of $1\text{M LiAlCl}_4\text{-P.C}$ with either $1\text{M LiAlCl}_4\text{-xylene}$ or $1\text{M LiAlCl}_4\text{-nitrotoluene}$ and charge-discharge experiments were carried out on lithium and copper chloride electrodes .

(a) Results and Discussions

Solutions of $1\text{M LiAlCl}_4\text{-P.C}$ and $1\text{M LiAlCl}_4\text{-xylene}$ could be mixed in volume ratios up to 15 percent of xylene solution. Increasing the xylene content in the P.C-xylene mixture resulted in phase separation. The data on the electrochemical formation and discharge of lithium and copper chloride half-cells in 15 percent xylene mixed solvent indicated that (1) the CuCl electrode efficiency was not altered by the use of the mixed solvent

and (2) the lithium utilization efficiency was reduced from 80 percent to 50 percent in the xylene containing electrolyte. Thus, the mixed solvent system would not be useful for the present purpose.

The lithium electrodes operated at 70-75 percent efficiency in 1M LiAlCl_4 -solutions in nitrotoluene. The utilization efficiency of pasted plate CuCl_2 electrodes was in excess of one hundred percent. This behavior led to the conclusion that the solvent participated in the electrochemical reaction, and it was considered to be unsuitable for use with P.C. Based on these conclusions further experiments employing nitro-compounds were discontinued.

IV. STUDIES ON CHEMICAL AND IONIC EQUILIBRIA

A. Electrolyte Studies.

1. The Problem: The utilization efficiency of lithium electrodes in 1M LiAlCl_4 - P.C has been found to be less than one hundred percent. This was a matter of concern since any parasitic reactions involved in diminishing the lithium electrode efficiency may influence directly or indirectly the shelf-life and cycle-life of cells. It was not clear from previous work what these parasitic reactions were and the question of the stability of the solvent or the nature and role of any impurities have remained obscure. This situation is due to the complexity of the system and the difficulties involved in identifying and differentiating chemical and ionic processes by simple experimental procedures. In the present section we report the experiments which provided information relevant to these problems.

2. Method of Approach.

Gas chromatography was employed to analyse the solvent and electrolyte solutions. The effect of the nature and concentration of the electrolyte salts, viz. AlCl_3 and LiAlCl_4 , on the extent of generation of impurities in P.C was analysed in the range of 0.01 to 1M solutions. Attempts were also made to determine whether purification of the electrolyte is feasible by chemical or electrochemical means. The variation of impurity content upon storage of purified electrolyte solution was also determined.

3. Results and Discussions.

a. Gas chromatographic analysis of 1M LiAlCl_4 - P.C.

Table 5 gives a comparison of volatile components present in 1M LiAlCl_4 solution in comparison with the technical grade of propylene carbonate and the distilled solvent. The data may also be compared with an electrolyte of 0.1M LiClO_4 in the same solvent.

TABLE 5

Comparison of the Impurity Contents of the Solvent
and the Electrolytes

Composition of the Test Sample	Volatile Component wt%* of the Test Sample									
	1	2	3	4	5	6	7	8	9	10
P.C (technical grade)	v	v	0.07	0.4	0.005	tr	0.5	tr	0	tr
P.C (distilled)	v	tr	0.005	0.085		tr	0.005	tr	0	0
0.1M LiClO ₄ - P.C	v	tr	0.05	tr		tr	0.005	tr	0	0
1M LiAlCl ₄ - P.C	v	N	0.5	0.2		1.5	0.5	2.5	N	2

* Approximate percentages

v Concentration not estimated - presumably unimportant

tr Trace amount

0 Not observed

N Total concentration of CO₂ and unknown (5 to 10% (wt)), the resolution did not permit an estimation of the concentration of the individual components.

Components based on retention times.

(1) air or argon, (2) CO₂, (3) water, (4) propylene oxide,
(5) allyl alcohol, (6) N-propyl alcohol, (7) propylene glycol,
(8) propionaldehyde, (9) unknown, and (10) other components
not yet identified

(i) Gas Chromatograph Conditions for Analysis.

Instrument - Perkin Elmer Model 801 with Hot Wire Detector,
Columns - 1/8" x 6" Stainless Steel packed with 80 mesh Porapak "Q".

Conditions:

Helium Flow - 20 ml/min
Injector Temp. - 230°
Detector Temp. - 200° at 250 ma. filament current.
Column Oven - Temp. Programmed:

Initial Isothermal Period of 2 min. at 120° followed by a linear rise
at 48°/min. to 230°; remainder of run at 230° isothermal.

Standard Sample Size = 2 µl

Limits: $\text{H}_2\text{O} = 5 \times 10^{-4}$ percent by weight.
(Hot Wire) $\text{P.O.} = 4 \times 10^{-3}$ percent by weight.
 $\text{P. G.} = 7 \times 10^{-3}$ percent by weight.

Retention Times for Well conditioned columns

Air, Argon N_2	- 21 sec.
CO_2	- 33, 36 sec; unknown = shoulder at 44 sec.
H_2O	- 88 (large peak) to 102 (small peak)
P.O.	- 258, 263 sec.
P. Ald.	- 274 sec.
Allyl alc.	- 293 sec.
P. G.	- 443, 435 sec.
P. C.	- 930 sec.

(i) Commentary on the Methodology.

It was observed that the retention times for the various volatile components in Table 5 tended to vary with the concentration of the solution and the column age. This may be attributed to the asymmetry of the shape of the peak in the former case, and to an increase in the polarity of the surface of the packing material in the latter. The components identified by the retention times under the given conditions of concentration and column parameters at the time of experimentation are given in the foot note of the Table.

The question of whether thermal decomposition of the electrolyte by the temperatures encountered during analysis contributes to the observed impurity content is resolved by the following observations.

1. Although propylene carbonate is thermally decomposed in bulk at temperatures of 100°C or above, it can be rapidly distilled at atmospheric pressure with only slight decomposition ("Propylene Carbonate", Technical Bulletin, Jefferson Chemical Co. Inc.).

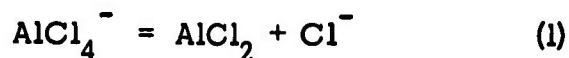
2. The analysis of distilled propylene carbonate shows no evidence of thermal decomposition products.

3. The analysis of 0.1M LiBF_4 or 0.1M LiClO_4 solutions in propylene carbonate shows only the expected increases in H_2O content and dissolved air or argon plus any traces of organics originally found in the purified solvent. See Table 5.

4. The variety of impurities observed in the analysis of LiAlCl_4 or AlCl_3 solutions is associated only with that salt system as a representative Lewis acid. Furthermore, the concentrations of impurities are observed to be proportional to the salt concentration.

5. The success of gas chromatography as an analytical tool is based largely on the use of extremely small sample volumes ($< 1.0 \mu\text{l}$ to $10 \mu\text{l}$) which, when injected into a small hot chamber with a rapidly flowing inert gas, are flash evaporated before thermal degradation can ensue to a significant extent. The use of excessive sample for a given injector volume leads to immediate evidence of decomposition such as new peaks, changes in relative concentrations of old peaks, etc.

A comparison of the impurity contents of the four types of samples clearly indicated that the addition of LiAlCl_4 to distilled propylene carbonate brought about solvent decomposition. The total concentration of volatile impurities in a 1M LiAlCl_4 - P.C solution was 5-10 (wt) percent. The strong Lewis acid liberated in the dissociation equilibria of the AlCl_4^- anions as in



is believed to be responsible for the observed impurities.

- b. The effect of the concentration of the electrolyte salts on the amount of impurities formed.

In order to understand the relationships between the nature and concentration of the electrolyte salts on the extent of the generation of impurities, analyses of solutions containing different concentrations (0.01 to 1M) of AlCl_3 and LiAlCl_4 were made. The thermal decomposition of the solvent due to the heat liberated during the preparation of the solutions was minimized by precooling the solvent to its freezing point with liquid nitrogen before mixing with the pre-weighed salts. After twelve hours of stirring under dry argon to insure complete dissolution, the solutions were analysed by gas chromatography. The results of the experiment are given in Figures 22 and 23. The following conclusions are possible from the data in the figures:

- (a) Both AlCl_3 and LiAlCl_4 generated nearly the same impurity contents in their reaction with P.C. Thus, the generation of impurities was not related to Li^+ ions of the LiAlCl_4 salt.
- (b) The concentration of impurities increased approximately linearly with the increase in the concentration of added salt. Thus, the generation of the impurities was not a catalytic process, but involved the participation of the aluminum ion species.

- c. The impurity contents of aged solutions.

Gas chromatographic analyses of the impurity contents of aged solutions depended on the conditions of storage. No change in the concentration of the

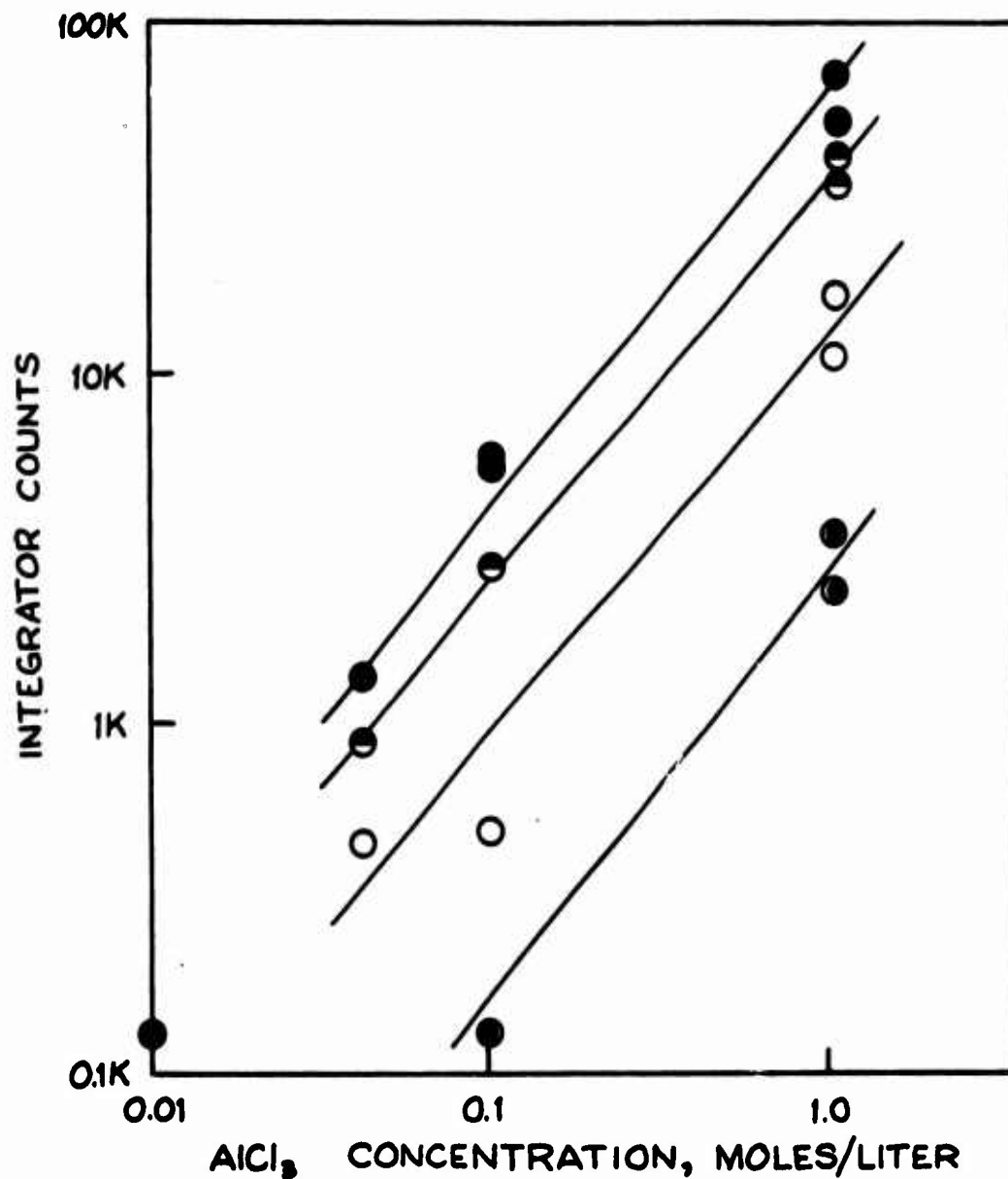


Figure 22. Salt-induced decomposition of Propylene Carbonate in AlCl_3 solution.

- Peaks at 34 + 44 Sec. ($\text{CO}_2 + \text{HCl}$?)
- ⊖ " 265 Sec. (Propionaldehyde)
- " 285 Sec. (Unknown)
- " 413 Sec. (Probably Propylene glycol but I.R. Spectra not obtained as yet.)

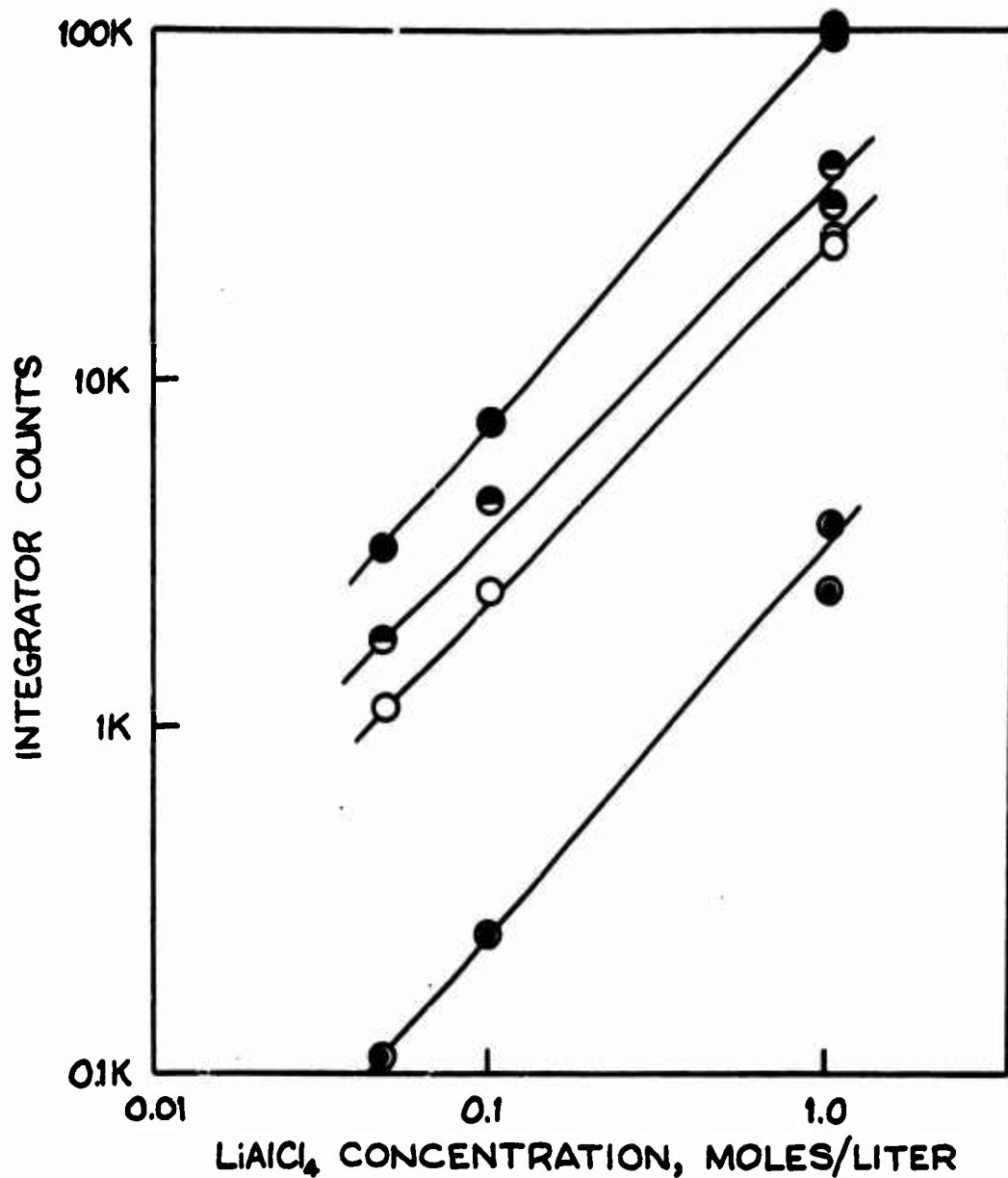


Figure 23. Salt-induced decomposition of propylene carbonate in LiAlCl_4 -P.C Solution.

- Peaks at 34 + 44 Sec. (CO_2 + HCl ?)
- " 265 Sec. (Propionaldehyde)
- " 285 Sec. (Unknown)
- " 413 Sec. (Probably Propylene Glycol but IR spectra not obtained as yet)

impurity content was observed in 1M LiAlCl_4 solutions stored in containers with air-tight lids. Solutions exposed to the air through leaky stoppers showed an increase in the concentration of HCl. These solutions were characterised by a lower utilization efficiency for the charge-discharge of lithium and an increased solubility of CuCl_2 . The formation of excess HCl may be explained by the reaction between aluminum chloride and the moisture in the air.

d. Efforts to eliminate the impurities from the solution.

It is seen from the Table 5 that most of the impurities present in 1M LiAlCl_4 - P.C were electroactive species. The possibility of removing these impurities by chemical or electrochemical procedures was examined as follows:

(i) The solution was passed through a long column (2 ft. x 1 in. dia.) packed with lithium powder.

(ii) Cathodic pre-electrolysis of the electrolyte solution was carried out employing large area (20 sq cm/500cc solu.) aluminum and copper working electrodes. The experiments were potentiostatic and were set at -2.8V vs. Ag in the same solution.

Experiments based on (i) and (ii) indicated that no efficient purification of the solution had occurred. This was probably because the lithium powder used in (i) or the pre-electrolysis electrodes in (ii) were deactivated by the impurities in the initial stages of the treatment. The occurrence of such a phenomenon was indicated by the decrease of the pre-electrolysis current to a low value from 150 mA to 10-15 mA during the first hour, even when large diffusion currents were possible as estimated from the total impurity contents of the solution. In essence, the exact conditions of the experiments necessitated a continuous renewal of fresh active surface during the experiment. This condition was provided by redesigning the pre-electrolysis experiment as follows.

Pre-electrolysis experiments were carried out using 50 ml of 0.1M LiAlCl_4 - P.C in a sealed single compartment all fitted with a stopcock arrangement for withdrawing samples for pre-electrolysis. The working and counter

electrode consisted of two identical strips of lithium ribbon each with 10 sq cm of immersed area. A silver wire reference electrode suitably positioned in the same solution was used to measure the potential of either of the working electrodes. After the cell was charged with 50 ml of electrolyte, stirring was begun and 1 mA of current was applied from a constant current source. The direction of the current was reversed every ten minutes with a dual clock switching arrangement. The initial potentials recorded at the working electrode were -3.5V on the charge and -2.9V on the discharge cycle. During the experiment lithium was electrochemically deposited or dissolved thus exposing fresh surface on a continuous basis. The pre-electrolysis was carried until G.C. analysis of aliquots indicated nearly complete removal of the electroactive impurities. During the latter stages of the electrolysis experiment it was observed that the electrodeposited lithium was poorly adherent and there was a necessity to filter the solution before analysis. The results of the experiment are shown in Table 6.

TABLE 6

Effect of Pre-electrolysis of 0.1M LiAlCl_4 -P.C.

Time of Electrolysis (Hours)	Concentration of Impurities (Integrator Counts)		
	CO_2 + Unknown	Propionaldehyde + Allyl alcohol	Propylene Glycol
-	7528	4800	2500
2.8	7500	4800	4072
43	6400	3360	4016
133	5040	1504	4446
206	4794	880	6784

It is seen from Table 6, that the pre-electrolysis reduced the net concentration of CO_2 and an unknown species. An examination of the gas chromatographic curves presented in Figures 24 and 25. showed that only the unidentified material was removed in the process leaving a CO_2 peak of constant area. The reduction of the concentration of propionaldehyde and allyl alcohol was effected by the

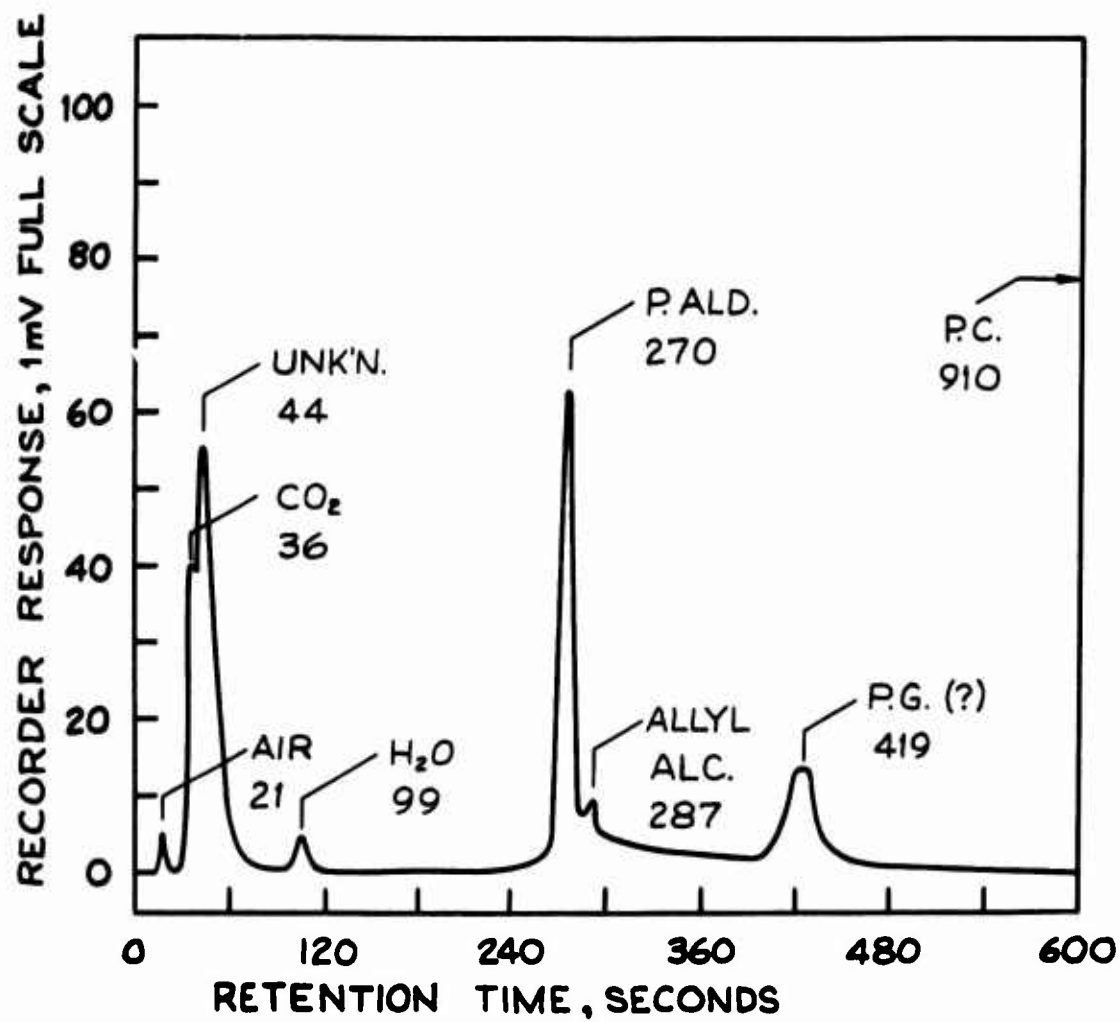


Figure 24. Chromatogram of 0.1M LiAlCl_4 -P.C solution before pre-electrolysis.

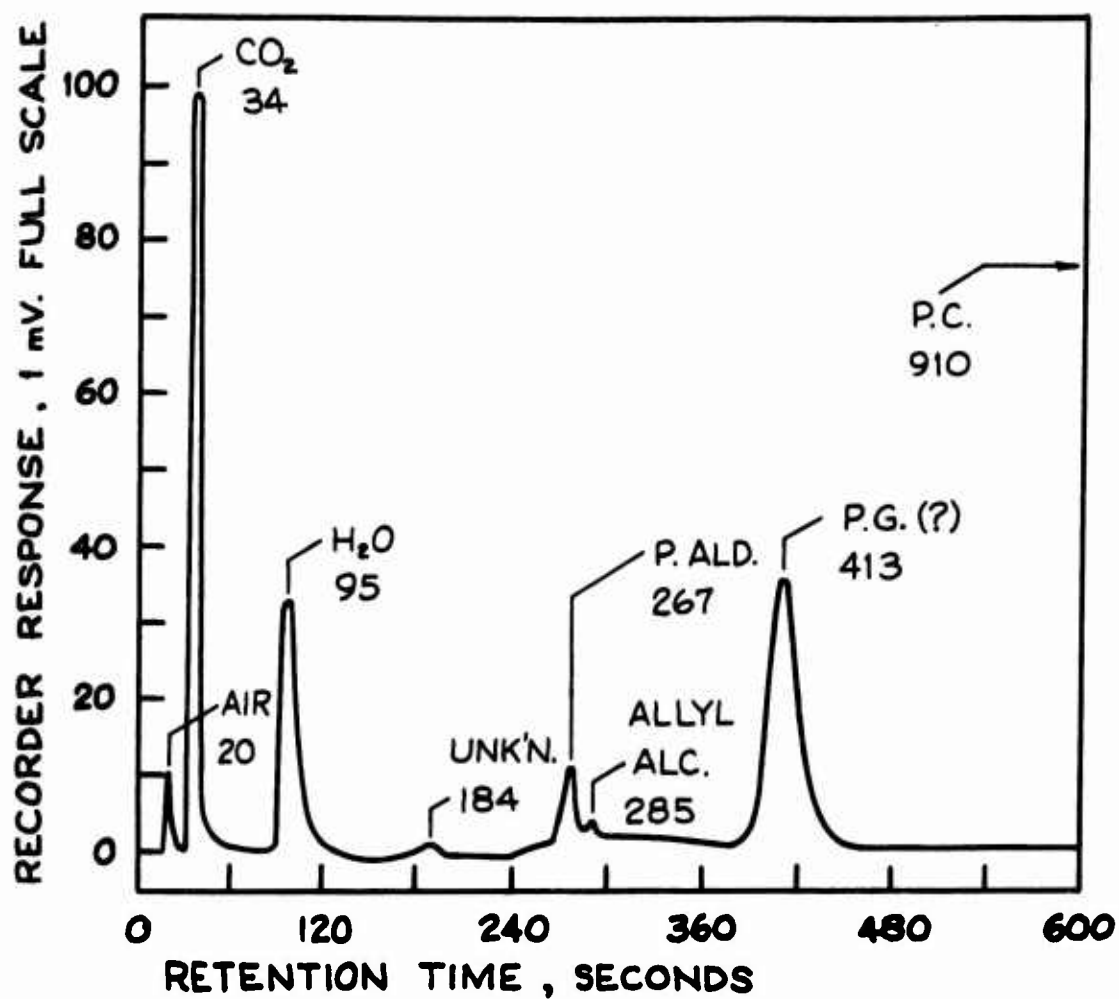


Figure 25. Chromatogram of 0.1M LiAlCl₄-P.C solution after 206 hours of pre-electrolysis.

pre-electrolysis. However, it is not clear why the peak thought to be glycol could not be removed by this technique. In this respect it is significant to note that no new peaks corresponding to reduction products of propionaldehyde or allyl alcohol were observed. Instead an increase in the area of the supposed glycol peak was obtained suggesting that this peak actually constituted the product of the reduction.

It was found that during 200 hours of proper storage no increase in the concentration of the unknown component, aldehyde, and the alcohol occurred; thus demonstrating that the electroactive impurities removed by the pre-electrolysis were not regenerated during storage.

e. Scale-up experiments for the purification of the electrolyte.

Based on the encouraging results of the purification by pre-electrolysis scale-up experiments were carried out in 500 ml batches of 1M LiAlCl_4 -P.C solutions. Two 30 sq cm area lithium electrodes and a 20 mA current were employed in these experiments. The solutions were analysed before and after sufficient current had been passed to remove the estimated quantities of impurities. It was found that the impurity content had not changed due to pre-electrolysis. The reason for the failure of the technique in the scale-up from 0.1M in 50 ml lot to 1M in 500 ml batch is not clear.

B. Investigations of the Chemical and Ionic Equilibria.

1. The problem: (a) Gas chromatographic analysis of the 1M LiAlCl_4 -P.C solution had indicated that the solution contained organic and inorganic impurities like aldehydes, alcohols, water, CO_2 and HCl. It was of interest to estimate the influence of these impurities on the performance of the lithium anode and on the copper chloride solubility.

(b) It was also of interest to examine whether the problem of complex formation was a particular property of copper chloride or a general phenomenon applicable to other cathode salts in electrolytes containing free chloride ions.

2. Method of Approach.

(a) The extent to which the impurities affected the lithium anode performance and copper chloride solubility could be measured by studying the effects of these factors in highly purified solutions and comparing the results with those from solutions containing known amounts of the impurities. As we were unable to purify the 1M LiAlCl_4 -P.C the direct experiment on the effect of the impurities could not be carried out. Instead, we estimated the relative impurity effects by adding known amounts of propionaldehyde, n-propyl and allyl alcohol to the unpurified solutions. The particular experiments were as follows:

- (i) The measurement of the self-discharge of electro-deposited lithium,
- and (ii) the estimation of the solubility of copper chloride.

(b) The method of approach for the study of the phenomenon of complexation was to examine the solubility of three different cathode salts in three different electrolytes. Three cathode salts and three different electrolytes were employed.

3. Experimental.

(a) Lithium anode self-discharge studies.

The self-discharge experiments were conducted by keeping electro-deposited lithium electrodes immersed in 1M LiAlCl_4 -P.C containing saturated CuCl and 0.1M quantities of known electroactive impurities such as propionaldehyde, allyl alcohol, and propylene oxide.

(b) The effect of impurity on the solubility of copper salt.

The solubility of CuCl and CuCl_2 in 1M LiAlCl_4 -P.C containing known amounts of addition agents such as AlCl_3 , HCl , H_2O , propionaldehyde, allyl alcohol, propylene oxide, was measured after equilibrating the solutions in the presence of excess salts and estimating the concentration of the dissolved salts polarographically.

(c) Studies on complex formation.

An examination of the extent to which complexation played a role in the cathode solubility was made in the case of AgCl , PbCl_2 , and CuCl_2 employing LiCl - γ -butyrolactone, LiCl -N-N-dimethylformamide and MgCl_2 -propylene carbonate as electrolytes. A quantity of cathode salt equivalent to 0.1M was added to known volumes of 0.01 to 0.25M solutions of the electrolyte and equilibrated for a period of more than a day. The concentration of the dissolved salt in these solutions was estimated polarographically.

4. Results and Discussions.

(a) The self-discharge of the lithium anode.

Figure 26 gives the charge retention on open circuit of electroformed lithium anodes under the influence of various impurities. A comparison of curves (1) through (4) with Figure 10 curve (2) indicated that the addition of CuCl , propionaldehyde, n-propyl alcohol, and allyl alcohol caused a much higher rate of self-discharge than was observed in the absence of these impurities.

Although both propionaldehyde and allyl alcohol caused drastic increases in the corrosion rates the difference in action rate suggested the existence of different mechanisms.

The greatly decreased efficiency at zero open circuit time for the alcohols indicated that their reduction occurred during the charge cycle whereas the high zero open circuit efficiency and large slope for propionaldehyde indicated that most of its influence was through reaction with the deposited lithium.

(b) Role of organic impurities on the solubility of CuCl_2 .

Data on the measurement of the solubility of CuCl_2 in the presence of added organic impurities are presented in Table 7.

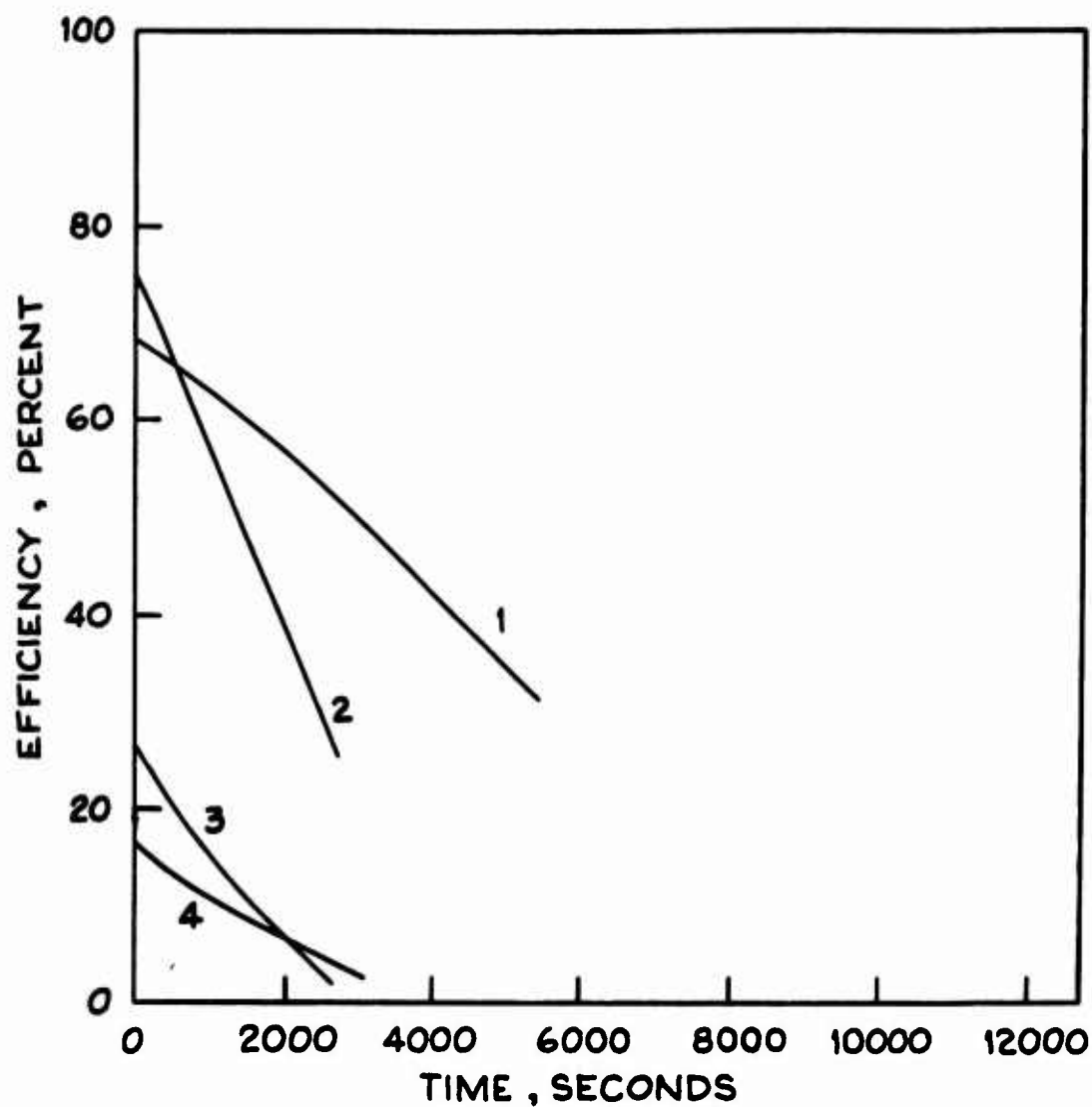


Figure 26. Self-discharge of lithium in 1M LiAlCl₄-P.C in the presence of added impurities. Curves (1) - (4) are for addition of CuCl (Saturated) propionaldehyde, allyl alcohol and n-propanol respectively to 1M LiAlCl₄-P.C solutions.

TABLE 7

Solubility of Copper II Chloride in 1M LiAlCl_4 -P.C in Presence of
Added Organic Impurities (5% by volume of organic component added)

Composition of Solution	Solubility M/l
P.C. only	0.008
1M LiAlCl_4 -P.C only	0.006
1M LiAlCl_4 -P.C + allyl alcohol	0.036
1M LiAlCl_4 -P.C + propionaldehyde	0.023
1M LiAlCl_4 -P.C + propylene oxide	0.037
1M LiAlCl_4 -P.C + propylene glycol	Gel like crust; no polarogram was taken

It may be seen from Table 7 that an increased concentration of organic impurities increased the solubility of cupric chloride.

(c) The role of inorganic impurities on the solubility of CuCl_2 .

Table 8 gives the solubility of copper chloride in 1M LiAlCl_4 -P.C in the presence of added inorganic impurities such as water, HCl and lithium chloride.

TABLE 8

Solubility of CuCl_2 in P.C and 1M LiAlCl_4 -P.C in the Presence
of Added Inorganic Impurities

Composition of Solution	Solubility of CuCl_2 . M/l
P.C only	0.008
P.C + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.0123
P.C + 5.3% (vol.) H_2O	0.125
1M LiAlCl_4 -P.C	0.006
1M LiAlCl_4 -P.C + sat. LiCl	0.008
1M LiAlCl_4 -P.C + 0.5% (vol.) H_2O	0.0125
1M LiAlCl_4 -P.C + 0.5% (vol.) 12N HCl	0.0372

The data in Table 8 indicate that the effect of LiCl on the copper salt solubility in 1M LiAlCl₄-P.C was small. This is probably so because of the low solubility of LiCl. The results show that the addition of water to P.C increased the copper salt solubility. An increase in the solubility of copper salt in 1M LiAlCl₄ in the presence of small quantities of water may be understood in terms of an increase in the inherent solubility of the copper salt in the mixed solvent or by complexation.

(d) The effect of AlCl₃ on the copper salt solubility in 1M LiAlCl₄-P.C.

During the studies on the formation and discharge of copper chloride in 1M LiAlCl₄-P.C on copper electrodes it was demonstrated that the addition of AlCl₃ improved the discharge efficiency. The reason for such an improvement was thought to be the preferential complexing of the Cl⁻ ions liberated during the discharge with AlCl₃ rather with CuCl₂ which would result in a decrease in the solubility of copper chloride. In the present experiments, a direct measurement of the solubility of copper chloride was made in 1M LiAlCl₄ containing 0.5M AlCl₃. The results are indicated in Table 8.

TABLE 9

The Effect of AlCl₃ on the Solubility of CuCl₂ in 1M LiAlCl₄-P.C

Composition of the Solution	Solubility of CuCl ₂ M/l
1M LiAlCl ₄ -P.C (solution stored 8 days)	0.018
1M LiAlCl ₄ -P.C + 0.5M AlCl ₃ (")	10 ⁻⁴

As seen from the results in Table 9 there was a suppression of the solubility of CuCl₂ in 1M LiAlCl₄ by AlCl₃. Furthermore, the low solubility of CuCl₂ in AlCl₃ containing aged 1M LiAlCl₄ solutions indicated that the excess AlCl₃ probably complexed with liberated HCl also to give AlCl₄⁻ ions, thus preventing an increase in the solubility of CuCl₂ upon storage of the LiAlCl₄ solutions.

(e) On the complex formation tendency of cathode salts in organic electrolytes.

Table 10 gives the solubility of AgCl , PbCl_2 and CuCl_2 in three different electrolytes.

TABLE 10

Solubility of Chloride Cathode Salts in Chloride Electrolytes.
(The concentration of cathode salt in the equilibrium mix = 0.1M)
(S = solubility 0.1M/l)

Electrolyte	Conc. of Electrolyte Salt	Solubility (M/l)		
		CuCl_2	AgCl	PbCl_2
MgCl_2 - P.C	0	0.008	0.0001	0.0001
	0.01	0.018	0.0003	0.004
	0.135	0.1	0.0003	0.005
LiCl -B.L	0	0.008	0.001	0.0005
	0.02	0.024	0.02	0.01
	0.27	0.1	0.1	0.1
LiCl -DMF	0	S	0.0001	S
	0.02	S	0.02	S
	0.27	S	0.1	S

Examination of Table 10 indicates that the presence of the electrolyte salt enhanced the solubility of the cathode salts. The solubility increased proportionately with the concentration of the electrolyte salt in the case of CuCl_2 , AgCl and PbCl_2 in LiCl solutions of γ -butyrolactone. A similar behavior was exhibited by AgCl in LiCl -N N-dimethylformamide, and CuCl_2 in MgCl_2 -propylene carbonate solution. The solubility of AgCl and PbCl_2 did not increase proportionately to the increase in the concentration of the electrolyte salt in MgCl_2 -P.C but the difference herein seemed to be one of degree rather than one of kind. These examples provided evidence that

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the tendency to complexformation is a general problem in case of chloride salts in chloride electrolytes.

V. CELL STUDIES.

A. The Problem:

In the previous sections the behavior of lithium anodes and copper chloride cathodes as well as the studies relating to the chemical and ionic interactions in the electrolyte solutions have been dealt with. These studies were useful in elucidating the inherent problems of the system.

A practical cell operates with a limited amount of electrolyte under which conditions the interaction of the reaction products, such as the chlorocuprate complex, play a significant role in determining the discharge efficiency, shelf-life and cycle life of the cells. In addition, operational and engineering parameters such as the current density, the nature of the separators, and the anode-cathode loading also play a role in influencing the cell performance. In this section, experiments are described which indicate the effects of these parameters.

B. Method of Approach:

The experiments were designed to determine the effect of the separators, the current density, the nature of the electrolyte, and the cycling on the utilization efficiency of the cells.

The first set of experiments were carried out to evaluate the performance of the lithium-copper chloride cell as a function of the distance of separation between the anode and the cathode. Teflon spacers were used to vary the distance between the anode and cathode. The purposes of these experiments were:

(i) To understand the transition of behavior between the excess electrolyte and the limited electrolyte conditions.

(ii) To serve as a basis for comparing the performance of different separators.

In the second set of experiments, separators of different kinds were used in place of the spacers and the performance of the cells was

determined.

The third set of experiments consisted of the evaluation of the effect of the variation of separator thickness on the cell performance.

Subsequent to the selection of a suitable separator, the effects of the current density, cycling, shelf-life, and the electrolyte composition on the cell performance were determined.

C. Experimental.

1. The Cell.

(a) Cell - 1:

The Li-CuCl₂ cell arrangement was similar to the one employed for the evaluation of the lithium electrode performance in the limited electrolyte configuration. For the present experiments, a parallel plate configuration was employed. The cells were cathode limiting in terms of capacity and consisted of 6.45 cm² active area pasted plate dehydrated CuCl₂ · 2H₂O electrodes. An extension of the graphite cloth substrate acted as the cathode terminal for making external connections. Lithium metal foil of dimensions similar to those of the cathode constituted the anode, and it had a capacity at least ten times larger than that of the cathode. The cathodes were separated from the anodes either by means of polytetrafluoroethylene spacers or by separators, depending on the purpose of the experiment. The thickness of the electrode assembly varied between 0.2 and 0.5 cm. The assembly was inserted into the cell container of dimensions slightly larger than 1" x 1" x 1". The electrodes were held in position by filling the empty space with teflon or glass inserts. The amount of electrolyte was restricted to the quantity absorbed by the separator and the crevices filling the teflon inserts. The cell had provisions for inserting a silver wire to measure the half-cell potentials during the cell operation.

The coulombic capacity of the pasted plate, dehydrated CuCl₂ · 2H₂O cathode ranged from 7.8 to 15.5 mA-hr cm⁻². The separators were conventional

filter materials. The current density ranged from 0.31 to 1.55 mA cm^{-2} .

(b) Cell - 2:

The cell container was of teflon and was smaller in capacity than cell - 1. Electrodes of 1 cm^2 superficial areas were used in this cell. The purpose of changing from the arrangement of cell - 1, was to reduce the capacity of the cell to collect representative data in a shorter period of time on the self-discharge of the system.

D. Results and Discussion.

1. Effect of the anode-cathode separation on the cell performance.

Two typical cathode limited cells comprising an anode and a cathode of one square inch area were assembled in parallel plate configurations employing polytetrafluoroethylene spacers of 2mm and 0.3mm thickness. The cells were of 80 mA-hr capability and were discharged at 5mA. The discharge performance of the respective cells is given in Figure 27 Curve (1b) and (2b). With a 2mm distance of separation, the cell discharged at two voltage plateaus with an overall utilization efficiency of 54%. The discharge curve was similar to that observed in excess electrolyte, suggesting that the cell was cathode limited. This was substantiated by the measurement of lithium half-cell in the cell. It was observed that the lithium anode exhibited a steady potential of -2.8V as in Curve (1a) during the entire period of discharge of the cell. It is interesting to note in Curve (2b) that the cell performance was adversely affected by a decrease of the anode-cathode separation from 2mm to 0.3mm. Half-cell measurements showed that the cell became anode limited as (2a) at small separations.

An examination of the cell components after discharge indicated that a film of copper had formed on the lithium surface. The soluble chlorocuprate complexes formed during the discharge of the copper salt probably discharged on the anodes causing the buildup of the copper film. It appeared that the poor cell performance in 2b, was connected with a higher rate of transfer of the chlorocuprate complex, occasioned by the smaller distance of separation between the electrodes

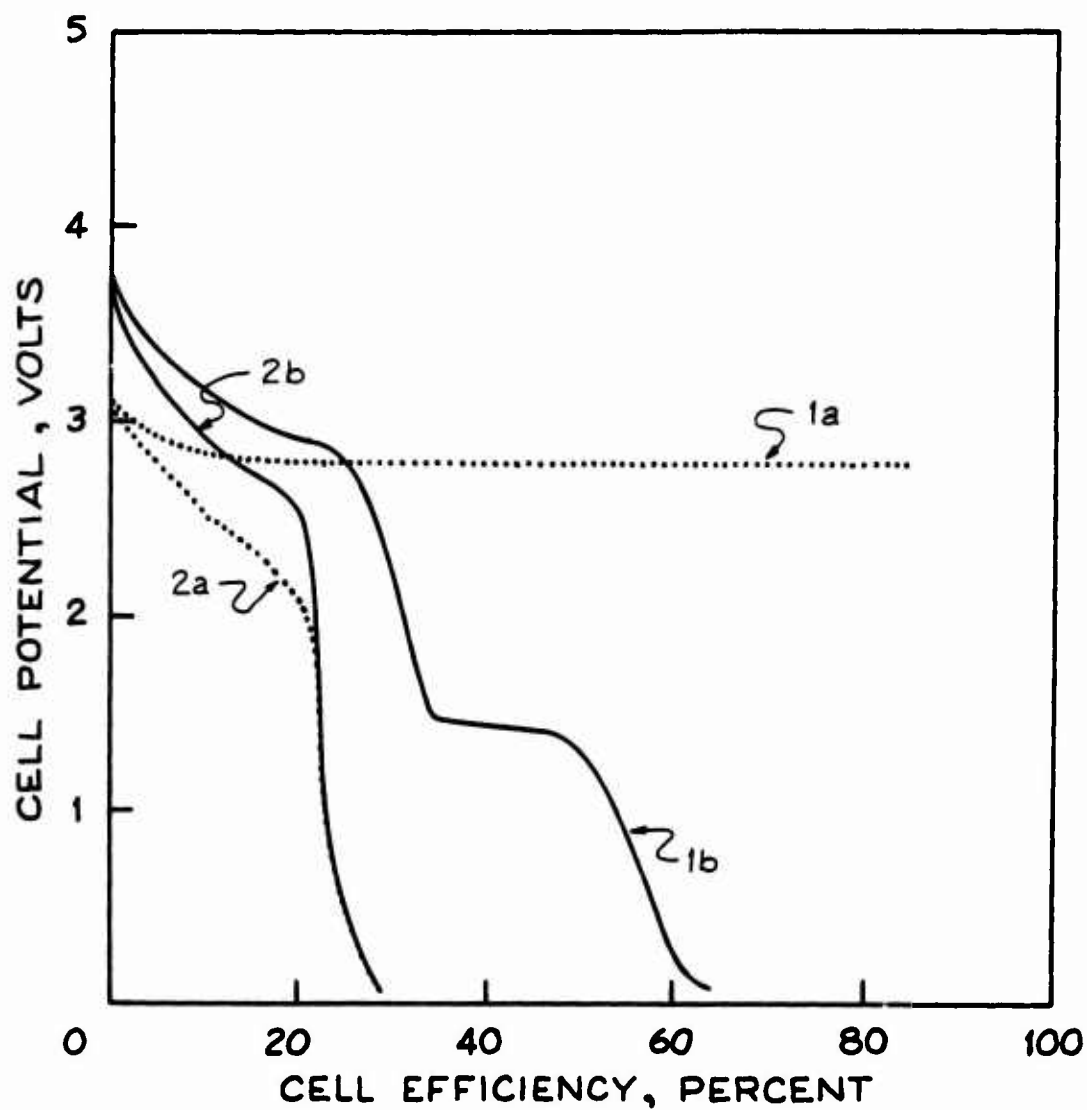


Figure 27. Effect of limited electrolyte on cell efficiency.

_____ cell performance, ... lithium half-cell performance.

1a and 1b are for 2mm separation of anode and cathode.

2a and 2b are for 0.3mm separation of anode and cathode.

in comparison with 1b. The high rate of transfer of soluble copper to the anode may result in a compact film of LiCl, or Cu⁰ on the lithium surface as in Equation 10.



2. The effect of the nature of the separator on the cell efficiency.

The separator materials used in the cell studies were conventional filter materials and are listed in Table 11. Short term tests over a period of a week indicated that the separators were stable in 1M LiAlCl₄-P.C. The cells used for the evaluation of the separators employed a single anode and cathode in a parallel plate configuration, with an area 1 in² and a cathode limited capacity of 80 mA-hr. The cells were discharged at 5mA. The utilization efficiencies of the cells in the presence of different separators are given in Table 11.

Table 11
Separator Studies

Nature of Separator	Utilization Efficiency
Millipore brand	
AP20	30
NCWPO	5
LCWPO	0
Whatman Brand - 41	12.0
Gelman Brand	
Acropore WR - 800	14.0
Synpor Brand	15

It is evident from Table 11 that among the various separator materials tested, Millipore AP20 (a glass Fibre Filter material) was the best one and it was chosen for the further experiments. The poor performance of the other separators may have been due to their relatively poor electrolyte wetting capability and their lack of mechanical strength to obstruct the growth

of copper filaments. The latter phenomenon was connected with the transfer of soluble copper ions to the lithium anode.

3. The effect of the variation of the thickness of the separators on the cell utilization efficiency.

In the above experiments two factors were found to cause a low utilization efficiency:

- (1) The poor wetting of the separator, and
- (2) Cell shorting by the growth of copper filaments through the separator.

It was of interest to examine whether the severity of these deleterious factors could be lessened by employing multiple layers of the fibre glass separator. The results of such experiments are given in Figure 28. It is seen that the cell performance did indeed improve from an efficiency of 30% to 85% upon increasing the separator thickness from 0.2 to 1.7mm.

As may be seen from Figure 28, a maximum efficiency of approximately 90% may be achieved with a distance of separation of 0.864mm - 1.0mm. Any further increase in the separation results in negligible improvements in the cell performance. Hence, detailed investigations of the cell behavior were carried out using 4 to 5 layers of the separator.

4. The effect of the current density on the cell performance.

Figure 29 gives the variation of the utilization efficiency with the current density for electrodes of capacity between 9-17 mA-hr cm⁻². It is seen that both of the cathodic reactions corresponding to the reduction of Cu⁺⁺ to Cu⁺ and of Cu⁺ to Cu⁰ follow the similar trend of a decrease of the efficiency with an increase in the current density. Lithium half-cell examination during the cell discharge indicated that at the higher current density, eg. 3.1 mA cm⁻², the anode polarized severely, and this limited the utilization efficiency of the cell. A higher rate of transfer of the CuCl₂ - complex to the anode and the consequent depolarization of the lithium leading to a compact LiCl or Cu⁰ film, as in Equation 10 may explain the observed behavior.

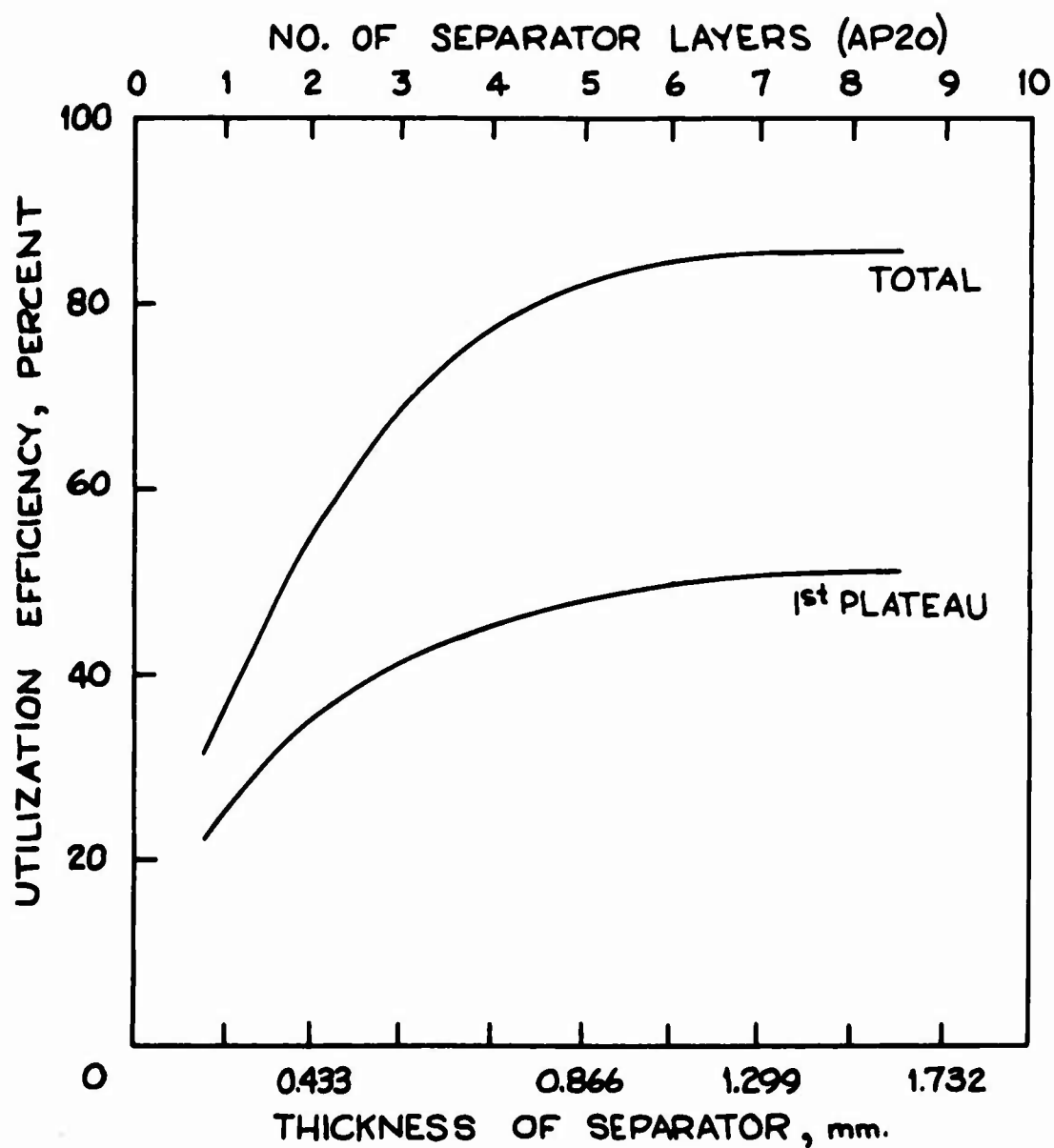


Figure 28. Effect of variation of thickness of separator on efficiency.

Cell capacity: 1.25 mA cm^{-2} Current density: 0.78 mA cm^{-2}

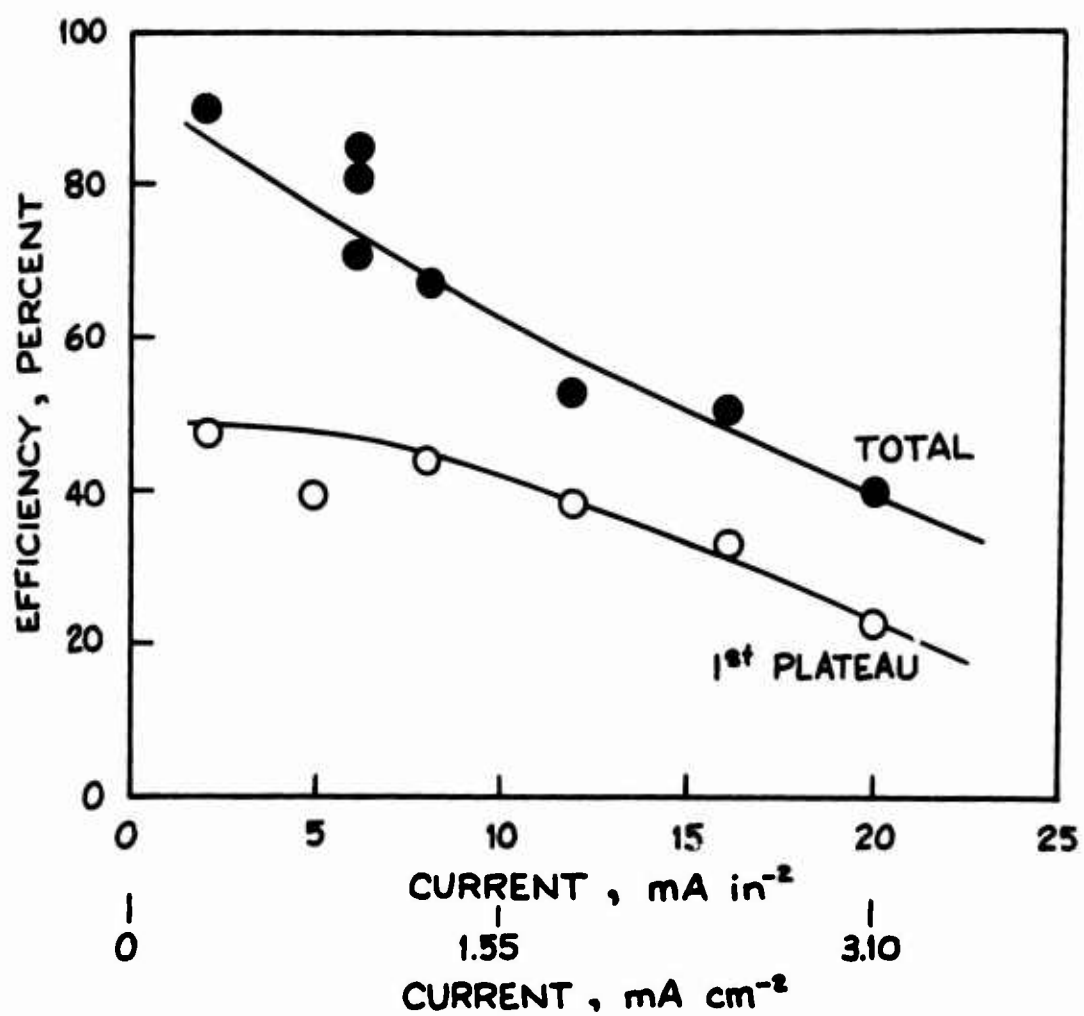


Figure 29. Effect of current density on the cell performance in 1M LiAlCl₄-P.C.

5. Self-discharge of the cell.

Cells assembled with a 30 mA-hr cm^{-2} capacity, configuration of cell - 2, were kept on open circuit to study their self-discharge. The cells had 4 layers of separators. The open circuit voltage of the cells changed from 3.3-3.4V to 0.5V in the course of 40-45 hours. Analyses of the copper transferred to the lithium during these experiments indicated that 80-90% of the cell capacity had been transferred to lithium by the self-discharge process during the interval. Based on these experiments, an average self-discharge current of $0.15 \text{ to } 0.2 \text{ mA cm}^{-2}$ was calculated. This value corresponded well with the order of magnitude of the steady state limiting current of 0.32 mA cm^{-2} calculated from the measured room temperature solubility of $8 \times 10^{-3} \text{ M/l}$ for the cupric chloride.

6. Cell Cycling.

The cycling of the cells was carried out at a constant current with an automatic cycling device. The cells were first discharged and then put on charge for a period of five hours. The current was then reversed to effect the cell discharge. When the cell potential reached 0.5V the current was again reversed for recharging to continue the cycling. These experiments employed cells which were similar in design and capacity to those of the previous experiments. Most of the experiments were carried out at 0.78 mA cm^{-2} .

A typical cell behavior during cycling is illustrated in Figure 30. The cell had a capacity of 61 mA-hr and employed five layers of separators. It was operated at 5 mA . The nature of the first discharge followed by the first charge and the second discharge is represented in Curves (1), (2) and (3), respectively. Based on the initial capacity and the discharge data, a utilization efficiency of 86% was realized during the first discharge. The five hours of charging at 5 mA was equivalent to a recharge of 40% of the initial capacity. In the subsequent discharge only 13.2% of the initial capacity was recovered instead of 40% of the initial charge. Thus, the current efficiency of the process was only 36%. It was observed that the cell voltage remained at approximately 0.5 to 0.6V after the first cycle for several hours, and no recharging took place.

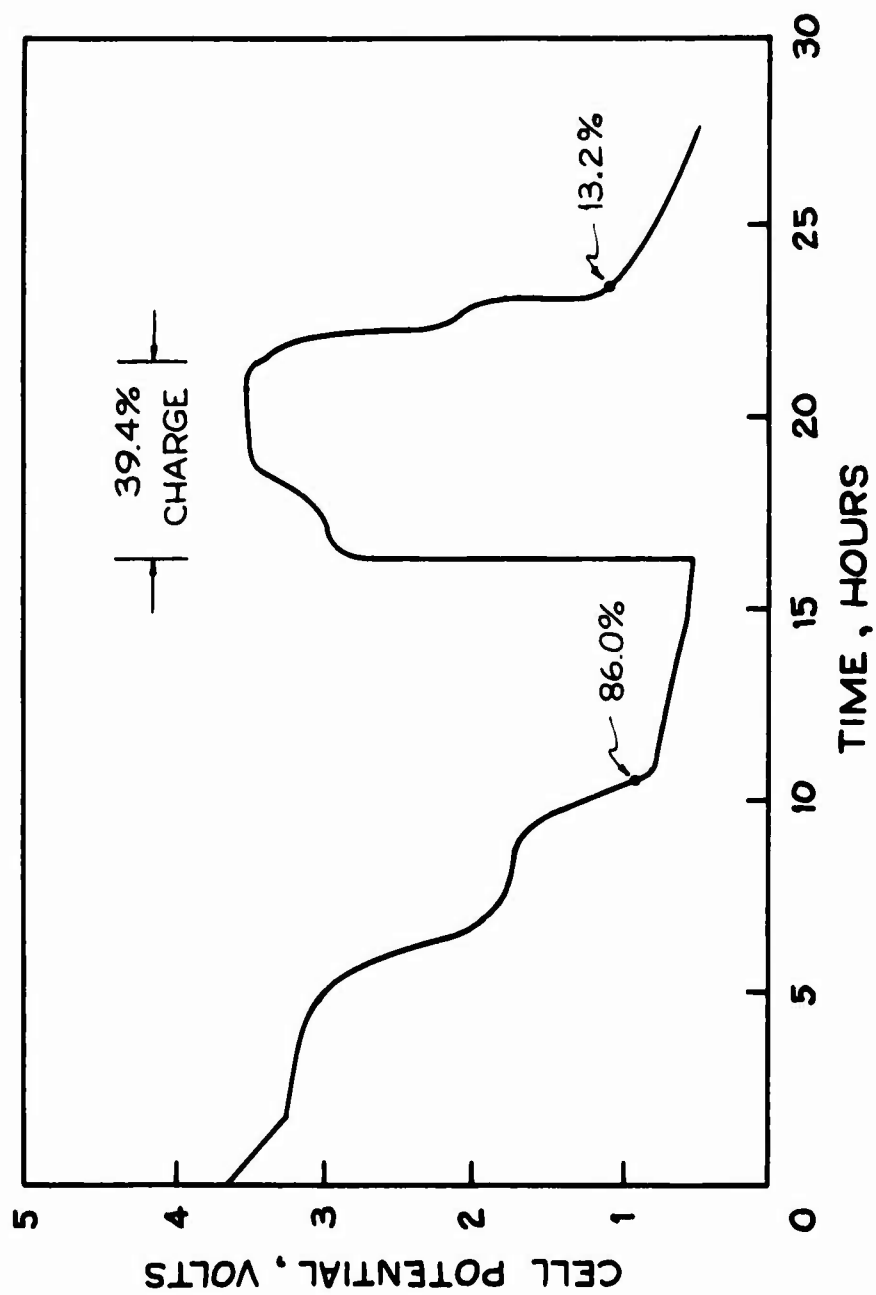


Figure 30. Cycling behavior of the cell in 1M LiAlCl_4 -P.C.

Capacity: 61 mA-hr. Current: 5 mA.

The cut-off voltage for the discharge was changed to 1 volt instead of 0.5 volts to overcome this problem. The results of the cycling are indicated in Table 12 for these conditions.

Table 12

Cell Cycling Data.

Anodic charge cut-off at the Cl_2 evolution voltage.

Cathodic discharge cut-off at 1.0 volt.

Initial capacity of the electrode 80 mA-hr current 0.78 mA cm^{-2} .

Cycle No.	Cell Charging % of initial charge up to Cl_2 evolution	Cell Discharge		Overall Current efficiency (<u>Hours Charge</u>) (Hours Discharge) %
		% of initial capacity 1st plateau	up to 1V.	
1st Discharge	--	44.8	75.9	--
1	30.6	6.6	16.7	55.3
2	12.5	3.8	10.7	85
3	6.6	1.9	6.5	98.2
4	5.4	1.7	5.4	100
5	4.1	1.3	4.1	100
6	3.5	0.95	3.3	95

It may be seen in Table 12 that the cell cycling was similar to that observed for the CuCl_2 half-cell in excess electrolyte: the current efficiency was high and the cell recharge capacity dropped below 10% during the course of three cycles.

The poor cycling capability of the cell was attributed to the discharge mechanism of the copper chloride electrode. In $1\text{M LiAlCl}_4\text{-P.C}$ which involved the formation of a soluble chlorocuprate complex. The formation and diffusion of the soluble copper species led to a film of copper on the anode. Upon recharging, this copper would not be returned to the copper chloride electrode because of the high cathodic potential of the lithium metal. Thus, with each discharge there was an effective loss of active material from the cathode. Since the cells were cathode

limited, the capacity for each subsequent recharge would be drastically reduced.

Other consequences of the above phenomenon are the disintegration of the cathode structure due to the continuous removal of the active material from its structure, and the shorting of the cell due to the growth of copper filaments from the anode to the cathode. The latter would be expected because the deposition of copper takes place from solution. Evidence for this effect was obtained from an examination of the discharged cells, and it is presented in Figures 31 and 32.

The cell under examination had four separator layers, a capacity of 60 mA-hr, and it was discharged at 5 mA. After the cell discharged to 0.5V, with an utilization efficiency of 85%, it was taken out, rinsed with propylene carbonate, and the anode and the cathode were removed from the separators. Figure 31 represents the separator layer facing the lithium anode. The dark region was found to be a film of metallic copper. The separator underneath this was removed for examination and it is represented in Figure 32. Figure 32, No. 1 illustrates the rear portion of the separator in Figure 31 and No. 2 is for the separator layer next to this. The dark spot once again was found to be copper. It may be seen from Figure 31 and 32 that the deposited copper had a tendency to grow from the anode to the cathode. The over-discharging of the cells resulted in shorting due to this effect.

In addition to the above causes, the growth of lithium filaments through the separators were observed to reduce the cycle life of the cells.

7. Cell behavior in other electrolytes.

During the course of the examination of the CuCl_2 half-cell we observed that the addition of AlCl_3 to 1M LiAlCl_4 -P.C or the operation of the CuCl_2 half-cell in 1M LiAlCl_4 -P.C in nitrotoulene resulted in an increased



Figure 31. View of separator facing lithium anode after discharge.



Figure 32. View of the two separator layers opened for examination after cell discharge.

utilization efficiency. Figure 33, Curves (a) and (b), indicates that this was true for cathode limited Li-CuCl_2 cells. The utilization efficiency of the cells was greater than 90%. Since the 120% utilization observed in nitrotoulene solution indicates the participation of the solvent in the electrode reaction, further experiments were discontinued with this solvent.

Figure 34 gives the effect of the variation of thickness of the separators on the utilization efficiency of Li-CuCl_2 cells in $1\text{M LiAlCl}_4\text{-P.C}$ containing 0.5M AlCl_3 . The observed effect was similar to that previously found for the utilization efficiencies of the Li-CuCl_2 cell in $1\text{M LiAlCl}_4\text{-P.C}$. However, it is noted that the utilization efficiencies reached 100%.

Figure 35 gives the effect of the cycling of the Li-CuCl_2 cells in $1\text{M LiAlCl}_4\text{-P.C}$ containing 0.5M AlCl_3 . The sequence of cycling was similar to that used previously. The current efficiency decreased gradually with an increase in the cycle number as indicated by the values of 76, 71, and 61% during the first, second and third cycles. For a recharge capacity of 45% of the initial capacity, the utilization efficiencies were 30.42, 28 and 25.4%, respectively. The fact that the cell reached potentials of the order 4.5 to 4.6V during the second and third cycle indicated that chlorine evolution probably occurred, which implied a loss of utilization efficiency. Further, for anode limited cells, the deposition efficiency of lithium in this electrolyte was anticipated to be poor as indicated by the half-cell measurement, and it was concluded that the electrolyte was unsuitable for rechargeable cells.

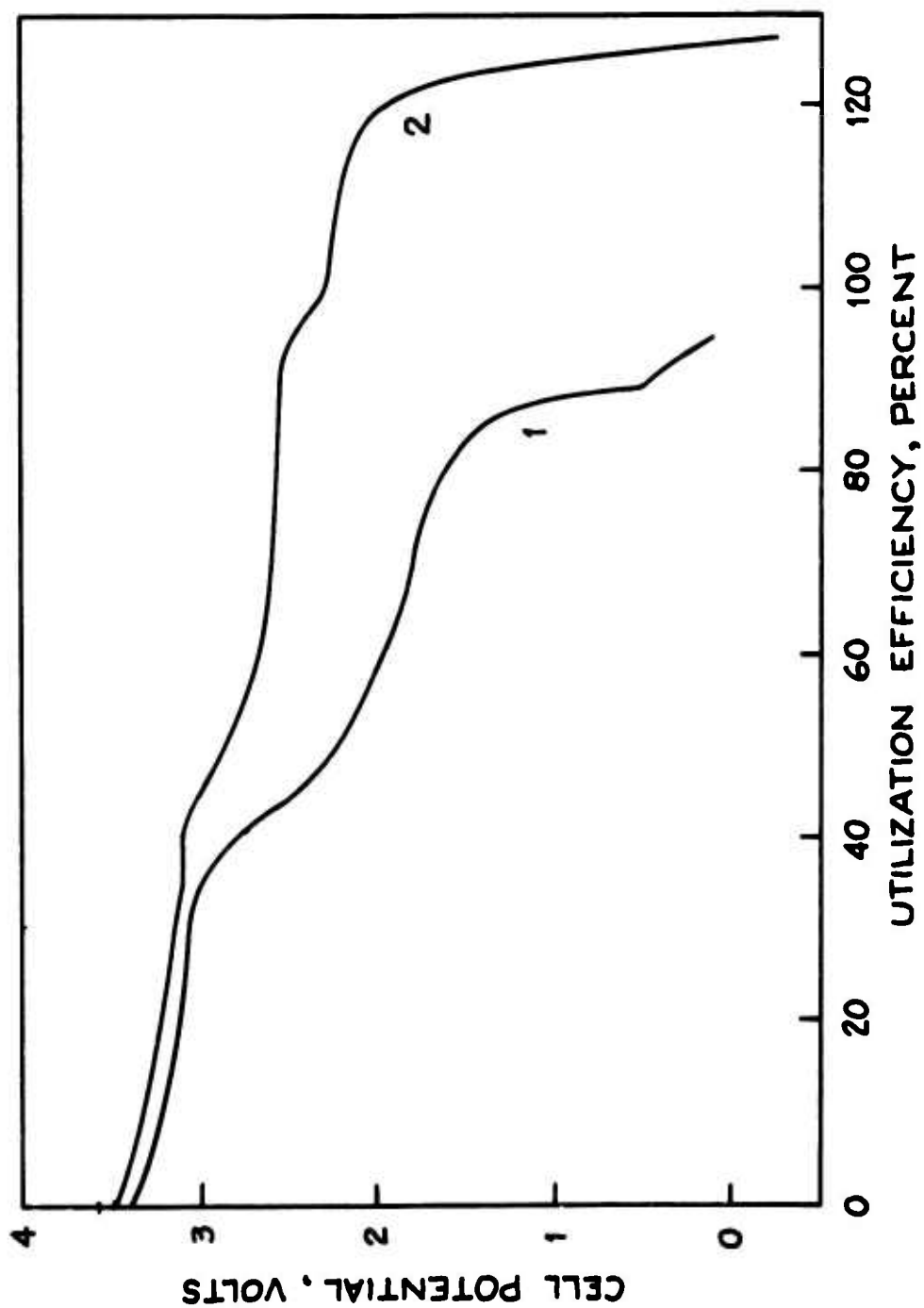


Figure 33. Cell discharge in different electrolytes.

1. 1M LiAlCl₄-P.C + 0.5 M AlCl₃

2. 1 M LiAlCl₄ - Nitrotoluene.

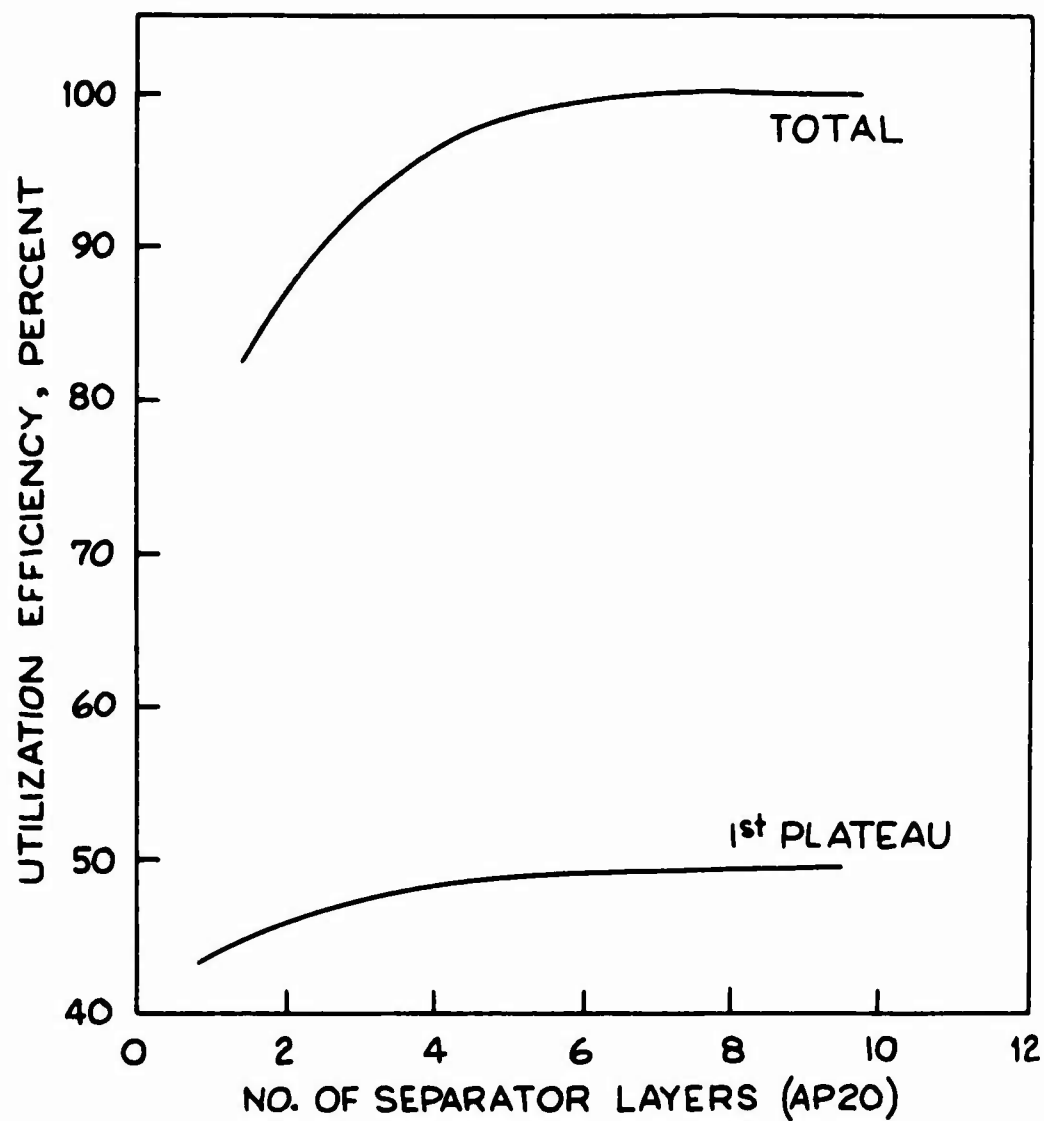


Figure 34. Variation of cell efficiency with separator thickness.

Electrolyte $1\text{M LiAlCl}_4\text{-P.C} + 0.5\text{M AlCl}_3$.

Cell capacity 80 mA-hr. Current density 0.78 mA cm^{-2} .

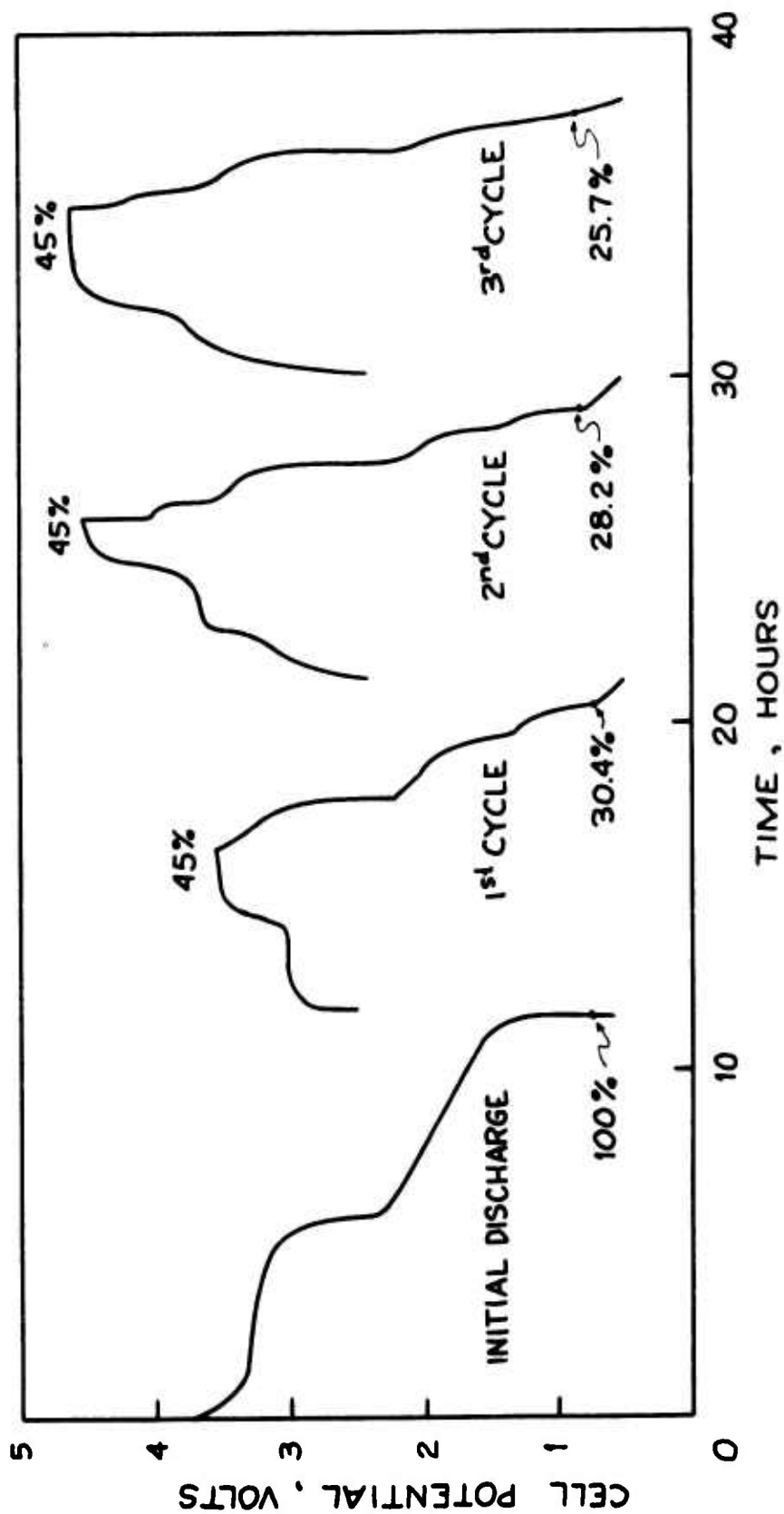


Figure 35. The cell cycling in 1M LiAlCl_4 -P.C containing excess AlCl_3 .
Cell capacity: 58.5 mA-hrs. Discharge current: 0.78 mA cm^{-2} .

VI. CONCLUSIONS AND RECOMMENDATIONS.

A. The Lithium Anode.

The electrochemical deposition and dissolution of lithium in 1M LiAlCl_4 -P.C. revealed that the utilization efficiency of the processes depended on the substrate used for deposition. No lithium deposition occurred on graphite. Utilization efficiencies of 40-85 percent were obtained on lithium, aluminum and copper substrates. A lowering of the utilization efficiency was observed as the current density and the charge density increased and as excess AlCl_3 was added to the electrolyte. The decrease in efficiency due to the increased loading appeared to be caused by the formation of a poorly adherent powdery deposit.

Lithium electrodeposition and dissolution experiments carried out on copper substrates in the presence of a limited amount of electrolyte gave results similar to those observed in the presence of an excess amount of electrolyte. However, cycling experiments indicated the existence of complications such as lithium growth through the separators. This led to the shorting of the cells.

The self-discharge studies of electrodeposited lithium showed that copper substrates were inferior to aluminum substrates. Further, the electroactive salts and impurities: CuCl , propionaldehyde, allyl alcohol, and n-propyl alcohol increased the self-discharge rate of the anode.

B. The Copper Chloride Cathode.

The anodic oxidation of copper metal in 1M LiAlCl_4 occurred at a current efficiency of one hundred percent and the principal product of the oxidation was CuCl . This salt could be oxidized to CuCl_2 by the use of suitable mixtures of the salt with an inert conductor like graphite. Chlorine evolution occurred on overcharge. The discharge of CuCl_2 to Cu^0 occurred stepwise with the formation of intermediate CuCl with an overall efficiency of 50-60 percent at 1-5 mA/cm^2 . CuCl_2 electrodes

formed from a mixture of salt and graphite could be recharged at a current efficiency of 90-95 percent. However, the material utilization efficiency decreased gradually with an increase in the cycle number. Detailed analysis of the discharge of CuCl_2 revealed the strong tendency of the salt to form highly soluble chloro-cuprate complexes. This phenomenon accounted for the low utilization efficiency and the poor cycle life.

Attempts were made to improve the utilization efficiency of the CuCl_2 electrodes based on considerations of ionic equilibria, salt-transformation cycles, and the use of mixed solvent systems. Only the addition of excess AlCl_3 to 1M LiAlCl_4 -P.C. led to an improvement. However, the addition of this salt was found to be incompatible with the operation of the lithium anode.

C. The Electrolyte:

Impurities such as propylene glycol, carbon dioxide, allyl alcohol, and propionaldehyde were generated in propylene carbonate by both AlCl_3 and LiAlCl_4 . The impurity concentration was found to be approximately proportional to the concentration of the added salt which suggested that the generation of the impurities occurred by means of stoichiometric rather than catalytic reactions. The purification of the electrolyte was found to be possible in 0.1M solutions. However, the purification of 1M LiAlCl_4 -P.C was not possible.

Studies on the electrolyte equilibria of AgCl and PbCl_2 cathodes revealed that these salts also generated soluble chloro-complexes in the presence of chloride ions. Thus, the tendency of chloro-complex formation in the presence of chloride ions was not peculiar to copper chloride, but a phenomenon of general validity in organic electrolytes.

D. The Cell:

The cell studies revealed that low utilization efficiencies prevailed. The loss of the cathode active material and its transfer to the anode limited the

rechargeability of the cell. Passivation of the lithium anode was observed at current densities of 3.1 mA cm^{-2} . The formation of a compact LiCl and/or a Cu^0 film on a lithium is thought to be responsible for this behavior.

It was possible to some extent to retard the rate of transfer of soluble copper species from the cathode by employing separators in a multi-layer configuration. The cell utilization efficiency was improved to 85 percent by this means. The measured self-discharge rate of the cell was high, and it corresponded to a corrosion current of approximately 0.2 mA cm^{-2} . This rate of self-discharge agreed with the limiting current computed from the solubility data.

The cells operated at a 100 percent utilization efficiency in 1M LiAlCl_4 -P.C containing excess AlCl_3 or in 1M LiAlCl_4 in nitrotoulene. These electrolytes were found, however, to be incompatible with the operation of rechargeable lithium anodes in non-reserve configurations.

E. System Performance.

It is clear from our work that organic electrolyte systems are not yet ready for development into prototype energy storage systems for vehicle propulsion. They exhibit neither the cycle life, the charge retention, nor the energy density to compete with existing rechargeable batteries. No attempt was made, accordingly, to describe their performance quantitatively in terms of the duty cycles required for vehicle applications.

It is especially clear that the ultimate performance attainable with organic electrolyte systems exceeds that of conventional systems by a considerable margin. The studies reported to date indicate unambiguously the course that must be followed to improve the performance of the systems.

The foremost obstacle to the successful operation of rechargeable, high energy density, organic electrolyte cells is the high self-discharge rate

of the cathode. Conceptually, this obstacle may be overcome by either or both of the following means:

1. The development of an electrolyte with the proper kind of specific interactions with the salts to suppress the dissolution of the copper species.
2. The development of an ion specific separator which inhibits the transfer of soluble cathode salts to the anode.

During the course of our studies of organic electrolyte systems we have examined item (1) in some detail. We have investigated various solvents, the use of mixed solvents, the effects of various anions and Lewis acids, the effects of various ratios of salt concentrations, and the possibility of operating the cathode in the salt transformation mode. The results have indicated that a fundamental, long range program is needed to provide the data required for the development of a satisfactory electrolyte. Yet, it is not at all certain that it can be developed.

There are reasons for believing that item (2) can be accomplished although quantitative statements cannot be made yet regarding the extent of any obtainable suppression of the self-discharge rates. It should be noted that the self-discharge of the copper chloride cathode is rather unconventional because it is discharge-assisted. Therefore, membranes are required with a high degree of selectivity.

Experience with ion exchange materials has shown that membranes can be developed which are specific for certain ions, and anion exchange membranes do exist which bind chlorocomplexes of various cations. Such membranes would be expected to retard the rate of transfer of the chlorocomplexes of copper. The internal geometry of membranes can also be exploited to retard the diffusive transfer of solutes, an extreme example being the possible use of molecular sieve membranes.

It is known that ion exchange substances can function in organic electrolytes, but there is no information available which is directly relevant to the operation of lithium/cupric chloride cells in organic electrolytes.

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13. **Abstract.** The electroformation and discharge of lithium and copper chloride was investigated in half cell and cell configurations in 1M LiAlCl₄-P.C. The utilization efficiency of lithium in a half-cell depended on the substrate, current density and the loading. In the operation of rechargeable cupric chloride electrodes the tendency of copper salt to form highly soluble chloro cuprate complexes was observed. Impurities present in the solution caused significant self-discharge of the lithium electrode and increased the copper salt solubility. The formation of highly soluble chloro-complexes was a general phenomenon found for other cathodes salts also such as AgCl and PbCl₂ in chloride containing electrolytes. This solubility problem affected significantly the Li-CuCl₂ cell performance. The transfer of dissolved copper species to the lithium anode by diffusion or migration resulted in the deposition of a copper film on the anode. It was possible to retard the rate of transfer and consequently to improve the 1st discharge of the cell by employing thick separators. At higher current densities passivation of the lithium anode occurred in the cell. The cells were rechargeable but the cycle life was limited due to loss of cathode active material. A course of investigation to effect possible improvements in the cell performance is suggested.

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