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**INVESTIGATION OF ELECTROCHEMISTRY  
OF  
HIGH ENERGY COMPOUNDS IN ORGANIC ELECTROLYTES**

**May 1, 1965 to October 31, 1965**

**by**

**R. T. Foley, L. E. Helgen, and L. Schubert**

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National Aeronautics and Space Administration  
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**Research Grant NGR 09-003-005**

**The American University  
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ABSTRACT

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The investigation of high energy compounds in organic electrolytes has been directed toward a clarification of the electrochemical and chemical properties of the cyclic esters,  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone and propylene carbonate. The range of electrolysis, that is, the voltage range, including anodic and cathodic potentials over which an electrolysis may be conducted without sensible Faradaic current contribution from the supporting electrolytic solution, has been measured. These values mainly from lithium perchlorate solutions are, for  $\gamma$ -butyrolactone, 5.78 v., for propylene carbonate, 5.25 v., and for  $\gamma$ -valerolactone, 6.82 v. Potentials have been assigned to  $\text{ClO}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{Cl}^-$ ,  $\text{BF}_4^-$ ,  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and other ions as indicative of their participation in electrode processes. The reaction of butyrolactone and propylene carbonate with Li, Na, K, Ca, and Mg has been studied at 100°C in a dry  $\text{N}_2$  atmosphere. Na, K, and Ca are quite reactive and the reaction products are being studied by infrared, gas chromatographic and chemical techniques. The suitability of these three metals or their salts in electrochemical systems is questionable. Over extended periods of time "molecular sieves" either decompose these solvents or dissolve in them to give appreciable electrochemical activity.

*Burton*

## I. SCOPE

This research deals with the electrochemistry of high energy compounds in organic electrolytes. The term, "high energy", is defined by, and restricted to, those elements and compounds useful in the conversion of chemical to electrical energy by electrochemical processes. In the first report (1) it was pointed out that, to achieve a high energy, a galvanic cell of high voltage, 3-5 volts, was necessary, and this immediately specified a non-aqueous system. So the first requirement was for a solvent and electrolytic solution which would be stable, in the electrochemical sense, over a large voltage range. Therefore the range of electrolysis of the non-aqueous electrolytic solution becomes a primary consideration. It is noted here that the term "range of electrolysis" is used instead of "decomposition voltage". This is not because the latter term is not sufficiently descriptive but rather because it has been used without precision in the electrochemical literature dealing with the electrolysis of aqueous solutions. The term "domain of electrochemical activity" has also been used, but appears more cumbersome. At any rate, we are defining here the range, including both anodic and cathodic potentials, over which the solvent and supporting electrolyte may be used in a high energy battery without itself entering into the galvanic reaction. The major attention during this period has been devoted to the cyclic esters for reasons given below. The range of electrolysis for a number of salt solutions in propylene carbonate,  $\gamma$  - butyrolactone and  $\gamma$  - valerolactone were measured. In addition, to electrochemical measurements, certain chemical reactions of the esters were investigated. These included the reaction at elevated temperature with Li, K, Na, Ca, and Mg metals. This behavior will further characterize the esters as electrolytic solvents providing basic information of value in the high energy field.

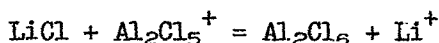
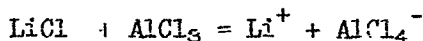
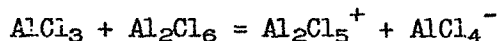
As was stated in the first report the aim of this research is to establish principles. The principles will describe the character of the organic solvent, the type and structure of the high-energy organic compounds that will operate at cathodes in these solvents and the kinetics and mechanism of the electrode processes leading to the utilization of the thermodynamically available energy.

## II. LITERATURE ON ELECTROCHEMISTRY OF CYCLIC ESTERS

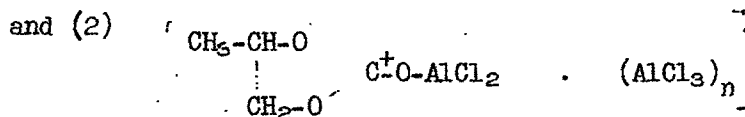
Harris (2) appears to have been the first to evaluate the cyclic esters as electrolytic solvents in a critical way, although work employing the compounds as solvents in aluminum electrolytic capacitors (3) must have been going on at the same time. Harris compiled literature data on, and measured experimentally, pertinent physical and electrochemical properties of ethylene carbonate, propylene carbonate,  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone, ethylene trithiocarbonate, and cyclopropanone. These included the solubility of a large number of inorganic salts, and viscosities, densities, conductivities, and dielectric constants of the solvents and various solutions. Further, electrodeposition studies of importance to electroplating and secondary battery technology were carried out. He investigated the deposition of Li, Na, K, Mg, Ca, Al, Zn, Cd, Fe, Mn, Co, Ti, Nb, U, Bi, Pb, and Sn from propylene carbonate solution. Of these, Li, Na, K, and Zn could be deposited electrolytically. From his work Harris drew the general conclusion that these solvents were promising ionizing media. The capacitor work mentioned above (3) refers to patents granted in 1960 in which aluminum electrolytic capacitors utilize an electrolyte of a condensed alkyl phosphate dissolved in propylene carbonate and a substituted ammonium salt dissolved in propylene carbonate, butyrolactone, or valerolactone. These solutions were claimed to be stable for long periods of time and able to operate at low temperatures.

Chilton and Cook (4) reported studies on properties of electrolytic solutions of propylene carbonate. Their studies were directed toward the development of a secondary battery with a long charge-discharge cycle life and a high energy per unit weight. The standard electrolyte used in their work was 0.75 M  $\text{AlCl}_3$  and 0.63 M  $\text{LiCl}$  in propylene carbonate. Lithium chloride is soluble to only 0.057 mole/liter (0.24 g per 100 cc) at 25°C while aluminum chloride is soluble to over 3 moles/liter. Aluminum chloride enhances the solubility of  $\text{LiCl}$  through the formation of  $\text{LiAlCl}_4$ . Both lithium chloride and lithium perchlorate decrease the conductivity of aluminum chloride solutions. The maximum conductance for the aluminum chloride-propylene carbonate system of  $7.5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  occurs at 150 g/liter. The conductance for aluminum chloride

solutions to which lithium chloride was added reaches a maximum of  $6.6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  at 120 g/liter. This behavior is explained by equilibria of the following type



Migration experiments conducted by Chilton and Cook indicate that the current is carried by species such as



$n = 0, 1, \text{ or more}$

Certain electrolysis experiments conducted in this study are pertinent. An aluminum chloride solution was electrolyzed with aluminum anodes and aluminum cathodes which were considered to be inert. A cell voltage of 10 volts was required for a current of 10 ma to flow and 5 volts for 2 ma. These voltages did not deposit aluminum at the cathode or dissolve aluminum from the anode. In the corresponding solutions containing lithium chloride or lithium perchlorate, lithium is deposited and a lithium anode dissolves. The anodic oxidation of metals to form cathodic reactants - Ag and Ni to form AgCl and NiCl<sub>2</sub> - for reversible systems were studied. Silver chloride was formed at 100% efficiency and nickel chloride at low efficiency except at very low current density. The current efficiency for the lithium anode was found to be about 100% between 20 and 80 ma/cm<sup>2</sup>.

Bauman et. al. (5) investigated propylene carbonate and nitrobenzene electrolytes with the objective of improving the lithium-silver chloride system. Their comments on the physical properties of these solutions are pertinent. They point out that the freezing points of the liquids reported in the literature are misleading. Propylene carbonate can be supercooled 25°C below its freezing point. Whereas the freezing point is given in the literature as -42°C, a crystal-liquid mixture exists at -60°C and propylene carbonate solutions of AlCl<sub>3</sub>·LiCl do not



freeze at dry ice temperatures. Electrolyte decomposition studies were conducted with propylene carbonate solutions of  $\text{AlCl}_3$  and  $\text{AlCl}_3 \cdot \text{LiCl}$  as solutes. On the anodic side a linear relationship between polarization and current density was found to exist out to about 30 ma. On the cathodic side in the  $\text{AlCl}_3 \cdot \text{LiCl}$  electrolyte there is a sharp rise in current at 4.5 v. With  $\text{AlCl}_3$  and platinum electrodes there is a linear relationship with 10 ma indicated after a polarization of 10 v. Some experiments were performed in  $\text{LiClO}_4$  electrolytes similar to those used in the present investigation. Silver salts are rendered insoluble by  $\text{LiClO}_4$ . When  $\text{AlCl}_3$  is added to the solution  $\text{AgCl}$  is formed. Some work was done with mixed electrolytes, e.g., propylene carbonate and butyrolactone, with the object of improving the adherence of Li on deposition. This was not successful.

Bauman (6) reported on electrolytic properties of  $\text{NaPF}_6$  solutions in propylene carbonate and butyrolactone in connection with the development of a Li-CuF<sub>2</sub> battery system. Saturated solutions in propylene carbonate (0.86 mole/liter) and in butyrolactone (1.14 moles/liter) were used. The conductivities of these solutions at 25°C were  $6.0 \times 10^{-3}$  and  $13.4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  respectively. There was no change in the infrared spectra of either solution after storing for 10 days at 165°F and the solutions did not react with lithium. The polarization of the lithium anode was measured (versus Li wire reference). Anodic polarizations of about 70 mv and 150 mv in propylene carbonate and butyrolactone, respectively, were measured at 1 ma/cm<sup>2</sup>.

Chilton et. al. (7) continued the work on the Li-AgCl system to the development stage mainly working with an electrolyte 0.63 M  $\text{AlCl}_3 \cdot \text{LiCl}$  in propylene carbonate. It was observed that additions of ethyl ether and toluene increased conductivity, e.g., the conductivity of a 0.63 M  $\text{AlCl}_3 \cdot \text{LiCl}$  solution was increased from  $6.0 \times 10^{-3}$  to  $10.0 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  by the addition of ethyl ether. In this study the reversibility of Li and AgCl electrodes was studied at length. In this connection the solubility of AgCl in propylene carbonate was determined to be  $10^{-21} \text{ mole}^2/\text{liter}^2$ .

Meyers et. al. (8) measured decomposition voltages of a large number of solutions of inorganic salts dissolved in propylene carbonate and butyrolactone. It is quite apparent that in the early work impure

solutions or solutions containing a fairly high water content were measured. For example, currents of over 100 microamp. were observed at applied voltages of 3.0 v for propylene carbonate and 2.5 v. for butyrolactone. Later work wherein solvents of higher impurity were used gave results in general agreement with those reported in Section III below. For example, a solution of 1.4 M  $\text{LiClO}_4$  in butyrolactone required a voltage of 5.2 v to yield 0.1 ma/cm<sup>2</sup>; a solution of 1.5 M  $\text{LiClO}_4$  in propylene carbonate in  $\text{CO}_2$  atmosphere a value of 5.2-5.4 v (9); a solution of  $\text{Al}_2(\text{SO}_4)_2$  in butyrolactone (argon atmosphere) a value of 6.10 v. (anode, 2.20, cathode, 3.90).

Towle (10) measured the solubilities and conductivities of  $\text{KPF}_6$  and  $\text{NaBF}_4$  solutions in propylene carbonate. A saturated solution of  $\text{KPF}_6$ , approximately 1 M, exhibited a maximum conductivity of  $7.25 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ , a saturated solution of  $\text{NaBF}_4$ ,  $1.77 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . In this investigation solutions in N-methyl formamide, propylene carbonate, dimethylformamide, and tetramethyl urea were also investigated. Elliott, Hsu, and Towle (11) report on the specific conductances of solutions of a number of salts in dimethylformamide, propylene carbonate, and benzonitrile compared with  $\text{H}_2\text{O}$ . The solvent (rather than the salt) determines the level of conductivity. Usually the salts arranged themselves in the same order in the three (aprotic) solvents. Ion size is important, compounds with larger ions having higher solubility. The ability of the ions to form complexes was emphasized. On the basis of measuring solubilities and conductances in a vast number of solutions, Elliott, Towle, and Hsu (12) formulated some general rules regarding these properties in non-aqueous solvents. They correlated conductance with viscosity and the tendency of ions to undergo specific interaction (coordination) effects and non-specific interaction (ion-dipole) type of bonding.

The deposition and dissolution of lithium anodes in solutions of  $\text{AlCl}_3\text{-LiCl}$  in propylene carbonate has been investigated at some length by Selim (13) as was the behavior of copper halide cathodes. An all chloride cell composed of Li anodes,  $\text{LiF}\cdot\text{BF}_3$  solutions in  $\gamma$ -butyrolactone with Cu cathodes was also studied (14). In this system background current thought due to the action of  $\text{BF}_3$  on the solvent were observed. Some experiments dealt with the anodic decomposition of a solution of  $\text{LiCl}$

in  $\text{LiClO}_4$ . For currents between 0.005 to 25  $\text{mA cm}^{-2}$  the following equation held:

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

In these studies the nature of the impurities in the solvent was observed to be of considerable importance and gas chromatographic techniques were used in analyzing for impurities that would affect electrode activity. The efficiencies of cathodic discharges of  $\text{CuF}_2$  and  $\text{AgCl}$  in propylene carbonate, dimethylformamide, butyrolactone, and acetonitrile were studied. Propylene carbonate was the least satisfactory because of lower efficiency.

Lyall et. al. (15) worked with solutions of aluminum chloride in propylene carbonate in connection with the development of a secondary battery using lithium anodes and nickel halide cathodes. They noted the instability of aluminum chloride solutions reported by others, i.e. aluminum chloride dissolution was very exothermic and the solution darkened with standing. They observed that the darkening could be partially eliminated by a procedure involving saturating the solution with chlorine after the aluminum chloride was dissolved, reacting excess chlorine with lithium metal, and finally saturating the solution with lithium chloride.

Eisenberg reported in 1964 (16) on an investigation with propylene carbonate, butyrolactone, and valerolactone using  $\text{LiCl} \cdot \text{AlCl}_3$  solutes. In discussing properties of desirable solvents he mentions stability from anodic and cathodic action as a requirement but does not give any decomposition measurements.

Farrar, et. al. (17) studied solutions of electrolytes in propylene carbonate (as well as acetonitrile and dimethyl sulfoxide) with the objective of developing a primary cell. They conclude that salts dissolve in these organic solvents to produce two large ions, for example,  $\text{AlCl}_3$  exists as  $\text{AlCl}_2^+$  and  $\text{Cl}^-$  and  $\text{Mg}(\text{ClO}_4)_2$  as  $\text{MgClO}_4^+$  and  $\text{ClO}_4^-$ . Various inorganic cathode materials such as  $\text{AgO}$ ,  $\text{CuF}_2$ , and  $\text{AgCl}$  were investigated in an electrolyte, 0.5 M  $\text{LiBr}$  in propylene carbonate. Severe polarization was observed (18).

Earlier this year Knapp reviewed (19) the status of the problem and reported on an experimental study comparing propylene carbonate

with dimethyl sulfoxide and acetonitrile as an electrolytic solvent. A number of solutes and cathode materials were investigated. The opinion that organic systems offered possibilities as practical primary cells was reinforced.

In this foregoing survey the attempt has been made to extract from the various investigation those items pertinent to the present area of investigation. Specifically, observations dealing with the chemical or electrochemical stability of electrolytic solutions of the cyclic esters propylene carbonate, butyrolactone, and valerolactone were sought. It would not be possible within reasonable space to even summarize the extensive measurements made by some Laboratories on hundreds of electrolytic solutions.

### III RANGE OF ELECTROLYSIS OF CYCLIC ESTERS

#### A. Experimental

The selection of solvents with desirable physical and chemical properties was discussed in the first report (1) and it was decided to devote our attention to acetonitrile,  $\alpha$  - picoline, dimethylformamide, propylene carbonate,  $\gamma$  - butyrolactone, and  $\gamma$  - valerolactone. In this period the latter three, the cyclic esters, were investigated. The purification of  $\gamma$ -butyrolactone has been discussed (1). In the work below redistilled samples were used with the exception of certain experiments in which commercial material were used for reasons mentioned.

Propylene carbonate was from Matheson, Coleman, and Bell (No. 7615 - PX 1705 b.p. 108-110°C at 10 mm) and was fractionated under reduced pressure as follows:

Cut No.	Temperature °C	Pressure mm Hg	Refractive index, 20°C
1	69	0.9	1.4223
2	69	0.9 - 1.0	1.4220
3 (residue)			1.4224
Reported (Reference 20)			1.4209

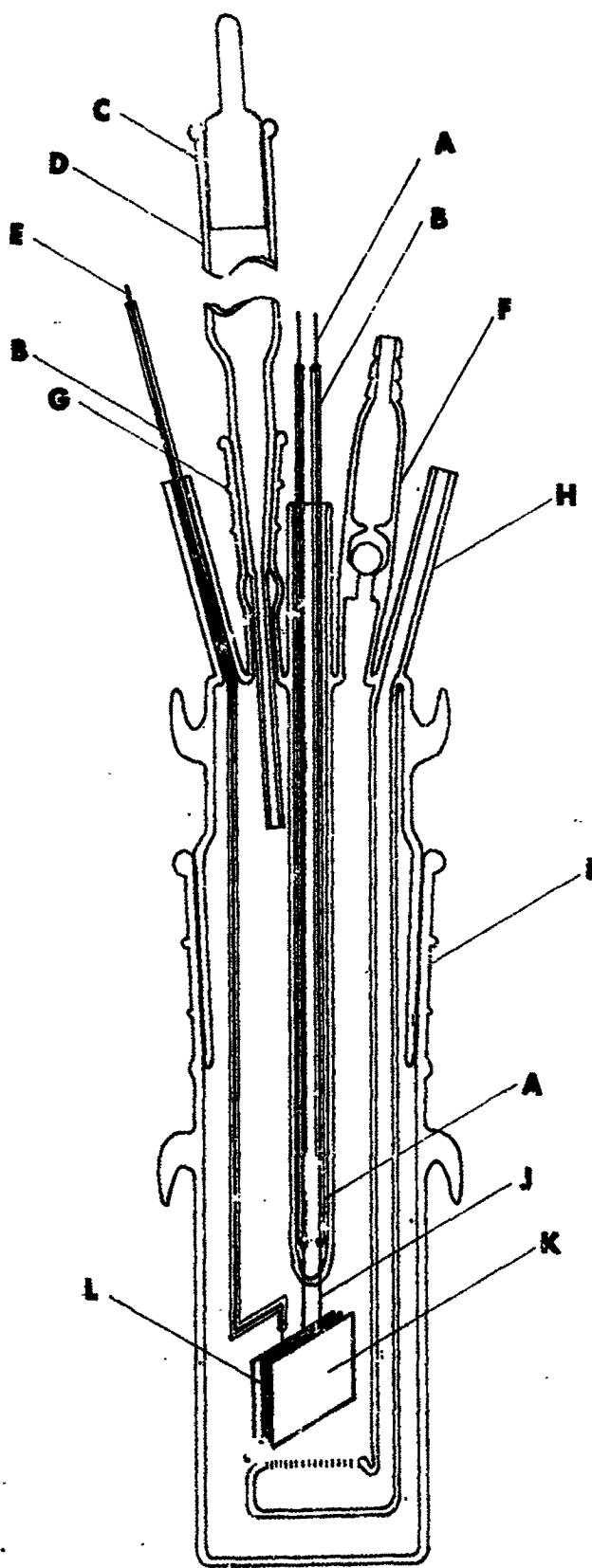
The second cut was used in the experiments below.

The  $\gamma$  - valerolactone was Eastman P 6123, and was fractionated under reduced pressure as follows:

Cut No.	Temperature °C	Pressure mm Hg	Refractive index,
1	39.75 - 43.0	0.475 - 0.770	1.4355
2	43.25 - 49.0	0.75 - 1.30	1.4315
Reported (Reference 21)			1.4301

The apparatus and procedures were generally similar to those described in the first report (1) with the following exceptions. A new electrolysis cell schematically depicted in figure 1 was constructed. In this cell the electrolytic solution was exposed only to glass and Teflon. The ground glass joints were separated by Teflon sleeves. The volume of the electrolytic solution was usually 100 ml. Measurements were made at 25°C. The potential was set manually and the current was

Figure 1 ELECTROLYSIS CELL



- A - Electrode lead (Copper)
- B - Teflon sheath
- C - Standard taper joint, 14/35
- D - Filling tube
- E - Silver wire reference electrode
- F - Check valve
- G - Standard taper joint, 10/30
- H - Gas diffuser tube
- I - Standard taper joint, 55/50
- J - Electrode lead (platinum)
- K - Electrode (platinum)
- L - Separator (glass fiber paper)

read after a wait of 4 minutes to approximate a steady-state measurement. In several cases measurements were made at a given potential by approaching from a higher potential as well as from a lower potential. Drying procedures were varied from the procedures outlined previously. The salts were dried in a desiccator over  $P_2O_5$ . This point is discussed more fully below.

## B. Results and Discussion

### Electrolysis of Butyrolactone Solutions

The behavior of butyrolactone solutions of lithium perchlorate\* on electrolysis is shown in figures 2 and 3. In figure 2 both curves A and B were obtained with 0.675 M solutions of  $LiClO_4$ . Curve A was obtained by making the working electrode first the anode then the cathode; curve B by the reverse procedure, that is, by making the electrode the cathode first and then the anode. These solutions were clear and colorless after electrolysis, with no evidence of colored decomposition products. The potentials at the arbitrary current density of  $0.1 \text{ ma/cm}^2$  were for A, anodic 2.36 v., cathodic 3.38 v., for curve B, anodic 2.67 v., cathodic 3.38 v. indicating total ranges of 5.74 v. and 6.05 v., respectively. Figure 3 shows a similar curve (A) for a 0.262 M solution with an anodic value of 2.38, cathodic of 3.65 and a range of 6.03. Curve B was obtained with the same solution which had been allowed to stand for 100 hours over type 4A molecular sieves and will be discussed below. On the anodic side there is what appears to be a diffusion limiting current caused by some impurity. This is evident when polarizing in the forward direction (from lower to higher anodic potentials) but is missing when polarizing from the higher (anodic) potentials. In both solutions there is a peak current at 1.4 to 1.6 v. on the cathodic side. The interpretation of this is uncertain but the best estimate is that it represents traces of  $H_2O$ . A solution 0.092 M in  $LiClO_4$  gave a similar behavior (not shown) on electrolysis. There was no trend observed with concentration of the solute.

Some measurements with  $KPF_6$  solutions in butyrolactone were given in the first report (1). Further measurements are given in figures 4 and 5. Curve A in figure 4 was obtained with 1.0 M soln of  $KPF_6$  in redistilled butyrolactone. Curve B was the same solution allowed to

\*Anhydrous lithium perchlorate from Foote Mineral Co.

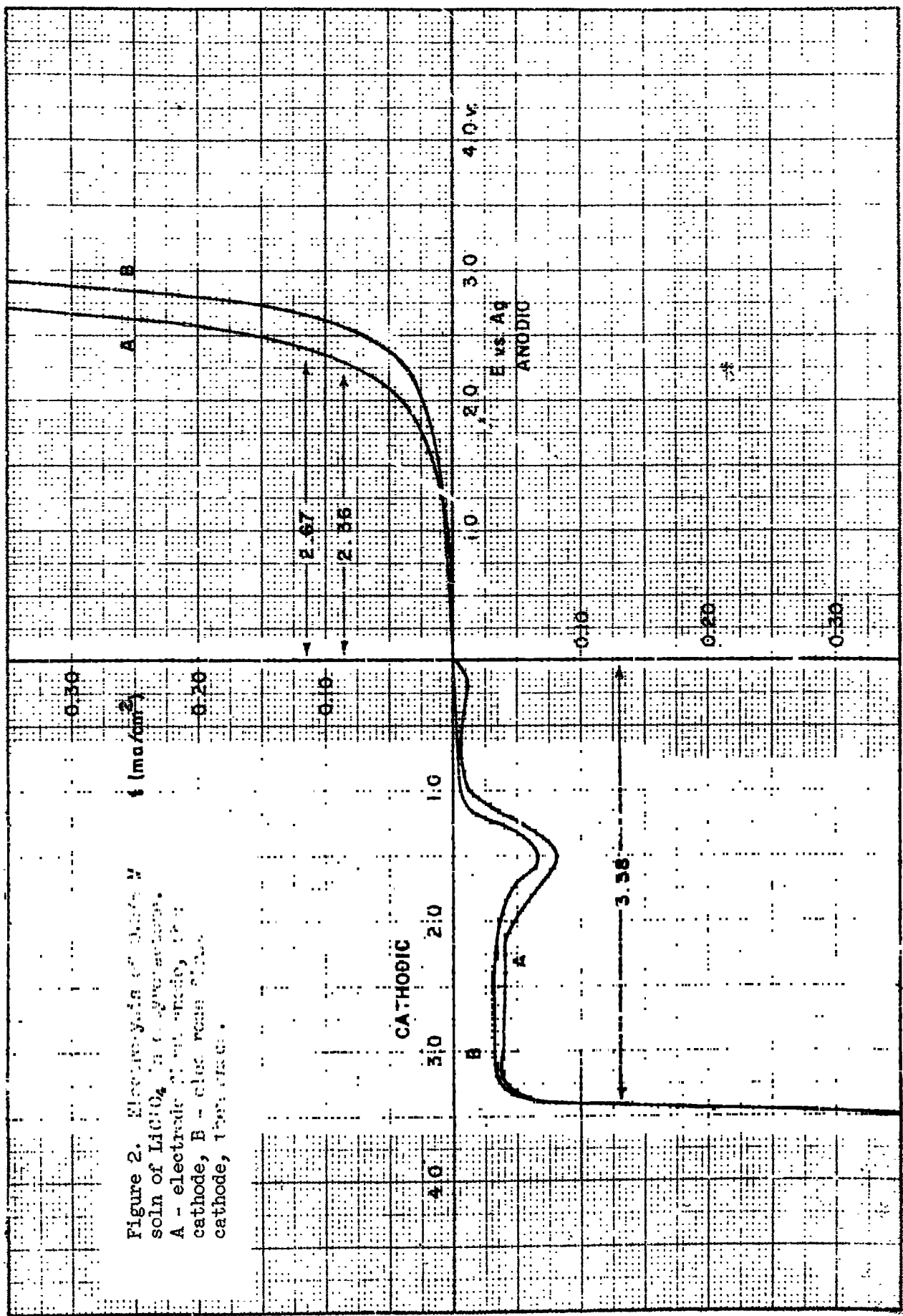


Figure 2. Electrolysis of 0.01 M  
soln of  $\text{LiClO}_4$  in  $\text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$ .  
A - electrode (near anode), B -  
cathode, B - elec near  $\text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$   
cathode, 1000 Hz.



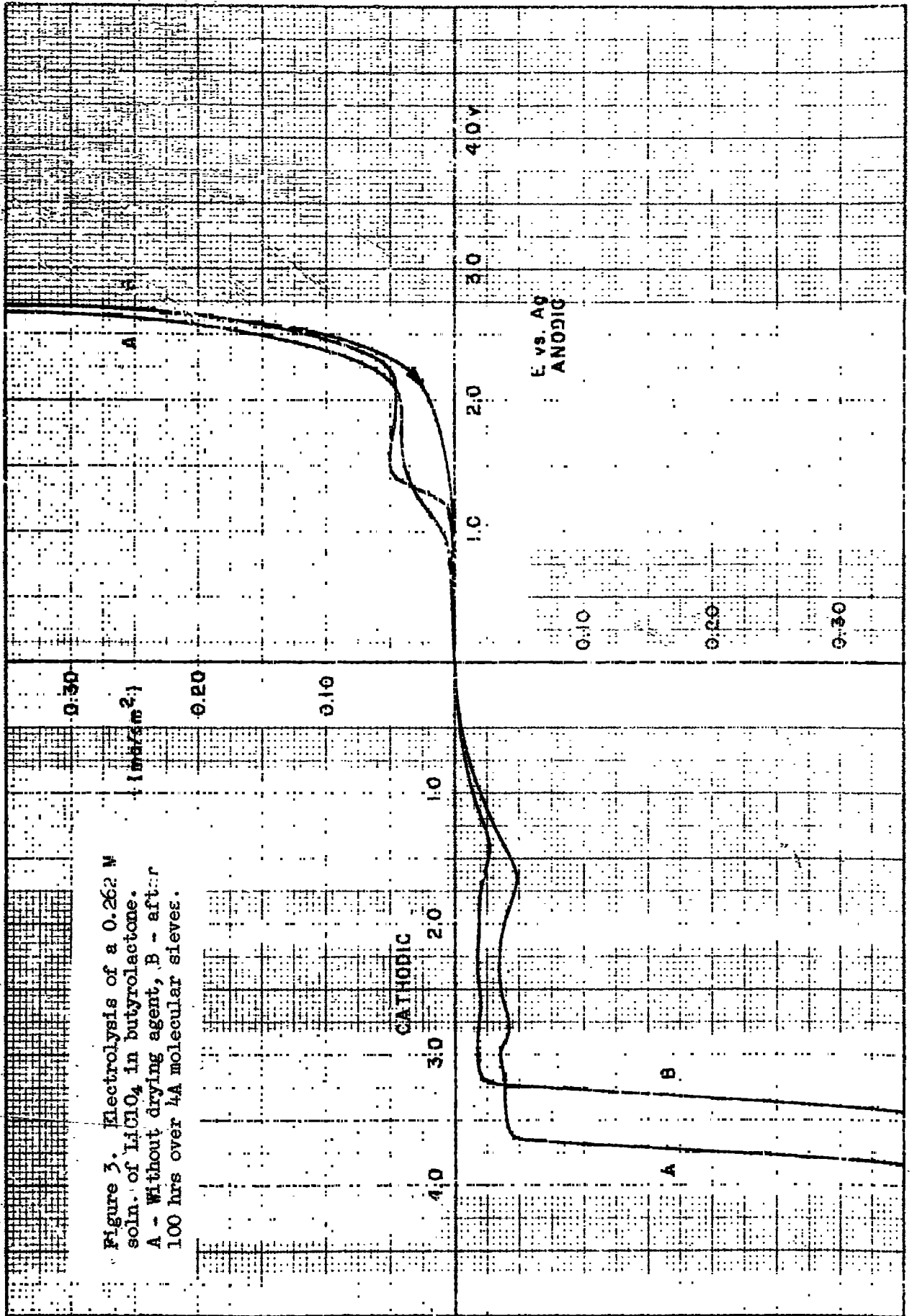


Figure 3. Electrolysis of a 0.262 M soln. of LiClO<sub>4</sub> in butyrolactone. A - Without drying agent, B - after 100 hrs over 4A molecular sieves.

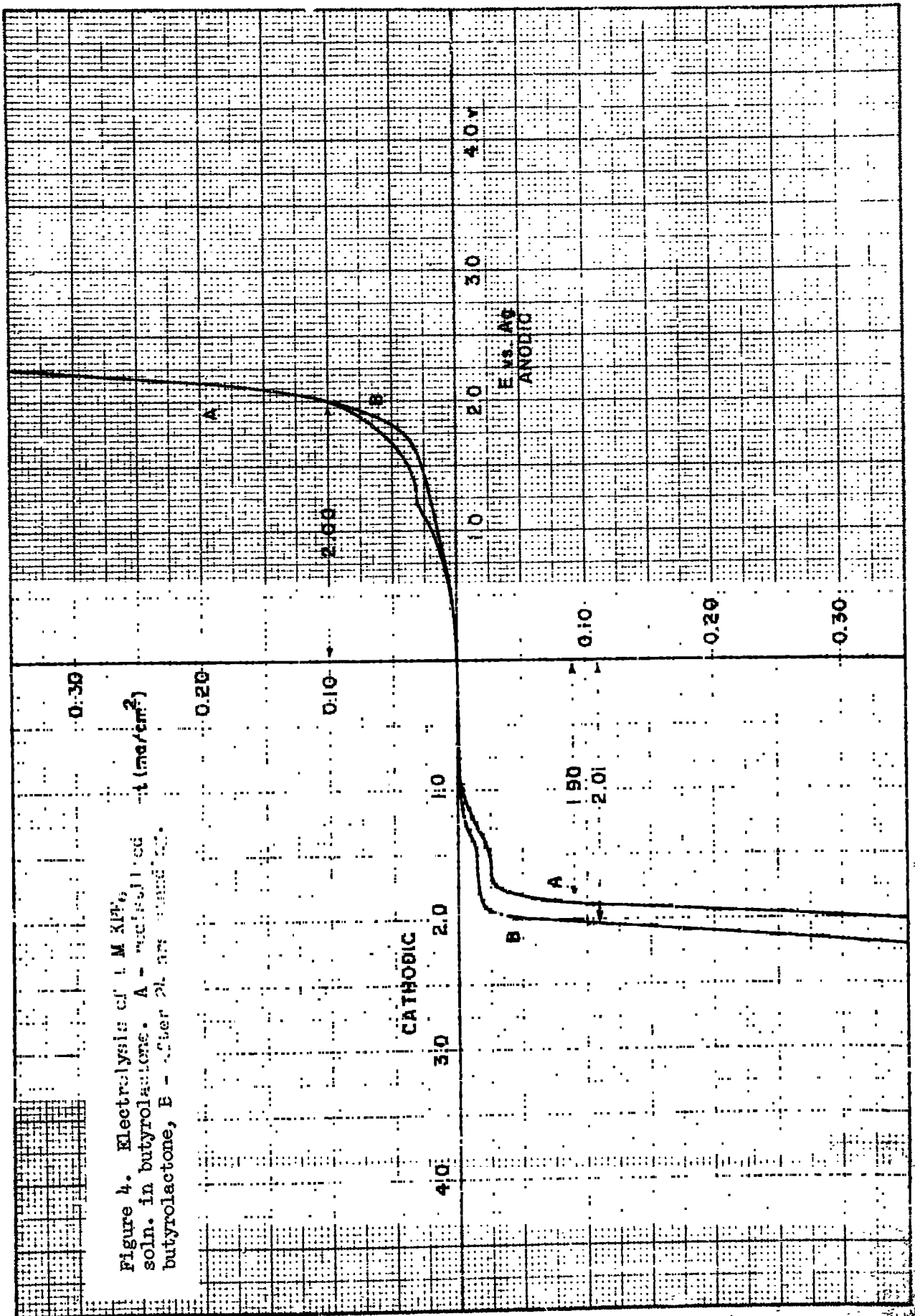
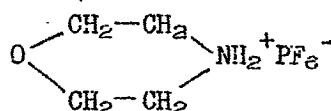


Figure 4. Electrolysis of 1 M KCl soln. in butyrolactone. A - reduced butyrolactone, B - after 24 hr. standing.

stand in the cell for 24 hours with the objective of allowing the reference electrode to come to equilibrium with the solution. Anodic potentials of 2.00 and 2.00 v., cathodic potentials of 1.90 and 2.01 v. for curves A and B respectively are observed. The ranges are 3.90 and 4.01 v. with sharp rises on both the anodic and cathodic side. In figure 5 is given a plot (curve A) for a soln 1.0 M in  $KPF_6$  with anodic, cathodic, and range values of 2.0, 1.82, and 3.82 v., respectively. This solution had been dried over type 3A molecular sieves for 12 days so that the oxidizable impurity observed at 1.2 - 1.8 v. on the anodic side should not be  $H_2O$ . Curve B is a similar measurement wherein the solution was prepared in commercial butyrolactone rather than distilled. There is a shift of the electrolysis range in the negative direction. Potential values of anodic, 2.5, cathodic 1.29 and range of 3.79 were recorded.

Solutions of morpholinium hexafluorophosphate\* in nonaqueous solvents are of interest because of the high conductivity of solutions formed with this salt (10-12). The formula



indicates acidic hydrogen. This is evidenced in figure 6 in which measurements are made in 0.5 M morpholinium hexafluorophosphate solutions prepared in doubly distilled butyrolactone (curve A) and commercial grade (curve B) are given. For curve A an anodic electrolysis potential of 2.33 v., a cathodic of 0.45 v., and a range of 2.78 v., are compared with curve B, with anodic potential of 2.60 v., cathodic of 0.30 v., and range of 2.90v.

Figure 7 gives a family of electrolysis curves for 0.5 M solutions of morpholinium hexafluorophosphate in commercial butyrolactone. Curve A represents the solution without any drying agent, curve B was developed by measurements made on a solution to which Linde molecular sieve type 3A (K, Na, zeolite) was added, curve C to which type 4A (Na Zeolite) was added and curve D to which type 5A (Ca, Na zeolite) was added. The pH's of these solutions were 5, 6, 6, and 6 respectively indicating that the zeolites functioned as neutralizing as well as drying agents.

\*Morpholinium hexafluorophosphate obtained from Ozerk Mahoning and is about 98.2% pure based on fluorine analysis.

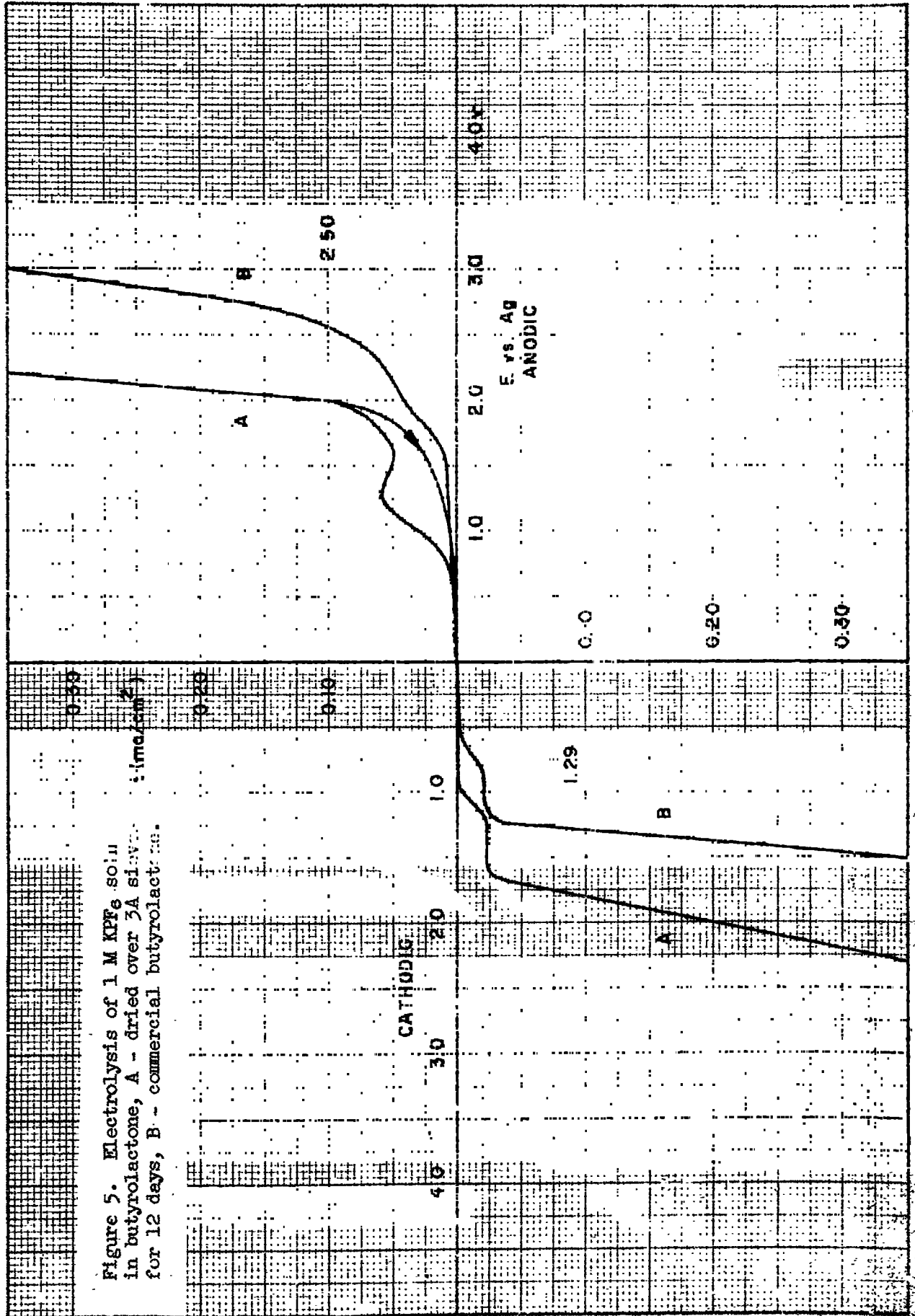
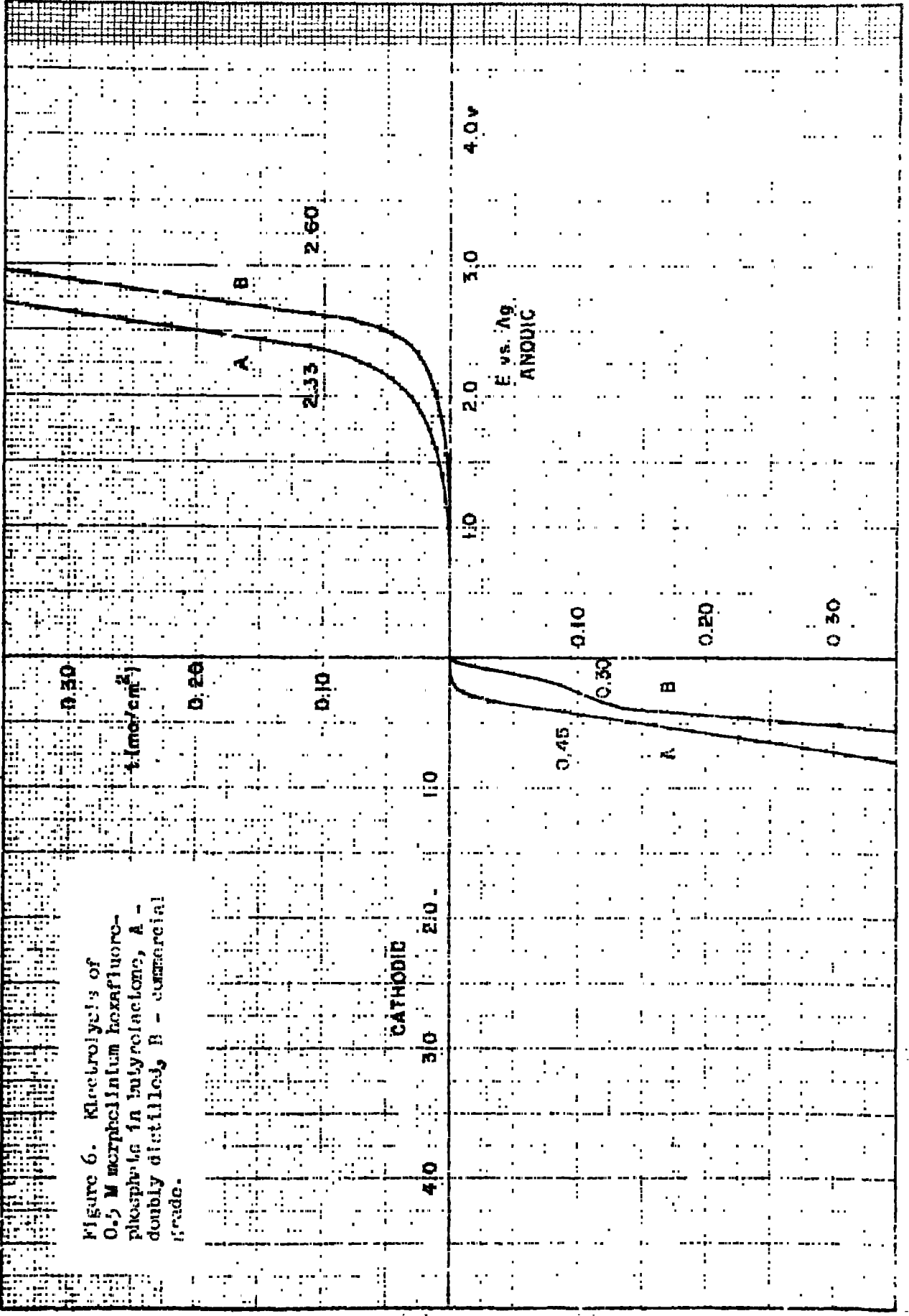


Figure 5. Electrolysis of 1 M  $KPF_6$  solution in butyrolactone, A - dried over 3A solvent for 12 days, B - commercial butyrolactone.

Figure 6. Electrolysis of 0.5 M mercurinium hexafluorophosphate in butyrolactone, A - doubly distilled, B - commercial grade.



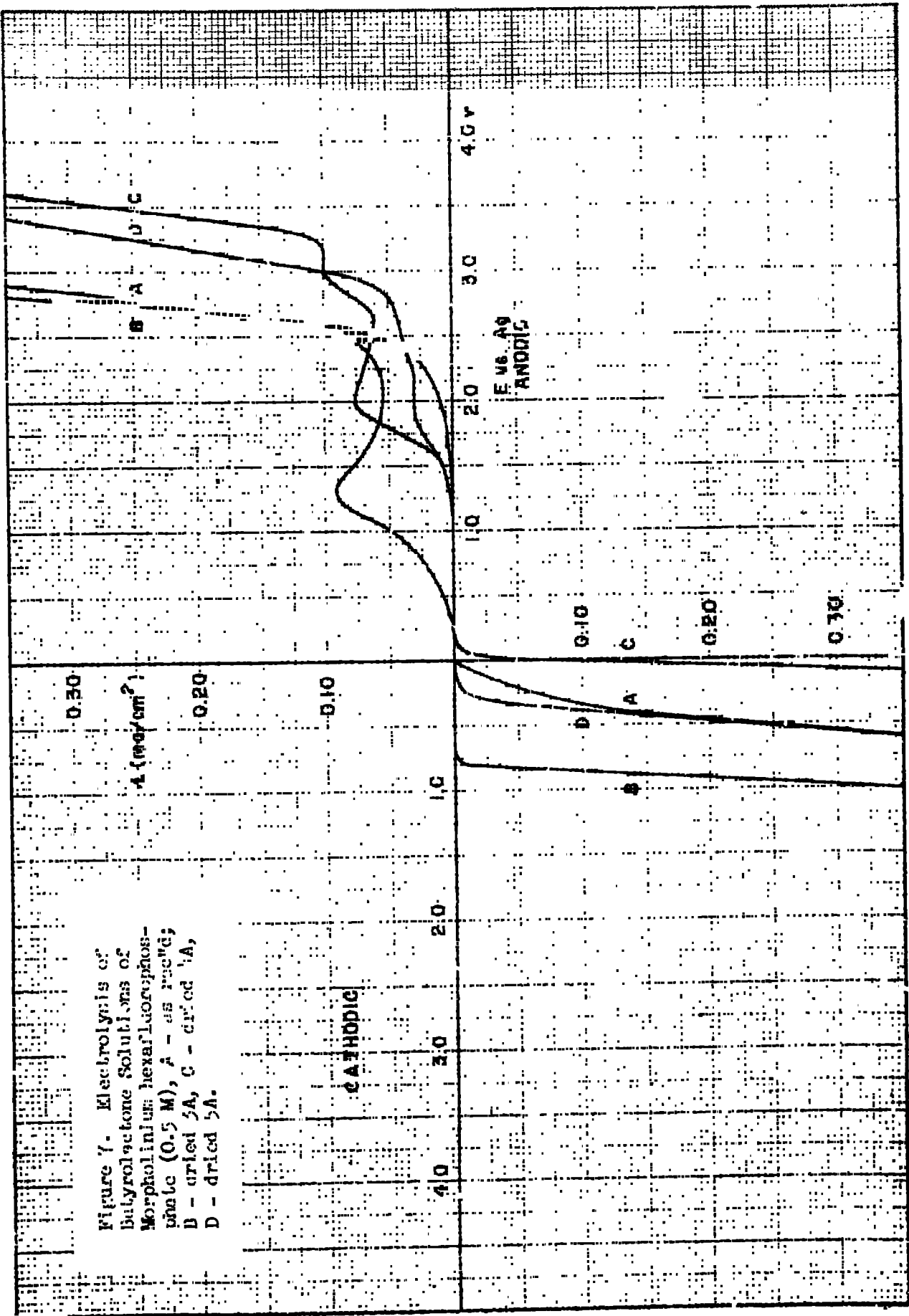


Figure 7. Electrolysis of Butyrolactone Solutions of Morpholinium hexafluorophosphate (0.5 M), A - as rec'd; B - dried 5A, C - dried 1A, D - dried 5A.

The significant result was that the molecular sieves introduced into the solution some impurity that gave an appreciable current on the anodic side of the electrolysis curve. Similar results are seen in figure 8 wherein the solvent was commercial acetonitrile. The legend with regard to the drying agent is the same. In both cases molecular sieves of the 3A and 4A type contributed to (diffusion limiting) currents on the anodic side.

#### Electrolysis in Propylene carbonate solutions

The electrolysis of a 0.455 M lithium perchlorate solution in propylene carbonate used directly after distillation is shown in figure 9. Curve A was from points collected over a period 2 - 4 hours after filling the cell, curve B 24 hours later. The shift is considered to be due to the equilibrating of the silver reference electrode with the solution. This shift in reference potential can be quite serious. For example, the electrolysis of a 0.637 M solution of lithium perchlorate in propylene carbonate gave an anodic potential at 0.1 ma/cm<sup>2</sup> of 2.92, cathodic of 2.20, range of 5.12 v. when run about 15 minutes after filling the cell. A second run gave values of 2.50, 2.68, and range 5.18 v. when made immediately following. The total range of electrolysis was about the same but the potentials at which the current density of 0.1 ma/cm<sup>2</sup> was measured was drastically altered by the "aging".

#### Electrolysis in $\gamma$ - Valerolactone Solutions

Measurements made with lithium perchlorate solutions in  $\gamma$  - valerolactone are shown in figure 10. Curve A was developed with a 0.305 M solution of LiClO<sub>4</sub> in Eastman practical-grade valerolactone with sufficient impurity content to produce a very misleading result regarding the range of electrolysis in this solvent. On the anodic side the current rises quite rapidly yielding a potential value of 0.75 v. This value, with a cathodic potential of 3.95 gives a range of 4.70 v. Purification of this solvent shows that the anodic rise is due to an oxidizable impurity. Curve B was developed with a 0.202 M solution prepared in newly distilled valerolactone. The oxidizable impurity at 1.3 v. is not recorded when the polarization path is reversed. Curve C refers to measurements made in the same solution which had been allowed to stand overnight in a closed cell in a dry N<sub>2</sub> atmosphere.

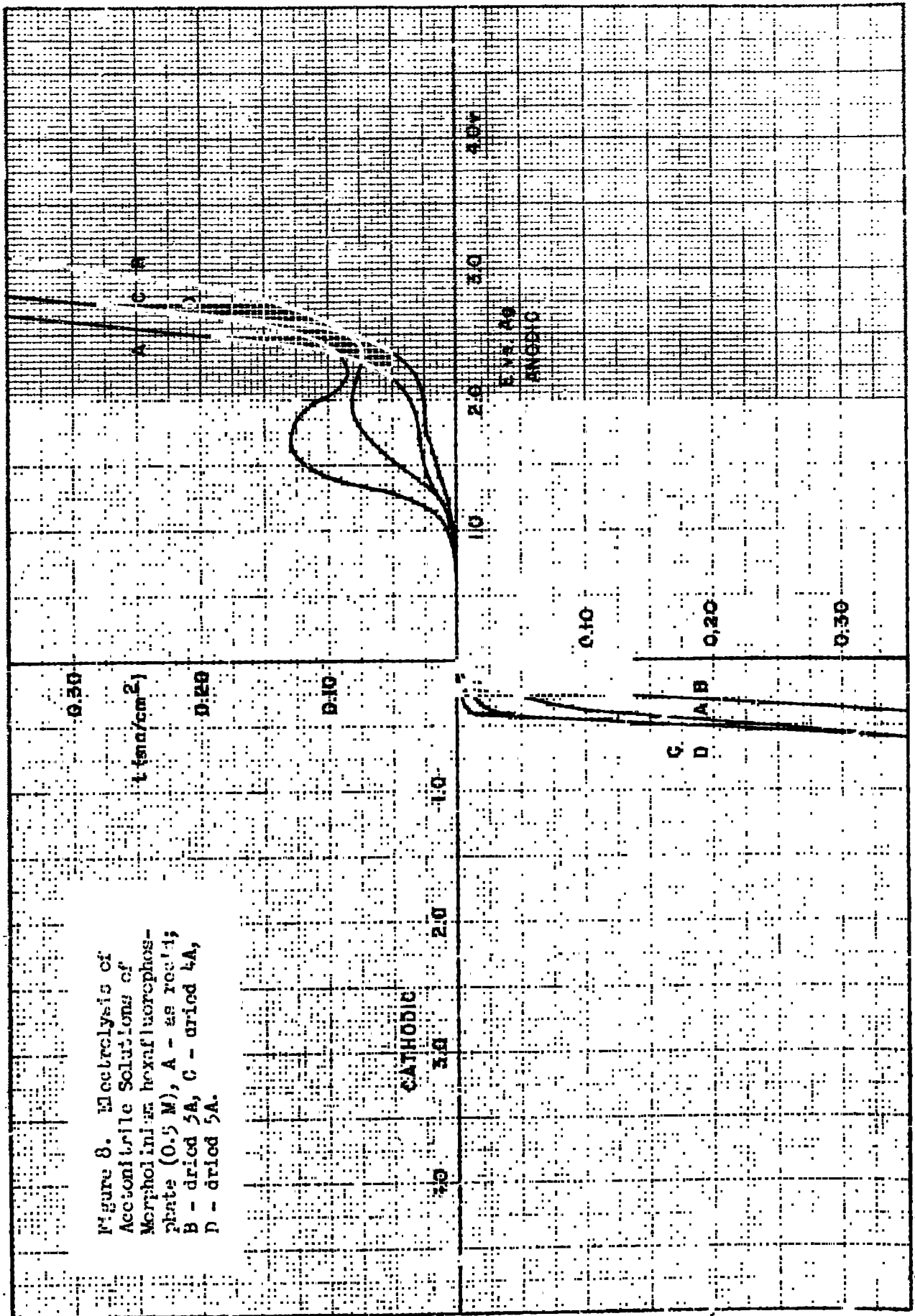


Figure 8. Electrocatalysis of Acetonitrile Solutions of Morpholine hexafluorophosphate (0.5 M), A - as rec'd; B - dried 5A, C - dried 4A, D - dried 5A.



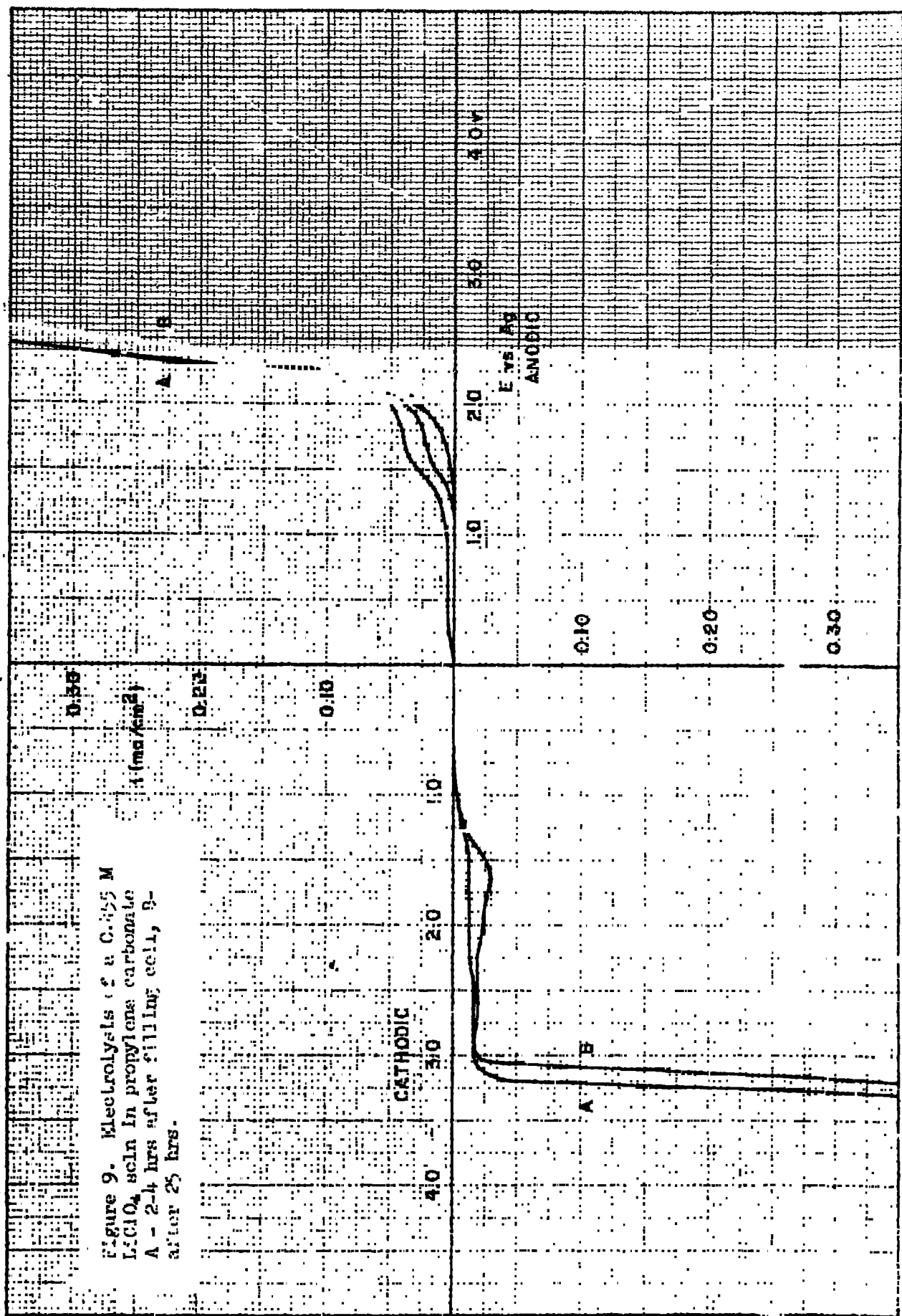


Figure 9. Electrolysis of a C-455 M LiClO<sub>4</sub> soln in propylene carbonate  
A - 2-4 hrs after filling cell, B - after 25 hrs.

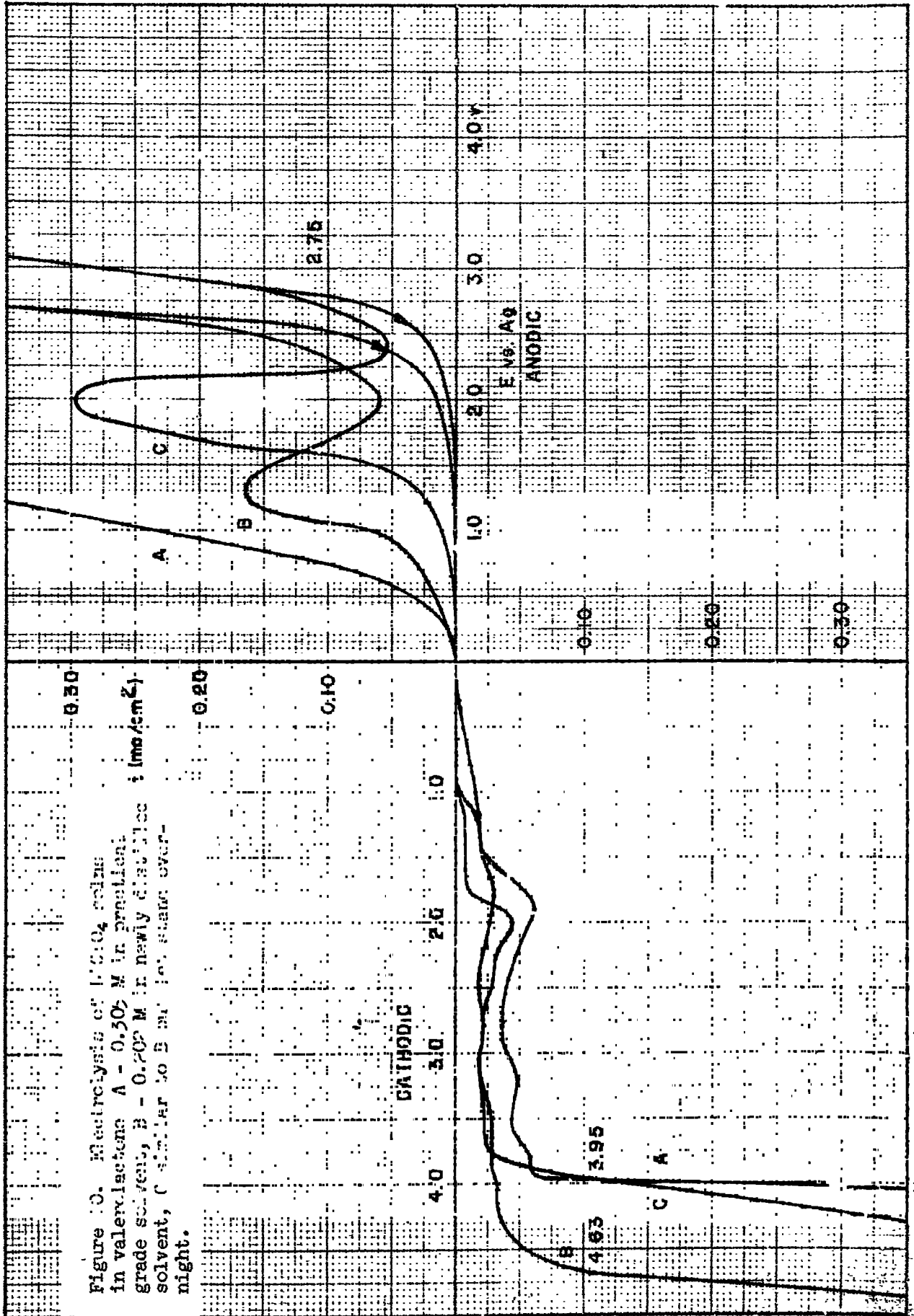


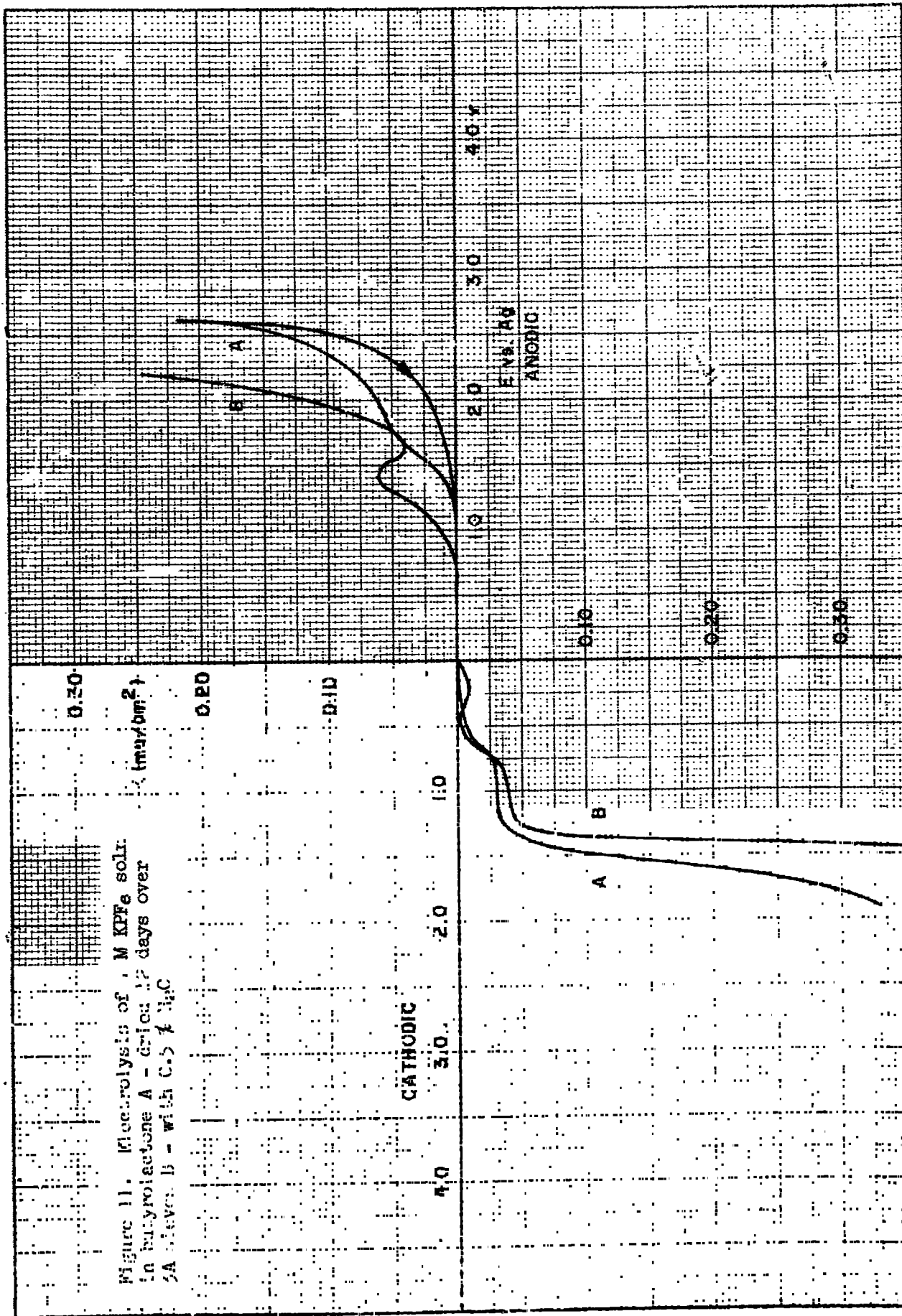
Figure 10. Electrocyclic of L-DIO<sub>4</sub> films in valerylactone. A - 0.30% M in proceliant grade solvent, B - 0.20% M in newly distilled solvent, C similar to B but for state overnight.

Two things are observed. The first is the effect of the limiting current at a greater concentration based on the (limiting) current, and second the shift in reference potential observed above. In this latter experiment an anodic potential of 2.75 v., a cathodic of 3.91, and a range of 6.70 v. is observed. The behavior, to the degree seen on the anodic side, appears to be specific to valerolactone as an explanation based only on water contamination is discounted. Whatever the reason, viz., overpotential of Li deposition on valerolactone, etc., it appears that the span of electrolysis in valerolactone is greater than that of butyrolactone and propylene carbonate.

#### Effect of Water Vapor and Drying Procedures

The presence of water in the solvent has the effect of shortening the electrolysis range and introducing limiting current constituents into the solution. Curve A in Figure 11 was obtained with a 1.0 M solution of  $KPF_6$  in butyrolactone which had been dried for 12 days over type 3A molecular sieves. Curve B was obtained from the same solution to which 0.5% by volume of water were added. The total range of electrolysis is shortened from 3.90 to 3.22 volts. It is intended to do more work on this effect particularly in studying the effect of water additions to solutions with a wide range of electrolysis.

It has been pointed out previously (1) that care must be taken in the employment of drying agent. Anhydrous calcium sulfate dissolves in most of these solvents to an appreciable degree;  $P_2O_5$  reacts chemically. Of the adsorbent type of drying agents the "molecular sieves" are the most suitable. However, at this stage they should be used with reservations. For extended periods of time it appears that the molecular sieves will introduce into the solution sodium and potassium salts which are evident on the cathodic side of the electrolysis curve. Figure 12, the electrolysis curve from a 0.298 M solution of lithium perchlorate that was prepared with distilled butyrolactone that had been allowed to stand for 3 months over type 4A molecular sieves is typical of a number of similar experiments. Figure 7 illustrates how oxidizable impurities may be introduced when solutions were treated with three types of molecular sieves for 15 days. On the other hand a lithium perchlorate solution in butyrolactone standing for 100 hours over type 4A molecular sieves did not suffer any adverse effect as seen from



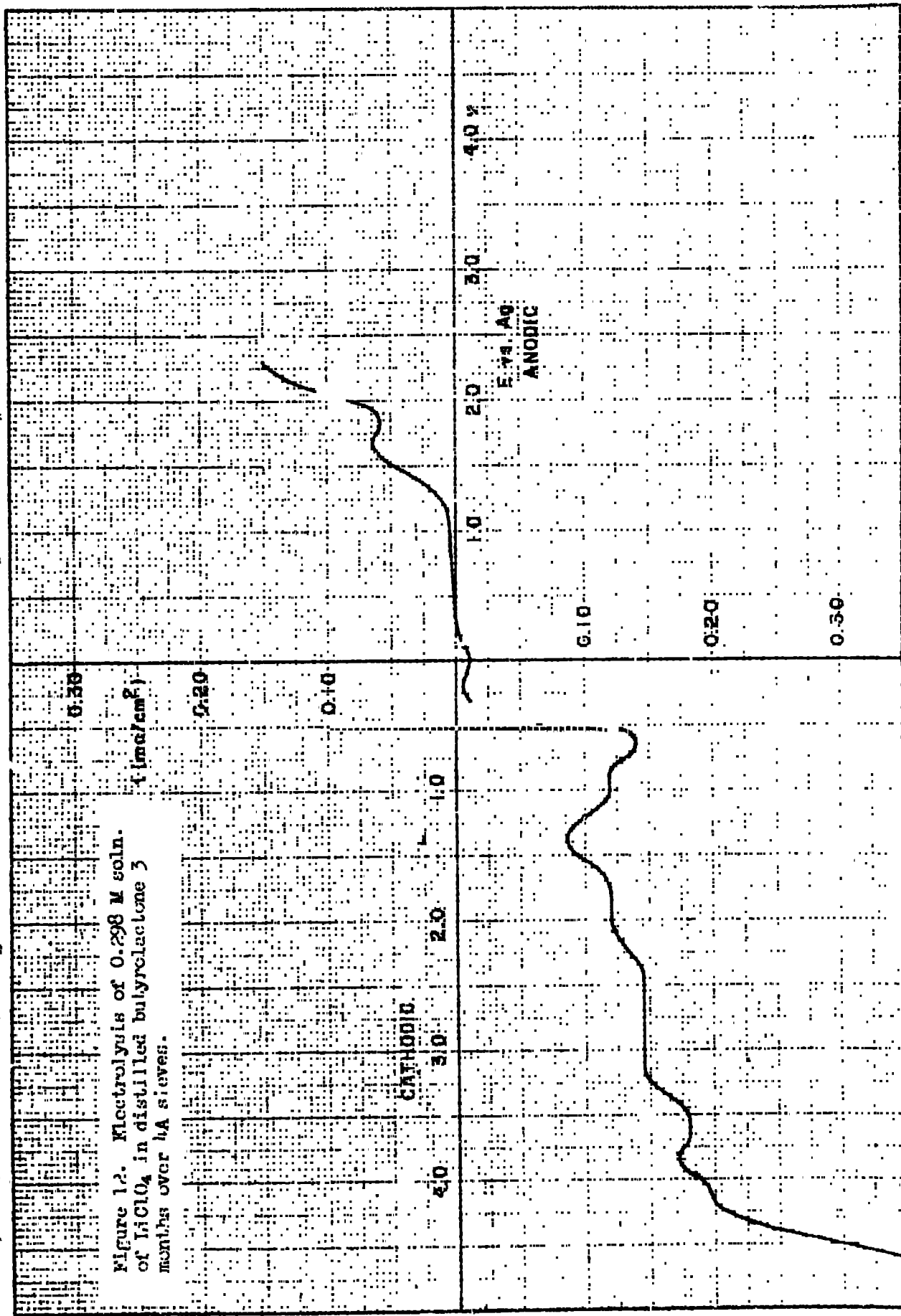


figure 5. Furthermore, in this case the possibility existed of exchange of Li ions with K or Na on the solid adsorbent. This whole area needs better definition. However, at this time it can be stated that the use of molecular sieves in contact with these solvents could well introduce complicating factors.

#### Effect of Chloride Ion

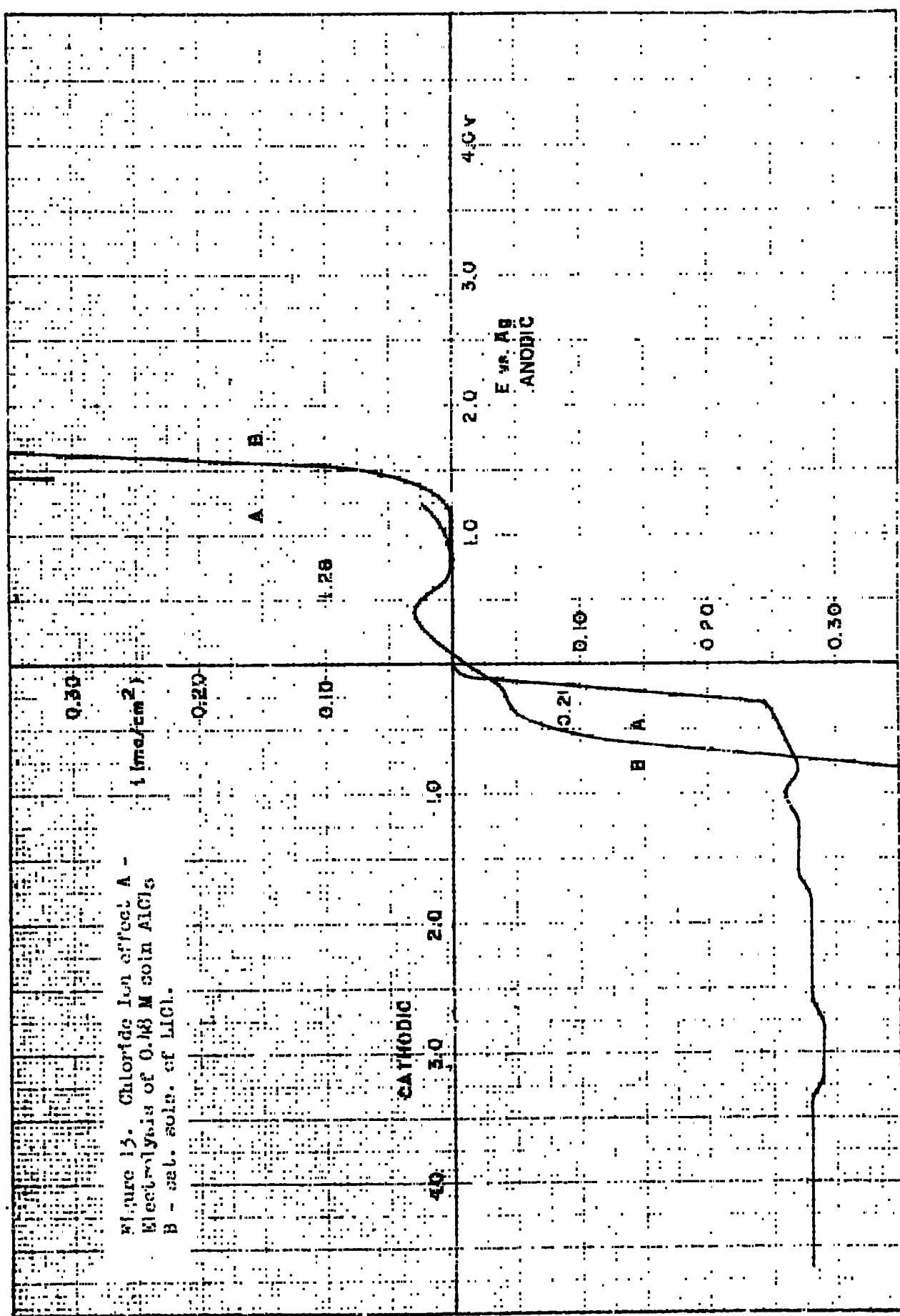
The effect of chloride ion is considered here by way of generalizing the electrolytic behavior of a number of chloride solutions. Unfortunately, these solutions are among those that would find employment in practical cells. Curve A in figure 13 was obtained with a 0.48 M solution of anhydrous aluminum chloride in  $\gamma$ -butyrolactone. In the preparation of the solution the exothermic effect and the solution darkening, reported by others, was observed. Curve B is a saturated solution of LiCl in the same solvent. The anode potential of 1.28 - 1.45 v. was to be expected but the cathodic behavior is difficult to explain unless a reaction with the solvent made hydrogen ions available.

#### Reference electrodes

In this work a silver wire situated about 1mm from the working electrode served as a reference electrode. This follows the thinking of Koch (22) who found that concentration cells based on Ag/AgNO<sub>3</sub> in acetonitrile followed the Nernst equation and of other investigators who employed this type of electrode in organic systems. Where the solute is constituted from halide salts the corresponding silver halide electrode can be used. However, the halide ion may have an adverse effect on the working electrode as discussed above. The AgCl electrode was used in the lithium perchlorate (0.319 M) solution in butyrolactone (see figure 14) and appears to be reasonably stable. Curve B was run 4 hours after curve A. It is interesting to note that in both cases polarizing from the high potential direction following polarization upward indicates that the oxidizable impurity was removed by electrolysis. An approximation at this time would be that the AgCl electrode was about 0.3 v. less positive than that of Ag. More work should be done in this reference electrode area particularly to eliminate situations of instability over long periods of time.

#### C. Conclusions and Direction of Future Effort

From the data presented above it is evident that the range of electrolysis, that is, the voltage range over which an electrolysis



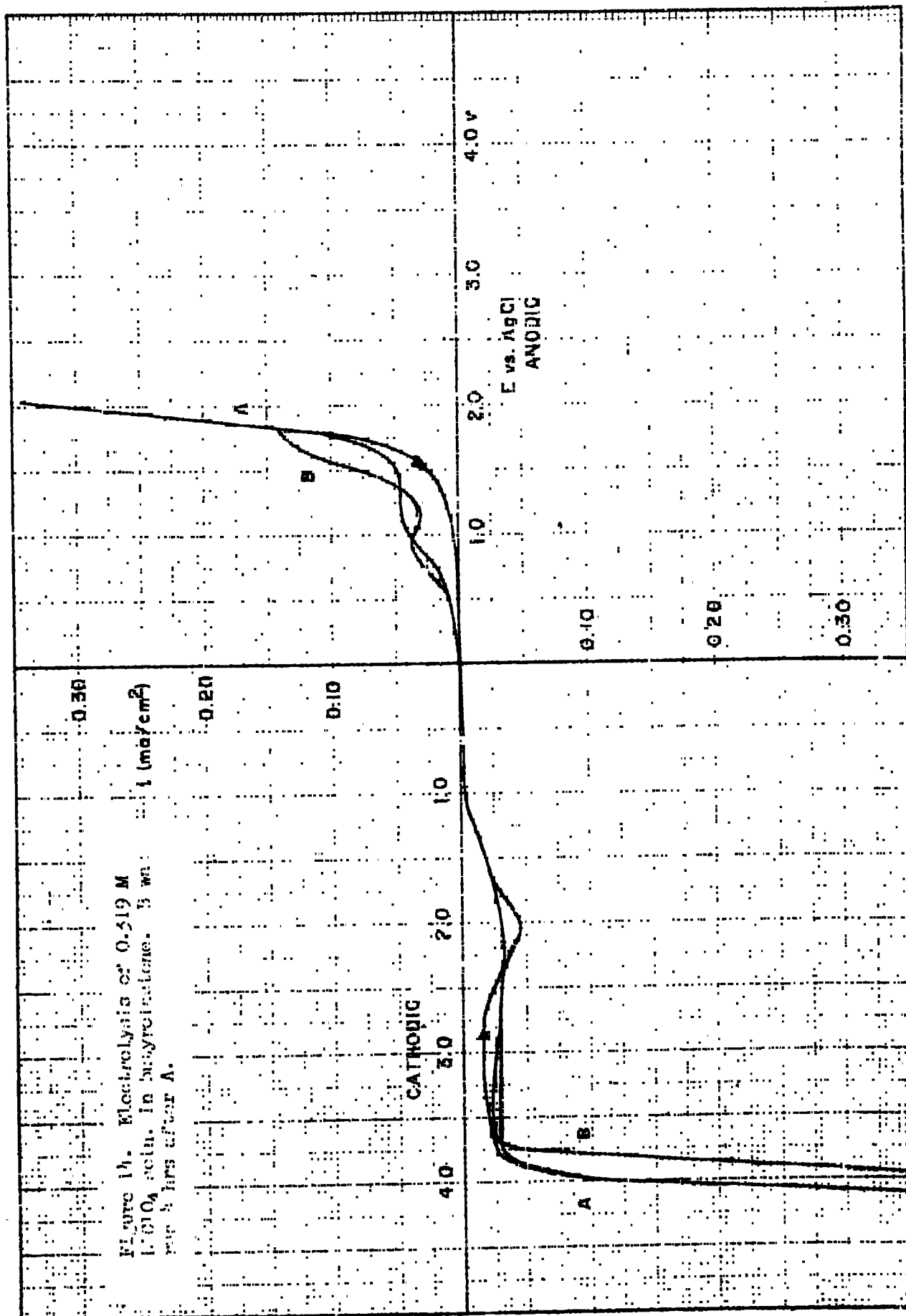


Figure 14. Electrolysis of 0.519 M FeCl<sub>3</sub> soln. in benzotrifluorene. B was run 5 hrs after A.



can be conducted without sensible Faradaic current contribution from the supporting electrolyte system, is a function of the solvent and the solute. Up till now we have worked with rather stable solvents so that most effects can be explained in terms of the dissolved salts. Although the danger of generalizing and talking in terms of averages is well recognized it is still of interest to attempt to draw some broad conclusions at this point.

First the ranges of electrolysis of the solvents, mostly based on  $\text{LiClO}_4$  solutions and averaging a number of measurements are as follows:

Butyrolactone	5.78 v.
Propylene carbonate	5.25 v.
Valerolactone	6.82 v.

The significance of these figures, i.e. whether valerolactone is actually 1 v. higher than the others will have to be confirmed by future work.

Turning now to the anodic potential limit as established by specific anions the following figures may be tentatively assigned.

$\text{ClO}_4^-$	=	2.40 v.
$\text{PF}_6^-$	=	2.47 v.
$\text{Cl}^-$	=	1.41 v.
$\text{BF}_4^-$	=	2.51 v.

The value for the  $\text{BF}_4^-$  ion is based on very few data. The cathodic potential limits as established by cations is as follows:

$\text{Li}^+$	=	3.44 v.
$\text{K}^+$	=	1.65 v.
$\text{Na}^+$	=	1.08 v.
* $(\text{CH}_3)_4\text{N}^+$	=	0.92 v.
* $\text{Al}^{+++}$	=	0.21 v.
* Morpholinium	=	0.40 v.

\* Cathode process not known.

With regard to the direction of future effort it would be very desirable to complete this phase of the project by making measurements with recrystallized samples of  $\text{KPF}_6$ ,  $\text{LiPF}_6$ , and  $\text{KClO}_4$ . These measurements correlated with what has been done will allow solvent limits to

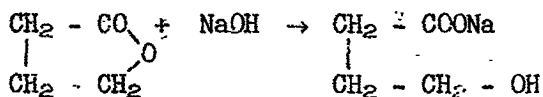
be established. It is intended to clarify the reference electrode situation from the viewpoint of checking adherence of the  $\text{Ag}/\text{Ag}^+$  electrode to the Nernst relationship in the electrolytes of interest. Whereas, the influence of water is roughly known, it will be essential to know the relationship quite accurately. On a longer term basis an understanding of the halide ion effect and how it affects the cathode activity will be considered.

#### IV. CHEMICAL STABILITY OF CYCLIC ESTERS

##### A. General

The objective of this phase of the program is to clarify some of those chemical properties and reactions that would be of significance when the cyclic esters are used as electrochemical solvents. Two obvious areas of concern are reactions with certain metals, namely, Li, Na, K, Ca and Mg and with the halogens. It is expected that anodes for many galvanic, power-producing cells will be drawn from the five metals listed here. Also, when an electrolyte, such as a KPF<sub>6</sub> solution, is employed in the galvanic cell the possibility exists of K being deposited. It is to this phase of the problem that attention was devoted during this period.

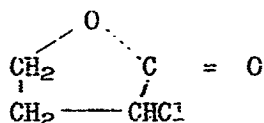
Some general comments can be made on the stability of the cyclic esters. It is known that a  $\gamma$  - hydroxy acid loses water between the carboxyl group and hydroxyl group in the same molecule to form the cyclic ester or inner ester called the lactone. Structurally, the cyclic esters, like normal esters, are intermediate between ethers and anhydrides. The reaction of the  $\gamma$  - hydroxy acid to form the lactone is quite spontaneous in aqueous solution. The  $\gamma$  - lactone is partially converted to the acid when boiled with water. The alkali hydroxides and barium hydroxides rapidly convert them to salts of the acids.



Ammonia converts the lactones into the amides of the corresponding acid.

Butyrolactone is stable at pH 7, but in alkaline solution hydrolysis is quite rapid. This is reversible when the pH is restored to 7. A typical analysis (23) for commercial butyrolactone gives only 0.1% of  $\gamma$  - hydroxybutyric acid. Halogen acids open the lactone ring, gamma-chlorobutyric acid being obtained with aqueous HCl. Alcohols react in the presence of sulfuric acid to yield the ester. In the presence of metallic sodium and a trace of sodium ethylate butyrolactone undergoes an aldol condensation. Sodium disulfide reacts to give the

disodium salt of dithiodibutyric acid. Chlorine reacts with  $\gamma$ -butyrolactone at 140°C to give alpha-chlorobutyrolactone.



Benzene, butyrolactone, and aluminum chloride give gamma-phenylbutyric acid (Friedel-Crafts type of condensation). Boron trifluoride forms double compounds with butyrolactone. Catalytic oxidation of butyrolactone yields succinic and maleic anhydrides.

Propylene carbonate (20) is a very good solvent for a number of resins. It reacts readily with ammonia and primary and secondary aliphatic amines to give 1-methyl-2-hydroxyethyl carbamate and derivatives. It is completely miscible with ethylene carbonate, a 10% mixture freezes at -53°C.

Propylene carbonate reacts with many compounds containing an active hydrogen to give the corresponding hydroxypropyl derivative, e.g. with phenol at 140-200°C or stearic acid at 170-200 (0.5% potassium carbonate catalyst in both cases).

The rate of hydrolysis apparently is the same order of magnitude as the lactones. Propylene carbonate, however, hydrolyzes with potassium carbonate. Traces of acid or base, as well as heat, tend to decompose the compound. Propylene oxide, propionaldehyde, allyl alcohol, and CO<sub>2</sub> are decomposition products. It is hydrolyzed rapidly in alkaline and slowly in acid solutions at 100°C.

#### B. Experimental

The reactivity of Li, K, Na, Ca, and Mg, was studied at 100°C in butyrolactone and propylene carbonate. The solvents were fractionated under reduced pressure and a middle cut was used for the experiment. The metals were obtained from the Fisher Scientific Co., as follows: sodium No. 206; potassium P-168; lithium L-111; calcium C-42; magnesium M-11. Weighed quantities of the solvent (about 50 g.) and the metal (usually 0.5 - 1.0 g) were held under reflux at 100°C, the three-neck flask holding the reaction mixture being held in a constant temperature oil bath. Nitrogen gas dried over P<sub>2</sub>O<sub>5</sub> was flowed over the reaction mixture at a rate of about 25-30 ml/min,

the top of the condenser being connected to a drying tube. Following the 100-hr reaction time the metals were reweighed and the solids and solutions were examined by chemical methods, infrared, and gas chromatographic techniques to learn the extent of reaction and the nature of the reaction products.

### C. Results and Discussion

The weight changes undergone by the different metals are summarized in Tables I through III.

Table I

Flask No.	Metal	Solvent	Weight of metal (g.)	
			(solid) Initial	Final
1	Li	Butyrolactone	0.473	0.483
2	Na	"	0.850	24.84
3	K	"	0.643	9.337
4	Mg	"	0.741	0.691
5	Ca	"	0.686	0.684
6	Ca	Propylene carbonate	1.007	1.160

Table II

Flask No.	Metal	Solvent	Weight of metal (g.)	
			(solid) Initial	Final
1*	None	Butyrolactone	-----	----
2*	None	Propylene carbonate	-----	----
3	Na	"	1.331	2.320
4	Mg	"	2.390	2.400
5	K	"	1.382	2.359
6	Li	"	1.207	1.353

\* Controls for reactivity of solvent in absence of metal

Table III

Flask No.	Metal	Solvent	Weight of metal (g.)	
			(solid) Initial	Final
1	Na	Butyrolactone	0.778	4.341
2	"	"	0.694	5.510
3	"	"	0.715	6.227
4	"	"	0.764	4.865
5	"	"	0.774	4.983

The third run was made to get sufficient product for analysis.

From these runs and the chemical and physical analysis of the solid products it is possible to draw general conclusions with regard to the reactivity of the five metals with the two cyclic esters.

Sodium and potassium definitely react with butyrolactone under the experimental conditions (100°C, and dry N<sub>2</sub> atmosphere). Li, Ca, and Mg are unreactive. Analysis of solid reaction products by infrared give indications of being salts of the carboxylic acid. The water solutions of these salts have pH's in the 7-8 range. In the reaction of Na with butyrolactone the metal appears to be directly responsible for gas evolution. The products obtained by reaction between Na and K and butyrolactone give positive unsaturation and ester tests but negative alcohol and carbonyl tests. Gas chromatographic study of the products of reaction between Na and butyrolactone in solution indicate the presence of at least 3 compounds, all lower boiling than the solvent. The gas chromatograms are compared in figure 15. The approximate proportion of these three compounds in a 50- $\mu$ l sample are 0.05, 0.19, and 0.24  $\mu$ l or in the range of about 0.4%.

Sodium, potassium, and calcium show visible signs of reaction with propylene carbonate whereas Li, and Mg are unreactive.

#### D. Conclusions and Direction of Future Effort

A tentative generalization at this time would class K, Na, and Ca, both the metals and, for reasons stated above, their salts, as adversely affecting butyrolactone and propylene carbonate when the latter solvents are used as electrochemical solvents.

It is planned to continue this work to identify, at least in terms of functional groups, the nature of the reaction products in the solid state (in combination with the metal) and in the solution. It is also intended to study the reaction of these 5 metals in the presence of an electrolytic solute such as lithium perchlorate because the extent of this reaction will be a critical point in battery technology as pointed out by King (24).

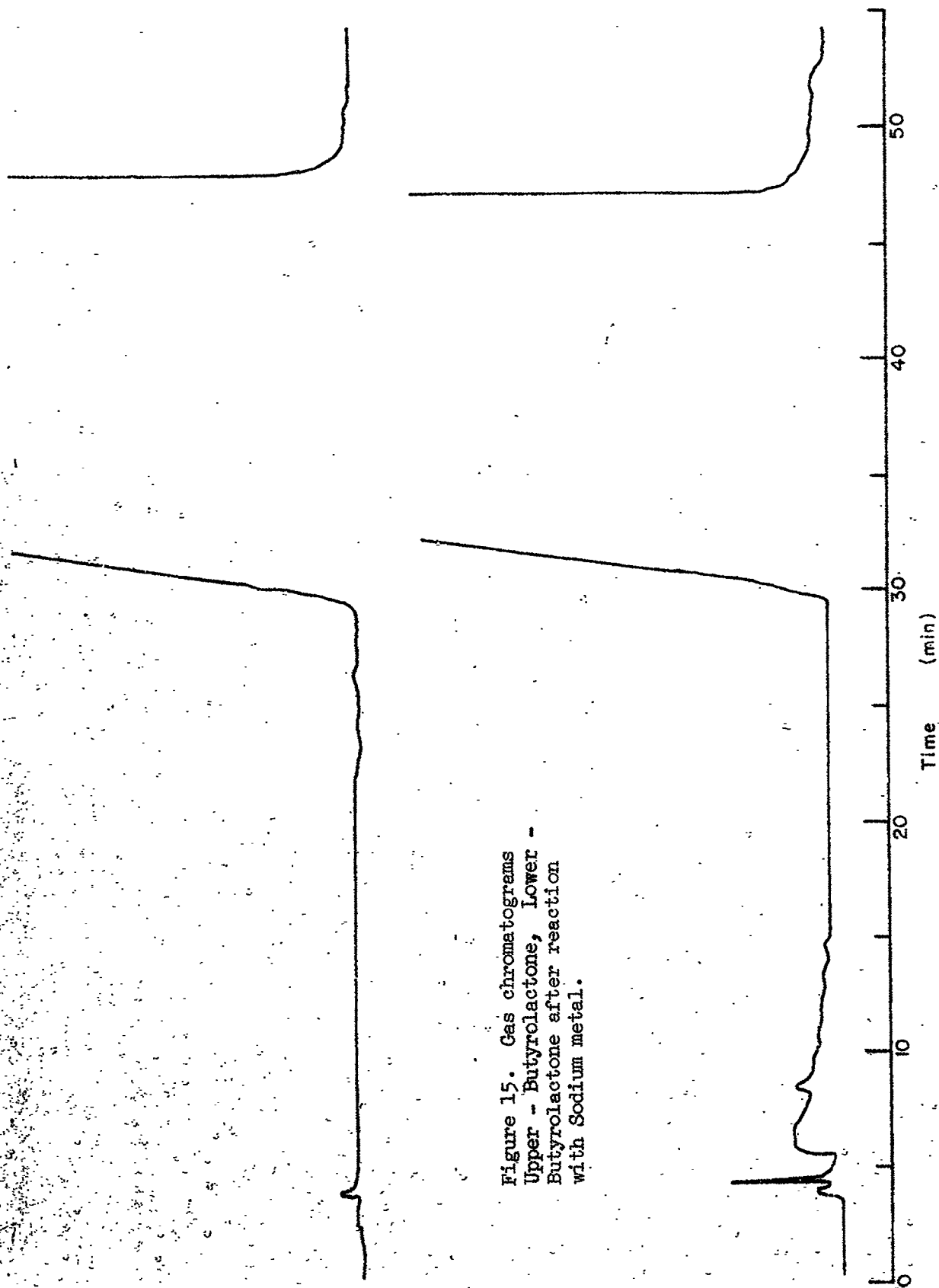


Figure 15. Gas chromatograms  
Upper - Butyrolactone, Lower -  
Butyrolactone after reaction  
with Sodium metal.

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