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HIGH ENERGY BATTERY SYSTEMS BASED ON PROPYLENE CARBONATE

Raymond Jasinski

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

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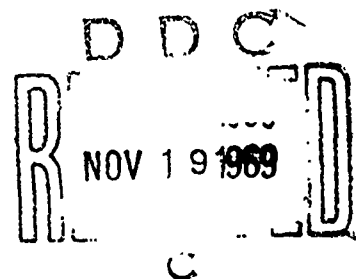
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ABSTRACT

The electrochemistry of electrolyte and electrode systems based on the aprotic organic solvent propylene carbonate is reviewed with emphasis on the application of such systems to high energy batteries. Topics discussed include electrolyte stability, purity requirements, purification procedures, solvent-ion interaction phenomena, and electrode reactions of inorganic positives, organic positives, and active metal negatives. Performance of primary battery systems is satisfactory for many purposes. The development of secondary systems and systems for operation at low temperature is discussed.

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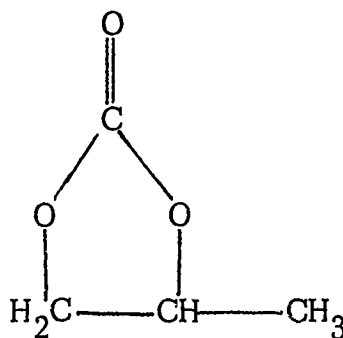
I. INTRODUCTION

The principal application of propylene carbonate (PC) in electrochemistry is its use as the primary electrolyte solvent for ambient temperature batteries employing, as the negative electrode, an alkali or alkaline earth metal (e. g. , Li or Ca). Electrodeposition of metal from PC is a relatively unexplored subject, and will be considered only in terms of recharging battery plates. PC has also found some application as a fill electrolyte for capacitors.⁸²

PC, a cyclic ester, is a clear, colorless (when pure) liquid capable of ionizing a variety of organic and inorganic salts. Its general properties are listed in Table I.

Table I. General Properties of PC

Formula



Molecular weight	102
Melting point, ⁵⁰ degrees	-49
Boiling point, ⁵⁰ degrees	241
Dielectric constant ⁸⁸	65.00 ± 0.08
Viscosity, ⁵⁰ cp	2.5
Density ⁵⁰	1.2

The dielectric constant is high: not too different from that of water. As will be shown, the solution chemistry of PC is, however, considerably different from that of water. The viscosity is significantly higher and some, although not all, of the differences in behavior can be explained by this property. The liquidus range is broad. The solvent can be supercooled by about 25°; solutes such as LiAlCl_4 depress the freezing point to at least -80 °C. Although the solvent boils at +241 °C, thermal decomposition can occur at and above +150 °C.

PC is produced in the United States by Jefferson Chemical Company via a reaction of CO_2 and propylene "under conditions that are proprietary." Processes have been described in the open and patent literature (e. g. , 72, 83) in which CO_2 and propylene oxide are reacted to produce PC at temperatures of 100 to 270 °C and 50 to 150 atm over a catalyst of an alkali or tetraalkylammonium halide plus an oxide or carbonate of a group II or group III metal.

The initial electrochemical studies of PC and similar cyclic esters are described in reference 50. This work was quickly followed in the early 1960's by a series of exploratory projects on the development of lithium batteries with PC as the principal ionizing solvent (e. g. , 29, 41, 80).

This initial work was mainly empirical in nature. More recently, some emphasis has been placed on the chemical and physical properties of this solvent, although mainly as they influence battery performance. The discussion given below will be based on this work. For discussions of prototype hardware, the reader is referred to references 54 and 56 as well as the original contract literature. A general bibliography of the contract literature is given in reference 55.

II. ELECTROLYTE REQUIREMENTS

The basic requirements for the PC electrolytes are: (1) compatibility with the electroactive plate materials, (2) high ionic conductivity, (3) insulation of the plates from the transfer of electronic charge, and (4) solvation, if possible, of at least some of the discharge products to prevent rapid passivation of the electrodes. Batteries with insoluble reaction products are common in aqueous systems. However, coulombic efficiency tends to be low ($\leq 30\%$), and high surface area electrodes are necessary to sustain prolonged current drains.¹¹⁴

As will be shown, PC appears to be at least kinetically compatible with lithium and this, of course, is a major reason for the interest in PC electrolytes. It has not yet been established whether PC and lithium are thermodynamically stable.

The discussion of compatibility given below will also consider decomposition of the positive via solvation of the plate material. This type of reaction, generally more prevalent than redox reactions at the negative, has a considerable effect on cell shelf life.

Considerable effort has been expended in surveying a host of solvent-solute combinations to uncover stable, highly conducting electrolytes. In order to simplify the quest, rules of thumb such as a high dielectric constant and a low viscosity were used to pick likely candidates. The rationale behind these rules is discussed in a variety of texts and in Section III.

Table XIX lists a number of measured conductivities at the point of maximum conductance. Few solvent-solute combinations have ionic conductivities much in excess of $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ (the majority have about $5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ ionic conductivity).

What limitation then does conductivity place on battery performance? Transferring ionic charge via diffusion plus migration in an electrolyte has been treated by Levich.⁷¹ The order of magnitude calculation given below is an application of his basic equation to the situation of a lithium electrode depositing ions into solution which are transferred across the electrolyte space and plated out at the cathode. The electrolyte chosen as an example is 1N LiClO_4 in PC:

$$i_L = \frac{nF D_1 Z_1 (2 C_0)}{\delta} \left(1 + \frac{Z_1}{Z_2}\right)$$

The electrode separation is taken as 0.25 mm, about the thickness of filter paper. C_0 is the initial concentration of solute. A linear concentration gradient is considered between the electrodes, hence $2 C_0$ is used in the calculation. Z_1 and Z_2 are the charges on the ions. There is very little information available on diffusion coefficients. A value of $3 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ is used (see Section III. 7); the electrolyte conductivity is $5.6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. From this data, a maximum electrolyte ionic current of 50 mA/cm^2 is computed. The applied potential required to pass 0.9 of this current in the absence of electrode overpotential effects is $\sim 0.1 \text{ V}$.

A. Electrolyte Stability

As mentioned often, a major (although not necessarily the only) reason for the increased interest in organic electrolytes is the opportunity to exploit the highly electropositive metals as battery negatives. The high negative potentials and the low equivalent weights of metals such as lithium and calcium imply a high energy density battery.

When coupled with transition metal fluorides, cell potentials of the order of 3.55 V are generally realized, at least on open circuit (Table II). Thus, the electrolyte is required to be stable to 81 kcal/equivalent. In these solvents, then, the fluorides are reasonable oxidizing agents. To put this point into context, the thermodynamic cell potential for chlorine, an active oxidant, coupled with lithium is about 4 V.

Stability to reduction is generally measured first by observing the presence or absence of gassing from the metal electrode immersed in purified solution, as well as alterations in the appearance of the solution. (The high purity of the solvent is to be emphasized. Besides obscuring results, the impurity can be directly involved in the decomposition of the bulk solvent and/or the coating of the negative described below.)

Table II. High Energy Density Electrode Couples at 25 °C^(41,54)

Reaction	Cell Potential, E°	Energy Density, W-hr/lb
2Li + F ₂ → 2LiF	6.05	2740
2Li + S → Li ₂ S	2.6	1350
2Li + CuCl ₂ → 2LiCl + Cu	3.06	505
2Li + CuF ₂ → 2LiF + Cu	3.55	754
2Li + NiF ₂ → 2LiF + Ni	2.83	620
2Li + NiCl ₂ → 2LiCl + Ni	2.57	437
3Li + CoF ₃ → 3LiF + Co	3.64	965
2Li + CoF ₂ → 2LiF + Co	2.88	633
2Li + CuO → Li ₂ O + Cu	2.25	587
2Li + NiO → Li ₂ O + Ni	1.79	492
4Li + Ni ₃ S ₂ → 2Li ₂ S + 3Ni	1.80	388
Mg + CuF ₂ → MgF ₂ + Cu	2.92	566
Mg + NiF ₂ → MgF ₂ + Ni	2.21	445
3Mg + 2CoF ₃ → 3MgF ₂ + 2Co	2.89	691
Mg + CuO → MgO + Cu	2.30	538
Mg + NiO → MgO + Ni	1.83	451
Mg + AgO → MgO + Ag	2.98	491
Ca + CuF ₂ → CaF ₂ + Cu	3.51	604
Ca + NiF ₂ → CaF ₂ + Ni	2.82	501
Ca + CuO → CaO + Cu	2.47	503
Li + AgCl → LiCl + Ag	2.84	231

A purified LiClO₄-PC solution was tested for compatibility with lithium by measuring, quantitatively, the rate of gas evolution in an equilibrated solution.¹⁴ No evidence of gassing was found after 5 days at 25 °C. Also, the surfaces of the lithium samples remained clean and bright with no signs of corrosion films. The same results were obtained with mixtures of PC and ethylene carbonate. Furthermore, the solutions were not discolored nor was there sediment or cloudiness present in the solution.

Decomposition reactions of an electrolyte by lithium need not involve gassing, but would generally involve charge transfer (oxidation of the lithium). Electrochemical techniques have been used to study this. Since the Li/Li^+ electrode is reversible, lithium test probes are difficult to use. The use of other metals such as platinum could possibly obscure results due to differences in overpotential for the decomposition reactions. Fig. 1 shows a cyclic sweep (80 mV/sec) on a platinum probe immersed in 1N LiClO_4 in distilled PC. Potentials are measured versus a Li/Li^+ reference electrode in the same solution.¹⁵ A detailed interpretation of this pattern is given in reference 17 together with confirmatory chronopotentiometric measurements. Briefly, cathodic peak no. 1 is due to the reduction of residual water, ~ 2 to 3 ppm. Peaks 2 and 3 are apparently due to the formation of lithium platinum alloy (a bright platinum electrode held at this potential develops a black coloration and, when immersed in water, will evolve gas). With time, this current decays to zero as the surface becomes saturated with alloy.

The anodic currents appear due to the oxidation of cathodically formed species, among them adsorbed hydrogen. From this data it is apparent that the electrolyte is kinetically stable from at least 0 to +3.8 V versus Li/Li^+ . The currents observed can be accounted for by the impurities in solution and by a specific alloying reaction.

In some cases, the solute can affect the electrochemical measurements of stability over and above direct participation in charge transfer reactions. This cyclic sweep experiment was repeated with tetraethylammonium perchlorate as the solute. A cathodic current characteristic of water reduction was not observed, even though small amounts of water were known to be present in the electrolyte (enough to cause considerable current flow in LiClO_4/PC). The addition of LiClO_4 restored the pattern to the form shown in Fig. 1. Tetraethylammonium perchlorate can also perturb the positive electrode. For example, the reduction of thin films of CuF_2 on copper were inhibited in an $\text{R}_4\text{NClO}_4/\text{PC}$ solution, even though R_4NF is more soluble than LiF (Table XV).

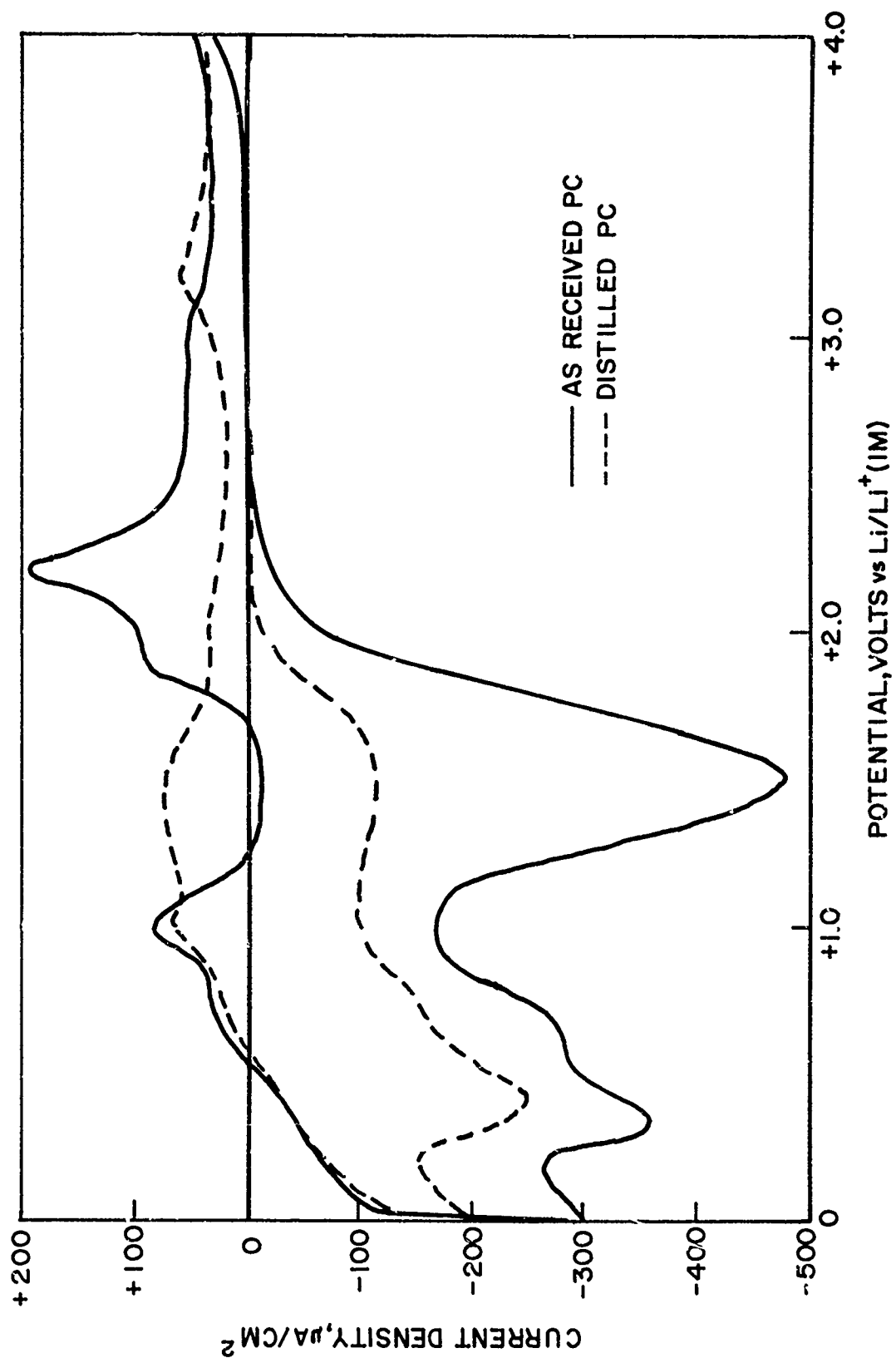


Fig. 1. Background currents recorded at Pt microelectrode in as-received PC and distilled PC containing dried LiClO_4 as electrolyte [scan rate = 80 mV/sec; scan was initiated at 0 cp (+2.7 V)]

Thermodynamic stability of PC solutions in the presence of lithium has not been established. The basis for raising this question is the repeated observation that clean lithium amalgam electrodes apparently decompose PC solutions at potentials of 1 V positive to the Li/Li^+ electrode.^{30, 100} This process has not yet been fully investigated, so the conclusions must be regarded as tentative.

Smooth, polished lithium electrodes were exposed to solutions containing ClO_4^- , PF_6^- , AsF_6^- , and BF_4^- . No particular incompatibility was noted.⁴ In the presence of potassium ions, a characteristic blackening of the electrode always occurred at or near the liquid surface. No other evidence of chemical activity accompanied this phenomenon: the solutions always remained clear. It is possible that the differences in potential between potassium and lithium may be sufficient to cause a displacement-corrosion reaction.

It is also required that the electrolyte be stable over the temperature of interest in developing battery hardware. For the purposes of this discussion, the temperature range of interest is -40 to $+160^\circ\text{F}$, essentially the ambient temperature range for the planet.

Little work has been done on the stability range of PC electrolytes. It has been shown⁵⁹ that the solvent itself will decompose at $+140^\circ\text{C}$ in an inert atmosphere. Decomposition between 70 and 110°C is slow, if it proceeds at all. (The lower temperature is that of the condenser in vacuum fractional distillation of the solvent; the higher temperature is that of the still pot.) It would seem, therefore, that PC itself should cause no major problem from the aspect of high temperature stability.

Unfortunately, high temperatures may result within the cell from the waste heat generated via the voltage inefficiencies of the plate discharge. A 100-W-hr/lb battery with an equilibrium potential of about 3.5 V discharging at an average cell voltage of 2.5 V will have to dump approximately 70 W-hrs/lb of waste heat. This may or may not be readily accomplished, depending on cell design and rate of charge and discharge.

Few battery systems have reached a development stage in which this factor is important. It has been observed, however, that in charging plates in PC-KPF₆, discoloration of the electrolyte would occur depending on cell configuration.⁷⁴

One of the more popular solutes used in conjunction with PC is LiClO₄. Perchlorates are strong oxidants when hot, and HClO₄ is routinely used to destroy organic matter in some analytical procedures. It would be expected that similar oxidation reactions would take place between LiClO₄ and battery materials at high temperatures. The use of this solvent-solute combination in practice would depend very much upon the temperature.

Testing thermal stability consisted of heating the electrolyte (1N LiClO₄ in purified PC) in an open container with various plate materials and observing the temperature at which violent reactions took place. It was found that the electrolyte could be heated to boiling with no problem other than slow thermal decomposition. However, the inclusion of carbon or finely divided sulfur produced a more violent reaction (see Table III). Although cells will not be operated at these temperatures, it has been observed that such decomposition reactions can take place in charging cells which are defective or which have high overpotentials in generating current.⁷⁴

Table III. Stability of 1N LiClO₄-PC Solutions

Material	Temperature, °C	Result
LiClO ₄ in PC	Heating to dryness	Stable
LiClO ₄ in PC	180 (5 hr)	Stable
LiClO ₄ in PC + Ni ₃ S ₂	Heating to dryness	Stable
LiClO ₄ in PC + Ni ₃ S ₂ (+ sulfur)	215	Burned
LiClO ₄ in PC + acetylene black	215	Exploded
LiClO ₄ in PC + sulfur (flowers)	260	Burned
LiClO ₄ in PC + aluminum (filaments)	260	Burned
LiClO ₄ in PC + lithium (sheet)	240	Stable

B. Solution Purity

As-received PC can contain a few tenths of a percent each of water, propylene oxide, propylene glycol, propionaldehyde, and others (e. g. , 59). Nonionized impurities such as these can be expected to influence plate performance as well as the measurement of electrolyte properties determined in dilute solution, e. g. , solvent conductivity, dissociation constant, solution ionic conductivity, diffusion coefficient, and ionic activity coefficients. When solutions of increasing dilution are formed for the appropriate extrapolation, a solute concentration range is eventually reached which approximates the concentration of impurities arising from the solvent. For example, 10 ppm water, the approximate limit of many distillation purification procedures, represents about 0.6 mM water. Thus, solute concentration above 6 mM must be used to ensure, a priori, that no more than 10% of the lithium ions in solution are free of chemically bound water. The inference of basic ion structure from conductance data generally requires data more precise than $\pm 10\%$.

The fact that water can interact with lithium ions, at least in LiClO_4 -PC solutions, has been demonstrated from chronopotentiometric data.³² The nature of the $\text{Li}^+ \cdot \text{H}_2\text{O}$ species apparently changes with water concentration¹⁷ and lithium ion concentration. Many equivalent conductance versus $C^{\frac{1}{2}}$ plots show a deviation from linearity at about the water concentration. This observation may be the effect of water or may actually represent the decrease in ion-ion interactions.

1 Positives

The most obvious interaction of water with positive plates is to increase plate solubility. An example of the solubilizing effect of water is shown in Table IV for CuF_2 . The concentrations of water in the first column represent added water. These values are probably low, since the salt, LiClO_4 , and the CuF_2 also contained water, some of which was accessible to the solvent. Nevertheless, the trend is apparent.

Table IV. Effect* of H₂O on CuF₂ Solubility⁴

Added H ₂ O, ppm	CuF ₂ Solubility		CuF ₂ , ppm/H ₂ O, ppm
	ppm	m mol/ml	
120	635	12.5	5.3
400	765	15	1.9
810	1270	25	1.57
2220	2640	52	1.19
6050	8900	175	1.47

* Equilibration time was 1000 hr.

The data on repetitive experiments are scattered. However, the ratio of concentrations shows the same general trends, i. e., a minimum of about 1.2 for water concentrations of ~2000 ppm where the effects of other impurities should be of minor importance.

The presence of other "natural" impurities in PC have also been reported⁹³ to increase the solubility of CuCl₂. The results are given in Table V. The solution was 1M in LiAlCl₄, containing 5% by volume organic component.

Table V. Solubility of CuCl₂ in PC Solutions⁹³

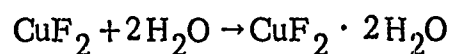
Composition	Solubility, mol/l
PC	0.008
1M LiAlCl ₄	0.006
1M LiAlCl ₄ + allyl alcohol	0.036
1M LiAlCl ₄ + propionaldehyde	0.023
1M LiAlCl ₄ + propylene oxide	0.037

It was suggested that the increase in solubility was due to specific interactions between the halide and the solvent.

The solubility of cadmium iodide is another example. It is quite soluble and forms a viscous solution in PC which has been dried, but not distilled. The solubility in carefully purified PC is low (0.166 g/100 g solvent).⁵⁰

The end result of increased solubilization of the positive is generally self-discharge of the negative via deposition of base metal ions onto the surface of the lithium negative. If sufficient base metal is in solution, the entire lithium electrode could be consumed. This is seldom the case. With lesser amounts, the lithium electrode could become isolated with an inactive metal coating. The more common effect is the development of base metal dendrites across electrolyte space, eventually short circuiting the battery. The amounts of water required for such effects have not been well established.

Effects of water on positive plates are also hydrate forming reactions of the type:



This reaction is not fast, but occluded water will eventually convert to water of hydration. The properties of the hydrate can be different from the properties of the fluorides themselves. It is often observed that the hydrate is not as electrochemically active as the parent compound.

A third mode of interaction is that of electrochemical discharge at the positive electrode. When coupled to a high potential negative, a cathodic current can be sustained by the presence of water. Indeed, this is the basis of early magnesium-sea water depolarized batteries. The detrimental result of such a discharge process is the buildup of pressure from the hydrogen reaction product. Fortunately, water discharges at a low potential, e. g. , 1.4 to 1.6 V versus Li/Li^+ (on platinum),¹⁷ and need not constitute a significant practical problem. However, with low potential positives such as the transition metal sulfides, the cathodic discharge of water must be considered in cell construction.

2. Negatives

Active hydrogen impurities will, by definition, react with lithium metal negatives to (1) consume plate material, (2) develop a film on the electrode, and (3) generate hydrogen.

Trace impurities, while not consuming much of the available plate material, can in principle develop insoluble films of reaction product on the electrode surface, thus isolating the electrode from the electrolyte or at least inhibiting electrode discharge. In this context, then, how much active hydrogen impurity is needed to form a film on the electrode? Both quantity of electrolyte and impurity concentration are important.

Consider the following order of magnitude calculation. A smooth lithium sheet of geometrical area 1 cm^2 with a roughness factor of 3 would have approximately 4×10^{15} lithium atoms (3×10^{-9} mol) exposed to the electrolyte. We will assume an electrolyte space of 2 mil ($5 \times 10^{-3} \text{ cm}$) which is filled with electrolyte (e. g. , LiClO_4 in PC). We will further assume that all the impurities are available for reaction with the lithium metal and that all of the lithium surface is available, i. e. , each lithium atom constitutes one reaction site. (The effect of lithium ion-water complexes on this reaction has not been established.) In such a system, a monolayer of film would result from 4 ppm water and/or 200 ppm propylene glycol.

Levels of purity below these values are achievable in practice;⁵⁹ in fact, 5 to 10 times the electrolyte could be used per cm^2 of exposed lithium within the purity levels achievable before a monolayer was developed. Note also the benefits of increasing electrode surface area: the more lithium exposed (per cm^2) the more tolerant the system will be to electrolyte impurities.

The exact nature of the reaction product at lithium in water-PC has not been established, i. e. , it is not known whether Li_2O , LiOH , or both are formed. In moist argon, it has been observed⁵³ that the first product formed on a lithium surface is LiOH . As the amount of water is increased, lithium hydroxide monohydrate is the product ($\text{LiOH} \cdot \text{H}_2\text{O}$).

Now, is a thin film of, for example, glycolate and/or hydroxide necessarily detrimental to the anodic oxidation of lithium? Very little quantitative data are actually available on this point. We have found, as have others, that there is no particular difficulty in discharging lithium electrodes in PC solutions containing sufficient impurity to form many monolayers of insoluble oxide and/or glycolate. During some experiments, visible gassing could be observed. The implication, then, is that the film is porous rather than passivating. Although some of the surface must be blocked, sufficient lithium is exposed to sustain discharges at least up to 10 mA/cm^2 .

Recent data²² have indicated an order of magnitude lower exchange current for the Li/Li^+ reaction on solid "clean" lithium in purified dimethyl sulfoxide (DMSO) than with a lithium amalgam. It has not yet been determined whether this effect is real or the result of surface impurity films.

At room temperature, lithium is inert to dry oxygen. Samples of metal heated to 40°C in dry oxygen showed no increase in weight. Nitride formation, however, is quite rapid.⁵³

In at least one instance the presence of water appears to actually increase solution stability of lithium anodes. A thoroughly dried solution of LiClO_4 in tetrahydrofuran (THF), when exposed to lithium metal, will decompose resulting in solid deposit collecting on the electrode. The same solvent containing traces of water ($\sim 50 \text{ ppm}$) is stable to all appearances and will sustain the anodic discharge of lithium. Similar observations have been made by others.⁴⁶ The oxide-hydroxide film may physically block the electrode from the solvent, and/or the water may interfere chemically with a step in the solvent decomposition mechanism. Since the lithium electrode discharges and solvent is needed at the electrode for discharge, the latter mechanism seems more likely. That the mechanism is complex is also illustrated by the qualitative observations that THF in the absence of solute is stable, as well as LiClO_4 solutions of THF containing 10% PC.

Another effect of the interaction between lithium and solvent impurities is the generation of hydrogen gas. The extent of this problem is illustrated by the following order of magnitude calculation. The 3 ppm of water in the volume of solution described above will generate about 4×10^{-5} cc hydrogen. Assume a battery of plates with (1) an electrolyte thickness of 0.25 mm, (2) a lithium ribbon anode thickness of 1 mm, thick and (3) a positive plate thickness of 2 mm. Assume further than there is a 2.5-mm gas space above each set of plates. The increase in gas pressure then from the generated hydrogen is only 4%, but from 300 ppm (0.02 M), i. e., at the levels employed earlier in the development stage of such batteries, the pressure increase is 400%.

Thus, with a configuration of the type described, and with present purification procedures (see below), gas pressure problems need not be significant. Indeed, the absence of gassing problems represents one of the significant advantages of lithium batteries over the conventional LeClanché and "mercury" batteries. However, it is to be emphasized that, in the example cited, a minimum amount of electrolyte was used as well as a parallel plate configuration, i. e., a minimum volume of plate material. The use of fully flooded plates or a LeClanché configuration, but with an excess of electrolyte to decrease ohmic losses, will increase practical gassing problems.

C. Purification Procedures

The effects of active hydrogen impurities have been discussed above. These materials can reach the electrolyte from a variety of sources: (1) the solvent, (2) the solute, (3) the positive plate materials, (4) the separators, (5) the binders, and (6) leakage through the seals.

1. Solvent

Most solvent impurities are generally byproducts of synthesis; water is most likely absorbed during handling and shipping. Purification is necessary for electrolytes intended for basic electrochemical studies as well as for battery construction.

Distillation, with and without prior chemical treatment, has been used extensively to purify the solvents commonly studied in organic electrochemistry, e. g. , acetonitrile (AN) and dimethyl formamide (DMF). A detailed survey of these procedures is given in reference 20. A substantial reduction in impurity content of PC is achieved by fractional vacuum distillation (~ 1 mm at 117°C).⁵⁹ The residual low boiling impurities are removable by stripping into a gas stream. The remaining 3 to 10 ppm water are reduced below the detection limit of the gas chromatograph (1.5 ppm) via percolating the solvent down a column of powdered molecular sieves (dried at 350°C under argon). Distilled PC remains colorless after this treatment, while the as-received solvent turns pink. This distilled product contains about 20 ppm of the 1-2 propylene glycol. Since the 1-3 glycol is satisfactorily removed by distillation, the 1-2 glycol must result either from azeotrope formation with PC or from slow continuous decomposition within the still.

Preparative gas chromatography may be particularly useful for accomplishing the more difficult separations such as acrylonitrile from AN and propylene glycol from PC.

Extensive application of preparative gas chromatography has been inhibited by a number of problems, e. g. , poor separations and low capacities. Most of these have been recently solved. The remaining problem anticipated is that of extensive decomposition of PC within the injection part at temperatures needed to vaporize large volumes of solvent. Co-injection with a low boiling aprotic solvent could also simplify matters.

2. Desiccants

The effectiveness of various dessicants in removing water from PC is summarized in Table VI.

Table VI. Desiccants for H₂O in PC* Solution⁵

Desiccant	Final Concentration, ppm
CaO · MgO	170
LiCl	200
Li powder	50

* Initial concentration of PC solution was 240 ppm.

The LiCl had been heated under vacuum for 15 hr at 110 °C; the water content was <0.002 at. %. The experiment consisted in agitating 50 ml of liquid with 2 g of desiccant for 5 days. Water concentration was monitored by Karl Fisher titration (this analytical technique may have a solvent "blank" of 10 to 20 ppm water).

Table VII shows the rate of water removal as a function of agitation time. The experiment consisted of agitating 1 g of lithium powder with 100 g of solvent in sealed containers.

Table VII. Removal of H₂O from PC With Li Powder⁵

Agitation Time, hr	H ₂ O Content, ppm
0	270
5	140
17	50
30	23*

* Limit of detection.

The possibility of ion exchange with the molecular sieves must be considered. Passing pure solvent down a dried column of sieves results in an increase in specific conductance to about $5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$, indicating some leaching of ionic material. Solutions of LiClO_4 in PC were analyzed via flame photometry before and after equilibration with sieves; no significant contamination by sodium ions was found. Similar results were obtained for LiCl in DMSO.

3. Solutes

The principal electroactive impurity arising from the solute is generally water. In some cases, other electroactive impurities are also found. For example, LiPF_6 as received has been observed to contain small amounts of electroactive impurities such as HF and HPF_6 . The presence of other contaminants was indicated by X-ray diffraction data,⁴⁰ although the materials were not identified.

The presence of soluble heavy metals is undesirable, since they can deposit out on the lithium negative. In practice, problems of this type seem to be minimal. When dealing with transition metal chlorides as positives, it is important to avoid soluble chlorides within the electrolyte which, as will be shown, have a solubilization effect on these positives. Fortunately, most of the alkali metal positives are relatively insoluble in PC.

A study was made of the residual currents at a mercury pool electrode as a function of LiClO_4 concentration (Fig. 2).¹³ It is evident that as the concentration of LiClO_4 increased, the residual current increased, indicating that some electroactive impurities can result from the solute as well as from the solvent.

A number of procedures have been devised to prepare dry LiClO_4 . The "anhydrous" salt, as received, contains about 1.5% water which cannot be removed by heating to 120°C under an inert gas or under vacuum.

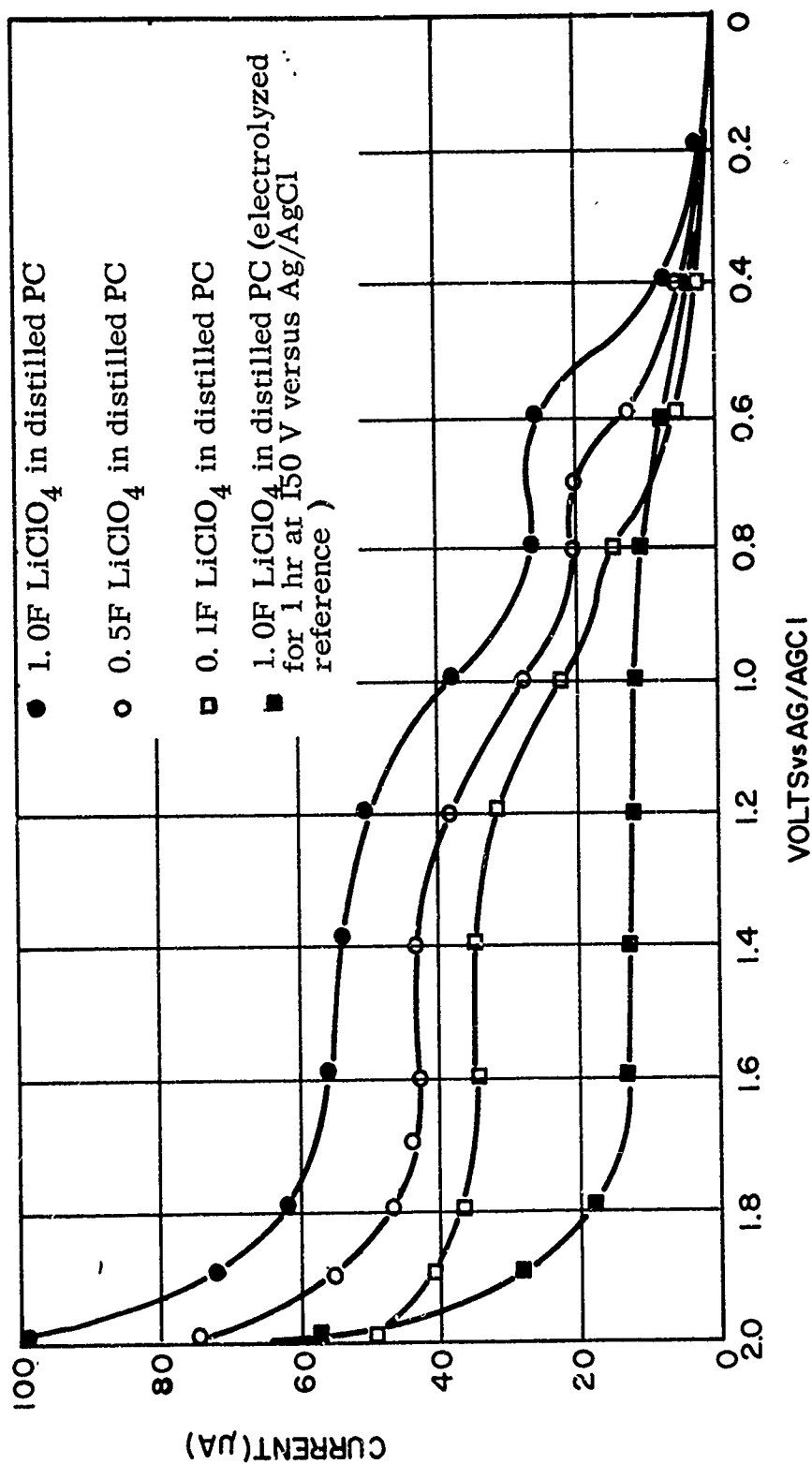


Fig. 2. Voltammetry - residual current curves at various electrolyte concentrations (scan rate = 4.07 mV/sec)

One successful approach has been to fuse the salt under vacuum and below its decomposition temperature.⁹⁵ A 1N LiClO_4 solution in PC, prepared from this commercially available material, had a water content of about 2 ppm.

Recrystallization, a classical technique for purifying solids, has also been applied.⁴ LiClO_4 recrystallized from ethyl ether apparently has a low but measurable water content.¹³

Dry LiClO_4 in PC can also be achieved by treating a solution prepared from the "anhydrous" salt⁵⁸ with molecular sieves. Repeated passes down the column are ineffective in reducing the water content below ~ 2 ppm. This implies a strong complex between lithium ions and water, which is consistent with spectroscopic⁵⁸ and electrochemical¹⁷ data. The amount of exchange with sodium and potassium ions in the sieves is apparently small and does not noticeably affect the performance of lithium electrodes.

Lithium chloraluminate (LiAlCl_4) has been extensively evaluated in prototype lithium batteries, particularly those employing rechargeable transition metal chloride positives.⁵⁴ This compound can be formed by the direct combination of LiCl and AlCl_3 . If done in situ, e. g. , by the addition of LiCl to a PC solution of AlCl_3 , considerable discoloration of the electrolyte is observed due to the high heat of formation of AlCl_4^- . If the procedure is carried out slowly and with considerable stirring, clear solutions can be obtained.

A more effective preparative procedure⁹² has been vacuum fusion of LiCl and AlCl_3 in the stoichiometric ratio of 340 °F. The addition of this material to PC produced no visible signs of chemical reaction as the salt dissolved.

AlCl_3 , as received, is usually about 98% pure. Among the impurities are aluminum hydroxide, aluminum oxychloride, and varying amounts of ferric chloride, e. g. , ~0.03%. The ferric chloride would be detrimental as mentioned; the hydroxide would probably be innocuous; little is known

about the electrochemistry of the oxychloride. Apparently, small amounts of organic material are present as well.

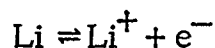
Probably the most effective method of purifying AlCl_3 is by sublimation under partial vacuum. Unfortunately, FeCl_3 is also sublimed. To some extent, the impurities can be removed by electrolysis of an AlCl_3 melt at 120°C .

In PC solutions, it would be expected that AlCl_3 (actually AlCl_4^-) would react with water impurity to produce aluminum hydroxide and HCl . The HCl should be more electroactive than water, possibly causing enhanced corrosion of lithium and support grids. Indeed, it was found that the addition of water to an LiAlCl_4 electrolyte enhanced corrosion of aluminum support grids.³⁸

The traditional purification technique used by electrochemists working with aqueous salt solutions has been in situ pre-electrolysis. Unlike aqueous systems, the reaction products formed by electrolysis of organic solvents between inert electrodes are not necessarily gases which leave the system but are generally soluble and often electroactive organic compounds. For example, electrolyzing a 1N LiClO_4 -PC solution of 5 mA/cm^2 between two platinum foil electrodes (2 cm^2 in area) for several hours resulted in minor improvement in the catholyte (lithium deposition) and a significant deterioration in the anolyte (electrolyte oxidation). A much larger "background" current was observed in the anolyte during a subsequent potential sweep on a platinum microelectrode, i.e., some of the decomposition products were electroactive. The anolyte was also observed to have changed from colorless to a light clear yellow. It is therefore important in carrying pre-electrolysis to provide acceptable half cell reactions if pre-electrolysis is to be used.

It is also important, from the same argument, to provide an acceptable counter electrode reaction in studying individual half cells, particularly if the counter electrode is in close proximity to the test electrode.

One set of acceptable charge transfer reactions is the dissolution and deposition of the principal cation, e. g. ,



This, of course, limits the choice of cations to those capable of redox behavior: magnesium, aluminum, and tetraalkylammonium ion solutions would be excluded. The available potential span is also limited to about ± 100 mV about the equilibrium potential. Nevertheless, it would be expected that active hydrogen compounds would be decomposed by the fresh metal surface continuously formed at each electrode. A preliminary study was therefore made of this technique with an electrolyte containing 1N LiClO_4 in PC.

A 5-mA constant current was passed for about 12 hr between two lithium wire electrodes (immersed area about 3 cm^2). After electrolysis, the lithium electrodes were removed and the background current recorded on platinum microelectrodes in both the anode and cathode compartments. It was found that the background current in the anolyte was slightly higher than before, but within experimental error, while that in the catholyte showed some decrease. When stirring was stopped for about 1 hr, a copious amount of finely divided lithium was deposited on the cathode, completely filling the catholyte compartment. Holding a lithium electrode at +1.0 V versus Li/Li^+ for several hours resulted in no significant improvement.

The main reasons for only a small improvement in background currents as a result of pre-electrolysis are probably the ease with which solid electrodes are passivated during electrolysis and the use of small electrodes.

A 1.0F LiClO_4/PC electrolyte was electrolyzed at a mercury pool for 1 hr at -1.5 V versus an Ag/AgCl past reference electrode (approximately +1.3 V positive to a Li/Li^+ electrode). As can be seen in Fig. 2, the residual current was reduced appreciably with this larger electrode.¹³

Most likely, this potential will not affect the discharge and removal of water due to the high overpotential of hydrogen on mercury.

4. Positives

The presence of impurities in the positive plate material may be beneficial, detrimental, or innocuous.

One of the more detrimental and ubiquitous impurities is water, either adsorbed or as a hydrate. The removal of trace quantities can be a major endeavor. Drying at 120 °C is usually ineffective. Transition metal fluorides are prone to form particularly stable hydrates which, rather than evolve water on heating, will form oxy- and/or hydroxy-fluoride compounds.

For example, it is observed that $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ decomposes to $\text{CuOHF} \cdot \text{CuF}_2$, CuOHF , as well as an unknown material.⁴

Drying transition metal sulfides at 120 °C also appears to be ineffective, at least for the nickel compounds. However, it appears that some of those compounds can be taken to ~300 °C without undue decomposition and with considerable evolution of water.

Treating cupric chloride with thionyl chloride has been used in an attempt to remove water.³⁷ It has been shown that this technique is not successful in drying nickel fluoride.⁷⁴

Probably the most effective answer to this water problem is to prepare the plate materials under anhydrous conditions. This philosophy is the basis of studies¹⁶ on the electrodeposition of CuF_2 from anhydrous HF-KF and the synthesis⁹ from copper metal and F_2 .

Note that the formation of decomposition products during preparation is not necessarily a serious problem unless (1) they consume a significant portion of the plate material, and/or (2) they form impervious surface coatings which screen the plate material from the electrolyte.

III. SOLVENT-ION INTERACTIONS

In the nomenclature of reference 86, PC, like DMF, DMSO, AN, acetone, and nitrobenzene, is a dipolar aprotic solvent. By definition, labile protons are not present so that hydrogen bonding cannot take place and interactions can only involve the less mobile solvent dipoles.

An estimate of the solvent-solvent interactions, i.e., whether such liquids are to be considered as structured, is given by the Kirkwood "g" factor.⁹⁷ This term, more precisely a measure of the hindrance of rotation for the polar solvent molecule, is defined in a modified form of the Onsager equation as:

$$g = \frac{(\epsilon - \epsilon_{\infty})(2\epsilon + \epsilon_{\infty})}{\epsilon(\epsilon_{\infty} + 2)^2} \frac{(9 kT)}{4 \pi N \mu^2}$$

where ϵ is the dielectric constant, ϵ_{∞} is the dielectric constant at infinite frequency, N is the number of molecules per cm^3 , μ is the dipole moment, k is the Boltzmann constant, and T is the absolute temperature. Molecules in which the charge distribution is exposed are characterized by "g" values differing from unity. Values of "g" greater than unity indicate association between molecules so that the dipoles reinforce one another. Values less than unity indicate a "contra-association" of the dipoles.

Values calculated for "g" for various liquids are given by Table VIII.

Table VIII. Kirkwood "g" Factor

Liquid	g	ϵ
H ₂ O	2.6	78
PC ⁽³⁹⁾	1.04	65
γ -BL ⁽³⁹⁾	0.71	39
EC ⁽³⁹⁾	1.19 (at 40 °C)	89 (40 °C)
Acetone	1.0	21
Nitrobenzene	0.8	35

Apparently, then, PC, like acetone, is a relatively unstructured solvent. Although the carbonyl group of PC constitutes a localized, exposed negative dipole, the positive end is spread over the remainder of the molecule and is quite diffuse. Thus, extensive "co-association" as in H_2O or HCN is not possible.

More direct estimates of solvent structure could be obtained from the temperature dependence of the refractive index, specific heat, density, and viscosity. These data are not yet available.

The dipoles are also the centers of interaction of solvent with ions. It would be expected, for example, that cations would be strongly solvated by the localized negative dipole. This is observed (see below). Similarly, it would also be expected that anions would be poorly solvated by the diffuse positive dipole. This is also observed.

Superimposed upon these ion-dipole interactions are the effects of the mutual polarizability of the ion and solvent molecule which determine the extent of interaction of the dipoles and ion charge centers.

Before listing data and presenting a general picture of solution structure, it is pertinent to consider briefly the concentration units. It is postulated that the solvent must be considered as a chemical reactant. Thus, for simple reactions such as salt dissolution, the most fundamental unit is that of mole fraction, i. e.,

$$N_B = n_B / (n_A + n_B)$$

where n_A and n_B are the number moles of solvent and solute. In those cases where $n_A \gg n_B$, i. e., in dilute solution, then

$$N_B \approx n_B / n_A$$

which is approximately proportional to the common molarity and molality scales.

Thus, the solution properties taken at dilute solution, e. g., ΔH° , Δ° , should be free of ambiguity from this "units" consideration. The extent of complication in concentrated solutions can be inferred from the following discussion on "density effects."

Much of the description of PC-solute structure is based on a comparison of measurements with those made in aqueous solutions. This cannot be done rigorously using the usual molarity and molality scales. The number of moles per unit weight or volume are considerably different for the two solvents. For example, 1 l of water contains 55.5 mol; 1 l of PC contains 11.77 mol.

Comparisons of properties are particularly influenced by this fact at higher concentrations. For example, the maximum solubility of LiBr in PC is about 2.4M. The mole fraction is approximately 0.18. The same mole fraction in water corresponds to about a 10M solution. Thus, it is solution properties at these concentration levels which should be compared, i. e., equal mole fraction not equimolar or molality solutions.

The data given in the following sections generally use molarity concentration units, since these were the units of the original work. Insufficient density data are available to make the transfer in units.

A. Density Effects

Table IX gives the densities of some solute-PC combinations considered for battery development. The density of PC has been measured by a number of groups; the reported data range from 1.198 to 1.203 g/cc.

Table IX. Densities of Solute-PC Solutions

Reference	Solute	Concentration	Density, 25 °C	Moles Solvent Displaced Per/ Mole Solute
99	—	—	1.1995	—
60	LiClO ₄	1M	1.259	0.46
50	LiBr	2.43M	1.372	0.15
	"	0.75M	1.235	
62	LiAlCl ₄	~1M	1.257	
37	"	1.25M	1.255	
40	LiClO ₄	0.25M	1.212	0.54
50	NaI	1.1M	1.336	0.28
50	KI	0.2M	1.227	0.30
50	ZnCl ₂	5.28M	1.602	
62	TMA·PF ₆	Saturated	1.209	0
74	TMA·PF ₆	0.1156M	1.206	0
74	Me ₃ N·PF ₆	1.8M	1.296	
41	KPF ₆	0.25M	1.227	0.68

From density data, it is also possible to get some feel for the changes in structure of a solvent upon addition of a solute. The general picture of an ion in solution is a sheath of solvent clustered about the charged species. This effect should result in a contraction of the solution. However, the space occupied by the bare ion can no longer be occupied by the solvent, resulting in a displacement. This displacement will be large if (1) the solvation energy is low, i. e. , there is a small degree of clustering, and (2) the ion size is large.

Table IX also shows the number of moles of solvent displaced per mole of solute. These data were calculated as follows. From the density of PC, there exists 11.77M/l. A 1-l LiClO_4 solution contains 1259 g of which 1153 g(11.31 mol) are PC. Due to the presence of salt, 0.46 mol is missing. It is possible to calculate, at least approximately from ionic radii, just how much PC would be displaced if the atoms and molecules were effectively billiard balls.

As can be seen, these data depend upon very accurate measurements of density, and the results can best be regarded as qualitative. Precise measurements at 25 °C of the density of PC solutions containing LiCl indicate the following relationship⁹⁹

$$d = 1.1995 + 0.047 m - 0.0949 m^2$$

where m is the molality.

Similar data are shown in Table X for salts in aqueous solution. Before these data can be compared, it is necessary to determine the relative volumes of ions and solvent. Table XI shows the computed volumes occupied by the 1 mol of salt ions based on ionic crystal radii. Also shown are the volumes occupied by a mole of PC and water.

Table X. Densities of Solute-H₂O Solutions

Solute	Concentration, M	Density	Moles Solvent Displaced Per Mole Solute
LiBr	1.235	1.0746	1.45
NaBr	1.05	1.0803	1.50
KI	0.65	1.0761	2.77

Table XI. Computed Volumes Based on Ionic Crystal Radii

Salt	Ion Volume of Salt, cc/ mol	Moles Solute per Equal Volume Solvent	
		PC	H ₂ O
LiBr	19.2	0.23	1.07
NaI	27.8	0.33	1.16
KI	31.5	0.36	1.70
NaBr	20.9		

These values are to be compared with the data given in Tables IX and X. Let us first consider the data for water. The amount of solvent displaced is greater than that computed from ionic radii, particularly for the larger ions. This is best explained in terms of disruption of the extensive hydrogen bond structure of the solvent.

The computed values for PC displaced by NaI and KI are essentially those observed; the values for LiBr observed are less than those predicted. It is difficult to say whether this difference for LiBr is outside experimental error. Qualitatively, the solvation energies in PC tending to contract the solution are probably of the same order as the solvent-solvent interactions.

The density of PC-tetramethylammonium hexafluorophosphate solution is essentially that of the pure solvent. Both the anion and cation are large, and the molecular weights of each are about the same as the solvent. The implication, then, is that they simply replace two solvent molecules with a salt of the same size and weight.

B. Heats of Solution

The energetics of ion solvation have been investigated by direct measurements of the heats of solution of a variety of alkali metal and tetraalkylammonium salts in PC.¹¹⁶ By comparison with similar data for water solutions, it is also possible to determine the enthalpy of transfer from one solution to another, and thus have a direct estimate of relative solvation. These data, it must be emphasized, are enthalpies of solution and not free energies. The importance of the entropy contribution should be major when dealing with structured liquids such as water (see below).

The calorimetric data were taken at a series of salt concentrations and extrapolated to infinite dilution, the standard state. Some of the data so obtained are listed in Table XII; standard enthalpies for transfer of salt from water to PC are shown in the fourth column.

Standard enthalpies of transfer for the individual ions (Table XIII) were obtained from these data by assuming that for Na to be zero. Admittedly, there is not a physical justification for this; nevertheless, the data should be self-consistent and give a relative order of solvation enthalpies.

It is not possible, however, to convert these $\Delta H^\circ_{\text{sol}}$ into enthalpies of solution for the individual ions in the exact way as Λ_0 and individual ionic conductances.

A semiquantitative estimate of the enthalpy of solvation for Na^+ has been calculated via the Born equation, i.e., -81.3 kcal and -101.7 kcal for H_{Na^+} in water and PC, respectively. The individual ionic enthalpies are calculated in Table XIV with this value for other ions in PC. In these calculations, the initial state is the gaseous ion.

The enthalpies of solvation for the alkali metal cations in PC are generally higher than for anions, as predicted. However, the differences between Rb^+ or Cs^+ and halogens are not all that large. This probably reflects a lower degree of specific solvation of these larger alkali ions by the solvent.

Table XII. Enthalpies of Solution and Transfer ¹¹⁶

Salt	$\Delta H^{\circ}_{\text{sol}}$		$\Delta H_{\text{tr}} (\text{H}_2\text{O} \rightarrow \text{PC}),$ kcal/mol
	H_2O	PC	
Trifluoroacetates			
Li	-6.33	2.36 ± 0.4	8.64
Na	-1.99	3.32	5.35
K	+1.24	3.73	2.52
Rb	1.89	3.78	1.89
C _s	1.53	3.04	1.52
Tetraphenyl borates			
Na	-4.79	-10.72	-5.93
K	+9.41	+0.74	-8.67
Rb	11.73	2.41	-9.32
C _s	12.40	2.38	-10.02
Perchlorates			
Li	-6.35	-9.51	-3.16
Na	-3.32	-3.05	-0.37
Iodides			
Li	-14.95	-15.05	-0.10
Na	-1.81	-5.04	-3.22
Me ₄ N	+10.08	+5.34	-4.74
Et ₄ N	6.67	6.08	-0.59
Tetramethyl ammonium			
Br	5.92	5.27	-0.65
I	10.08	5.34	-4.74
Tetraethyl ammonium			
Cl	-3.07	+3.30	6.37
Br	+1.49	4.90	3.41
I	6.67	6.08	-0.59

Table XIII. Relative Ionic Enthalpies of Transfer ($\text{H}_2\text{O} \rightarrow \text{PC}$)

Ion	H°_{tr} kcal/mol
Na^+	0
Me_4N^+	-1.45
Et_4N^+	+2.65
Cl^-	+3.83
Br^-	+0.35
I^-	-3.22
ClO_4^-	-6.37
CF_3CO_2^-	+5.35
BPh_4^-	-5.93
Li^+	+3.17
K^+	-2.80
Rb^+	-3.43
Cs^+	-3.96

Table XIV. Individual Ionic Enthalpies of Solvation in PC

Ion	H°_{solv} (Relative to Gaseous Ion), kcal/mol
Li^+	-124.8
Na^+	-101.7
K^+	-84.3
Rb^+	-79.0
Cs^+	-75.0
Cl^-	-79.4
Br^-	-74.4
I^-	-68.0

The solvation enthalpies for Li^+ and Na^+ are substantially more negative than for the anions, possibly indicative of definite solvate formation. Li^+ is known to form strong solvates with acetone and DMSO.¹⁰¹ Strong solvent interactions have been reported for Na^+ in DMF and DMSO.¹⁰²

It has been shown on the basis of aromatic nucleophilic substitution reactions,⁸⁶ that the solvation energies in some dipolar aprotic solvents increase in the series $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. The enthalpy data in Table XIV for anions in PC are somewhat consistent with this order, except that solvation of Cl^- is greater than Br^- and I^- .

Interpretation of the ΔH_{tr} between water and PC requires consideration of the additional solvent-solute interactions in protic solvents. In such solvents, anions are solvated by ion-dipole interactions on which are superimposed a strong hydrogen bonding, greatest for small ions.

If, to a first approximation, the solvation energies for the halide ions in PC are considered equal (see Table XIV), then the expected order of transfer enthalpies for the halides and ClO_4^- ions is consistent with this hydrogen bonding explanation. This assumes that the entropy effects on ion transfer are essentially the same for each of the ions discussed. This assumption would be less valid as ion size is increased, since breaking of the water-hydrogen bond structure would make a significant contribution to the overall free energy change.

C. Solubility of Salts

A salt dissolves in a solvent if either the ion pair solvation or the total anion solvation, cation solvation, or "dissociation or ionizing power" of the solvent, which is usually reflected in its dielectric constant, exceeds the crystal energy of the salt.

Of the many theories and equations that have been used to predict changes in solubility and variation with solvent, the majority depend only upon changes in the electrostatic properties of the solvent. These should be, and indeed are, valid only for a group of solvents of similar coordination power. To some extent, water and the n-aliphatic alcohols have similar coordination properties, and the solubilities of ionic salts in these media are a smooth function of the dielectric constant. Solubilities of ionic salts

in five cyclic esters: ethylene carbonate, PC, γ -butyrolactone, γ -valerolactone, and cyclopropanone, are not a smooth function of the dielectric constant.⁵⁰

Table XV lists the solubilities of a number of salts in PC. The most obvious feature of these data is that the maximum solubilities of salts in PC are much less (2 to 3M) than those in water, even though the dielectric constants are similar.

In Table XVI, some of these solubilities have been converted into approximate free energies. Comparing these with the measured enthalpies of solution (Table XII), it is apparent that entropy effects can have a considerable bearing on the net solubilities, at least for the iodides and perchlorates. For example, the lower solubility of these salts in PC in water implies that ΔF for the process: salt (H_2O) $\rightarrow$ salt (PC), is a positive value. Since ΔH_{tr} for some of these reactions is negative with $LiClO_4$, $NaClO_4$, and LiI , then, from

$$\Delta F = \Delta H - T(S_{PC} - S_{H_2O})$$

S_{H_2O} must be greater than S_{PC} . In these cases, the solvent-solute structure in water must be more disordered than in PC. It is generally concluded⁹⁷ that ions dissolving in water increase disorder by interrupting the hydrogen bond structure. In PC, dissolving salt must not lead to as much disorder or it may actually increase order via orientation of the solvent. It should be noted, of course, that those structural properties of the water molecule leading to a more ordered initial state are also those involved in solvating ions, e. g., hydrogen bonding centers to anions, and thus this one structural parameter of the solvent influences both ΔH and ΔS .

The solubilities of a series of alkali metal salts appear to follow more the order expected from entropy considerations than the measured enthalpies of solvation (Table XIV), i. e., the larger halide anion salts are more soluble even though ΔH°_{solv} are lower. For a given halide, the relative solubilities tend to follow the enthalpy of solvation of the cations. The fluorides are exceptions to this generalization: RbF is more soluble than LiF .

Table XV. Solubilities in PC

Salt	Concentration	Reference
LiF	$<5 \times 10^{-6}M$	62
LiCl	$3.8 \times 10^{-2}M$	62
	$4.0 \times 10^{-2}M$	25
LiBr	1.43m	50
LiI	1.365m	50
	0.02M	116
LiPF ₆	0.763M	74
LiPF ₆	0.55M	8
LiClO ₄	2.1M	63
LiBF ₄	0.42M	8
NaF	$\sim 5 \times 10^{-5}m$	50
NaCl	$\sim 3 \times 10^{-6}m$	50
NaClO ₄	$>2M$	116
NaBr	0.08m	50
NaI	1.10M	116
NaI	1.11m	50
NaBF ₄	0.093m	50
NaPF ₆	0.86M	8
KCl	$4 \times 10^{-4}m$	50
KBr	$6 \times 10^{-3}m$	50
KI	0.23M	116
KI	0.223m	50
KBF ₄	0.012m	50
KPF ₆	1.2M	41
RbF	0.061M	74
Tetramethylammonium fluoride	$6.5 \times 10^{-2}M$	62

Table XV (Cont.)

Salt	Concentration	Reference
TMA. PF ₆	0.15M	63
CaCl ₂	4.9×10^{-3} m	62
CaF ₂	2×10^{-4} M	65
CaF ₂ (1M LiClO ₄)	2.7×10^{-3} M	65
CaBr ₂	0.745m	50
Ca(BF ₄) ₂	6.45×10^{-2} m	50

Table XVI. Approximate Free Energies of Solution and Solvation

Salt	ΔF_{sol}	ΔF_{solv}
LiCl	+3.87 kcal/mol	-30
LiF	>+6.3	
NaF	+5.4	
NaCl	+7	
KCl	+3.81	-38
KBr	+2.0	
NaClO ₄	+0.4*	
NaI	+0.8*	
KI	+1.3*	
LiBr	+0.3*	-30.7
LiI	+0.6*	-37

* Assume $\lambda_{\pm} \sim 0.5$.

D. Complex Ions

The transition metals tend to form complex ions with anions and with solvents. The equilibria of silver chloride in PC solutions containing excess chloride have been studied potentiometrically¹⁹ in a constant ionic medium (0.1N tetraethylammonium perchlorate) at 25 °C.

From these data, only mononuclear complexes (AgCl_n) were found corresponding to the reactions:



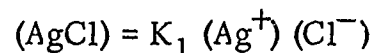
The solubility product for AgCl in Eq. 1 was computed to be $10^{-19.87}$. The overall formation constants for the soluble complexes are:

$$\log \beta_1 = 15.15 \pm 0.15$$

$$\log \beta_2 = 20.865 \pm 0.015$$

$$\log \beta_3 = 23.39 \pm 0.06$$

Here, β_1 is defined as the equilibrium constant for K_1 for



Similarly,

$$\beta_2 = K_1 K_2$$

$$\beta_3 = K_1 K_2 K_3$$

In pure PC, the solubility of AgCl is $2 \times 10^{-5}\text{M}$, and the predominant species is the undissociated AgCl complex. In chloride solution, the total solubility of AgCl is approximately equal to the chloride concentration, with AgCl_2^- as the predominant species. Reference 19 gives the concentrations of the various soluble species in saturated AgCl solutions containing excess chloride.

Table XVII is a comparison of these data with those observed in water.²³

Table XVII. Solubility and Complex Formation Equilibria²³ for AgCl in H₂O and PC*

Item	H ₂ O	PC
Dielectric constant	78.54	65.0
$\log K_{s0} [\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-]$	-9.42	-19.86
$\log K_{s1} [\text{AgCl(s)} \rightleftharpoons \text{AgCl}^-(\text{sol})]$	+1.0	-4.7
$\log K_{s2} [\text{AgCl(s)} + \text{Cl}^- \rightleftharpoons \text{AgCl}_2^-]$	-4.70	+1.00
$\log \beta_1 [\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}(\text{sol})]$	+2.85	+15.15
$\log \beta_2 (\text{Ag}^+ + 2 \text{Cl}^- \rightleftharpoons \text{AgCl}_2^-)$	+4.72	+20.86
$\log \beta_3 (\text{Ag}^+ + 3 \text{Cl}^- \rightleftharpoons \text{AgCl}_3^{2-})$	+5.04	+23.39

*Conditions: 0.1M ionic strength, 25 °C.

It is apparent that the solubility and complex formation equilibria are vastly different in the two solvents. Because of the strong complexes, the total solubility of AgCl is greater in PC even though the solubility product is more than 10 orders of magnitude smaller in PC compared to water. Since the dielectric constants of the two solvents are not markedly different, this tendency to stabilizing complex ion formation can be interpreted in terms of low specific solvent-cation solvation energies; low at least when compared to the free energy of chloride ion complex formation.

The studies of AgCl equilibria were extended to PC-water mixtures to evaluate the specific solvation properties of the two solvents.¹⁰⁷ The water concentration range was varied from 0.0004 to 3.57 M/l. Above this concentration, two phases exist with the perchlorate supporting electrolyte. The details of the experiments were essentially as described above.

The variations in specific formation constants with water content are described by formulas of the type

$$\log \beta_1 = +15.3 - 3.25 (C_{\text{H}_2\text{O}})^{\frac{1}{2}}$$

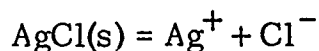
The expression for the solubility product is

$$\log K_{s0} = -20.0 + 3.25 (C_{\text{H}_2\text{O}})^{\frac{1}{2}}$$

It is a curious coincidence that the total solubility of AgCl in the absence of added chloride is almost exactly the same ($2 \times 10^{-5}M$), independent of the composition of the solvent. This coincidence is even more remarkable because in PC the predominant species are Ag^+ and Cl^- ions.

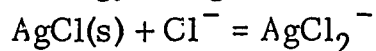
Although large changes are observed as the water concentration is increased from zero to the two phase boundary (approximately 3.6M), the equilibrium constants for solubility and complex formation of silver chloride in these water saturated PC solutions are still very different from those in pure H_2O .

A qualitative explanation of these large changes may be found in a discussion of the factors influencing the free energy of solvation of ions in the mixed solvents. The solubility product K_{s0} reflects the free energy change for the reaction



and is larger (less negative $\log K_{s0}$) the more strongly the ions are solvated. Thus, a medium of higher dielectric constant, or stronger specific interactions between the ions and solvent, would tend to increase K_{s0} . As the medium is changed from propylene carbonate to water, the dielectric constant changes very little, but the hydrogen bonding of the solvent to chloride ions is very much less in propylene carbonate than in water. Thus we may attribute the observed changes in K_{s0} largely to the differences in hydrogen bonding between chloride ion and solvent. Since propylene carbonate is probably a relatively weakly coordinating ligand, the free energy of solvation of the cation probably does not change very much as the composition of the solvent changes. Of course, the separation of the observed variation in K_{s0} into contributions from solvation of the cation or anion is a nonthermodynamic procedure, and we can discuss rigorously only the variation of the sum of the two free energies of solvation.

The other constant for which simple qualitative arguments may be clearly made is K_{s2} , which reflects the free energy change for the reaction



Here we observe directly the difference in free energy of solvation for two anions. If there were no specific interactions with the solvent, we would expect K_{s2} to be somewhat greater than unity simply because $AgCl_2^-$ is a larger ion than Cl^- . As the dielectric constant of the medium increases, we would expect the effect of size to be less and thus expect K_{s2} to approach closer to unity. The

observed values of K_{s2} decrease below unity at water concentration around 0.5M, and are nearly five orders of magnitude smaller than unity in pure water. Hydrogen bonding of the solvent to Cl^- would tend to decrease K_{s2} , and this apparently causes the overwhelming change as the solvent is changed from propylene carbonate to water. Coordination of the solvent to silver would be expected to increase K_{s2} and this may be a partial contribution to the observed value $K_{s2} = 10$ in the anhydrous solvent, but is certainly a much smaller effect than hydrogen bonding. This observation tends to confirm the previous statement that most of the increase in K_{s0} with increasing water content was attributable to increased solvation of Cl^- and not Ag^+ .

The intrinsic solubility of AgCl reflects the free energy of solvation of the neutral complex AgCl and this varies only slightly over the range from anhydrous propylene carbonate ($K_{s1} = 10^{-5}$) to water ($K_{s1} = 10^{-6.5}$). If anything, this variation implies that the coordinate bonding of propylene carbonate to silver is greater than water, but the effect is much smaller than the variations involving the solvation of the chloride ion.¹⁰⁷

Such chloride complexes may also exist with lithium ions, although they are probably weaker than with silver. For example, it has been observed that when the titration experiments of the type described above are done with LiClO_4 rather than Et_4NClO_4 , the unsaturation-saturation section is much distorted; the break occurs at a lower $C_{\text{Ag}}/C_{\text{Cl}}$ ratio.

The presence of Li-Cl solution complexes or strong ion pairs is also consistent with the departure from linearity of Λ versus $C^{1/2}$ plots above 0.025 M LiCl in PC. Unfortunately, the influence of trace water on these measurements is not known.

1. PbCl_2

The solubility of this material in pure PC is about $7 \times 10^{-5}\text{M}$. In 0.1M chloride, the solubility²⁵ rises to about 10^{-2}M . A PbCl_4^{2-} complex has been suggested.⁹¹

2. TlCl

Thallous chloride (TlCl) has also been studied.²⁴ The equivalent weight of this material is too high for use in lithium batteries. However, preliminary studies⁹⁹ indicate that the Tl/Tl^+ couple may be of value as a well poised reference electrode, e.g., $\pm 0.02\text{ mV}$ for aged $\text{Tl}(\text{Hg})/\text{TlCl}$. Table XVIII shows the solubilities of TlCl in PC containing varying

amounts of Et_4NCl and a constant $0.1\text{M Et}_4\text{NClO}_4$.

Table XVIII. Solubility of TlCl in PC

C_{Cl}	S
0	$7.6 \times 10^{-7}\text{M}$
0.0109	6.28×10^{-7}
0.1004	7.86×10^{-6}

As can be seen, the solubility is very low, and the solubilization by chloride ions is also very low. Apparently, the chloride complexes, if they do exist, are weak.

The equilibrium constants are: $K_{s0} = -12.2$, $K_{s1} < -6.4$ and $K_{s2} = -4.1$.

In this regard, TlCl seems to resemble NaCl which has a solubility in PC of $\sim 3 \times 10^{-6}\text{m}$. No data are available on possible Na-Cl complexes. By analogy with aqueous systems, these are expected to be weak.

3. CuCl

The solubility of CuCl_2 in PC was determined⁶² by chloride ion titration to be $4.9 \times 10^{-3}\text{M}$ at 25°C . The solubility of CuCl in LiAlCl_4 has been reported⁹³ as $4.62 \times 10^{-3}\text{M}$. From the discharge of CuCl electrodes it was concluded that, like AgCl , the solubility of CuCl is equal to the free chloride ion. Apparently, CuCl_2^- complexes are formed.

4. Physical methods

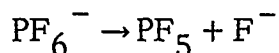
Aluminum trichloride is soluble ($\sim 3.2\text{M}$) in PC. Because of its Lewis acid properties, it would be expected to coordinate strongly with the negative dipole of PC.

A direct study of ion structure has been made with NMR techniques⁶⁵ for the products of AlCl_3 dissolution in PC. From the Al^{27} spectra, it was inferred that the major ionic species are $\text{Al}(\text{PC})_n^{3+}$ and AlCl_4^- , and these ions are quite similar to those found in AN. High resolution H^1 spectra of 1M AlCl_3 -PC indicate peaks due to coordinated PC as well as bulk PC. From this and the Al^{27} data, it is shown that the Al coordination number (n) is six, in agreement with the coordination number of Al^{3+} in AN and other solvents.

NMR studies of LiCl solutions of AN containing AlCl_3 are consistent with the formation of AlCl_4^- from the coordinating species Al(AN)_6^{3+} . The observed population of this aluminum state decreases linearly to zero at 1M LiCl.

Further studies⁶⁴ indicate that the population of the coordinating species is reduced by the addition of LiClO_4 to the AlCl_3 -AN solution. The implication is that $\text{Al(ClO}_4)_4^-$ is formed in spite of the ordinarily coordinating tendencies of ClO_4^- . It was noted, however, that ClO_4^- was less effective than Cl^- in complexing Al(AN)_6^{3+} .

NMR studies⁶⁴ were made of the F^{19} resonance for tetramethylammonium hexafluorophosphate ($\text{TMA}^+ \text{PF}_6^-$) in PC and in DMF. A doublet was found as expected from splitting by the presence of phosphorous, and no other peaks. Thus, the fluoride atoms are all chemically equivalent and the equilibrium for the dissociation reaction



is well to the left.

Direct evidence of Li^+ -water interactions is also available for similar solvents from NMR data. For example, the effect of water in AN on shifts of the Li^+ NMR spectra has been interpreted⁵¹ to indicate either some preference of Li^+ for water compared to AN in the solvation sphere, or an overwhelming preference for water in the inner solvation sphere.

5. Activity coefficients

Very little data are available on activity coefficients in PC electrolytes. One study⁹⁹ has determined $\gamma_{\pm}$ for Li^+Cl^- from equilibrium

potential measurements on the cell $\text{Li}/\text{Li}^+, \text{Cl}^-/\text{TlCl}, \text{Tl}(\text{Hg})$. Representative data at room temperature are shown in Table XIX.

Table XIX. Activity Coefficients for LiCl-PC Solutions (25 °C)

Concentration, m	$\gamma_{\pm}$
0.01631	0.6046
0.02003	0.5647
0.02718	0.4801
0.03197	0.4420

Even at low concentrations, there is a significant departure of $\gamma_{\pm}$ from unity. This is explained in terms of a strong ion pair or complex ion formation between chloride and lithium ions.

E. Conductance: High Concentrations

Extended data on the specific conductance of concentrated salt solutions are of obvious value in selecting electrolytes for batteries and in designing specific cell configurations. The acquisition of such data in nonaqueous solvents is relatively straightforward. Table XX shows the maximum conductance for a variety of salts in PC. Further listings are given in reference 54. Of interest is the observation that dissolving the gases PF_5 and BF_3 in PC gives rise to conducting solutions,¹⁰⁷ presumably through $2 \text{PF}_5 \rightleftharpoons \text{PF}_4^+ + \text{PF}_6^-$.

Almost all solute-PC combinations have maximum specific conductances below $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. Most conductance maxima are of the order of 1N, implying very little strong specific solvation with ions in solution. Contrast this situation with the specific conductance of LiClO_4 dissolved in THF—a solvent which does appear to coordinate with lithium ion. Unlike the PC solutions, conductance continues to increase with concentration until saturation is reached.

At high concentrations, ion association becomes important. Neutral ion pairs are formed as well as larger charged ion multiples. In effect, the solvent becomes unable to satisfactorily shield one ion from another. As a result, the specific conductances versus concentration plots

Table XX. Conductivities in PC-Salt Solutions

Salt	Concentration	Conductivity, $\text{ohm}^{-1}\text{cm}^{-1}$	Reference
LiClO_4	1N	5.6×10^{-3}	66
	1.1N	4.97×10^{-3}	66
	0.9	5.2×10^{-3}	2
	0.25m	4×10^{-3}	79
LiPF_6	0.76N (saturated)	5.83×10^{-3}	74
LiPF_6	0.55 (saturated)	4.49×10^{-3}	8
LiBr	2.4m	5×10^{-4}	50
LiBr	1.15m	1.8×10^{-3}	27
LiBF_4	0.42(saturated)	2.5×10^{-3}	8
LiAlCl_4	1N	6.57×10^{-3}	66
	0.75m	5.1×10^{-3}	47
AlCl_3	1.01N	7×10^{-3}	6674
N_2PF_6	1N	1.67×10^{-3}	74
NaPF_6	0.86 (saturated)	6.8×10^{-3}	8
NaI	1.1m	5.8×10^{-3}	50
	0.1N	1.5×10^{-3}	74
NaClO_4	1.22N	6.75×10^{-3}	2
KI	0.1N	2.3×10^{-3}	74
KI	0.2m	4.4×10^{-3}	50
KPF_6	0.5N	6.8×10^{-3}	74
KPF_6	Saturated	3.12×10^{-3}	8
KPF_6	0.25m	4.7×10^{-3}	79
	0.7m	6.8×10^{-3}	40
KCNS	1.55m	8.95×10^{-3}	29
KCNS	0.96m	7.25×10^{-3}	29
KBr	Saturated	1.8×10^{-4}	29
PF_5	0.056m	7.9×10^{-4}	WH#3
	0.5m	1.3×10^{-3}	107

Table XX. (Cont.)

Salt	Concentration	Conductivity, $\text{ohm}^{-1}\text{cm}^{-1}$	Reference
TMAPF ₆	0. 1N(Saturated	2.8×10^{-3}	74
PhMe ₃ PF ₆	0. 25m	5.37×10^{-3}	111
RbF	0. 06m(Saturated	7.4×10^{-5}	74
CaBr ₂	0. 75m	3.3×10^{-4}	50
Mg(ClO ₄) ₂	0. 4M	4.7×10^{-3}	27

Table XXI. Critical Distance of Approach for Ion Pair Formation

Solvent	D	$r_c, \text{\AA}$
H ₂ O	78.3	3.52
AN	36.7	4.2
Pyridine	12.0	23
Benzene	2.27	121

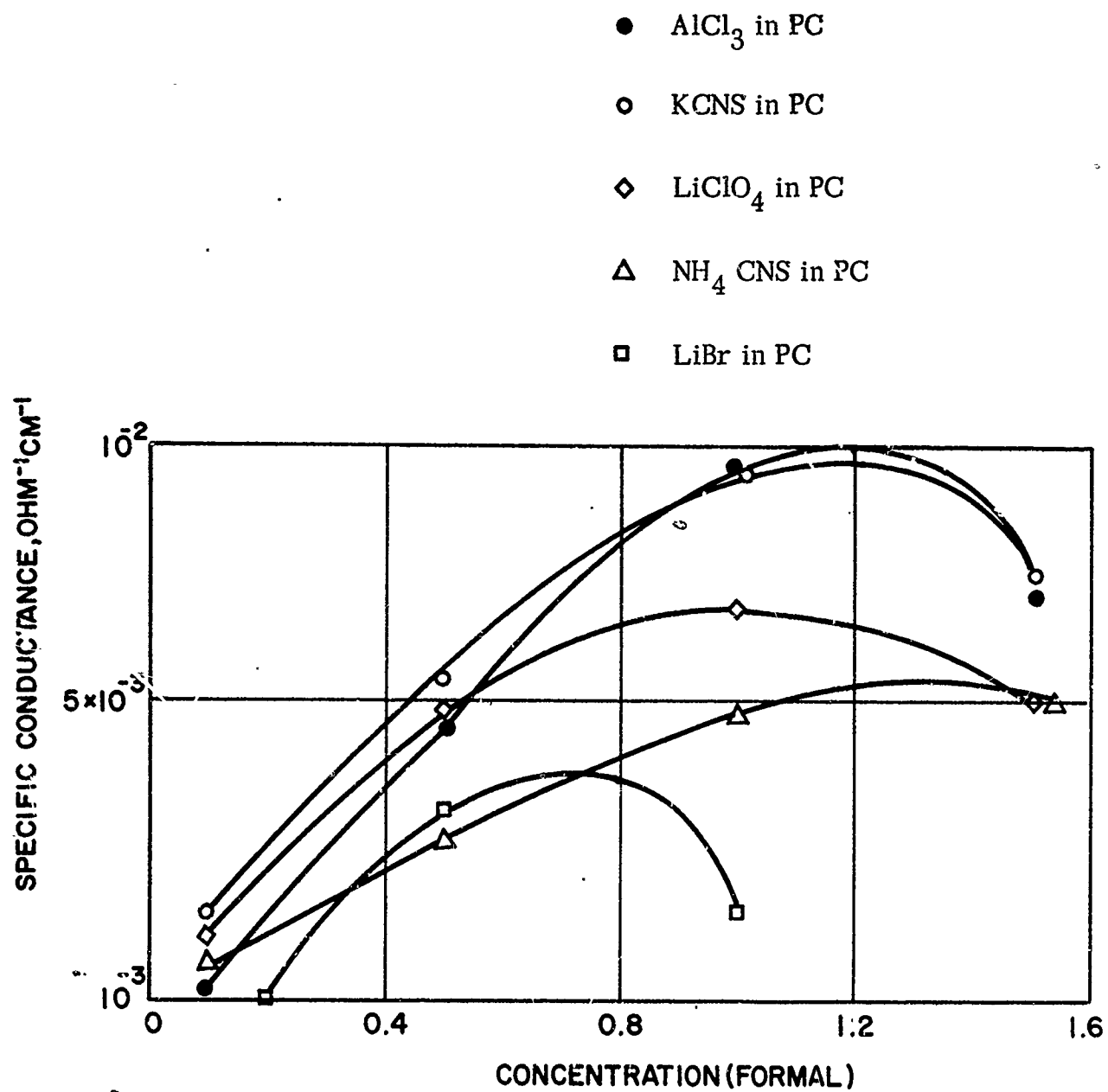


Fig. 3. Specific conductance of various solutes in PC

turn over and σ decreases with increasing salt concentration.

The relative effect of the dielectric constant on this shielding-ion association question can be estimated with following relationship for the critical distance involved in ion pair formation⁹⁷

$$r_c = \frac{Z_1 Z_2 e^2}{2DKT}$$

At this distance, the mutual electrical potential energy of the two ions is equal to 2 kT. Some values for r_c are given in Table XXI for a 1:1 solute such as LiClO_4 .

Obviously, ion-ion interactions in PC are going to be effective over greater distances, i. e., at lower solute concentrations. Note, however, that the critical distance for PC is only 1.2 times larger than water, yet the maximum conductivities achieved are much lower and ion association is much more pronounced.

The difference at high concentrations can be explained in terms of the lower specific solvation energies of ions in PC. The solvent molecules, being less strongly held by the ions, are more readily displaced by the coulombic attractions between ions of opposite charge and neutral ion pairs are formed. Furthermore, the solvent is unable to prevent more extensive complex ion formation between these neutral ion pairs and the poorly solvated anion. These molecular scale interactions are also manifest by an increase in the macroscopic viscosity (see, for example, Table XXVI).

As mentioned, there are also about five times fewer solvent molecules per unit volume of PC as compared to water.

The differences in ionic conductivity at low concentrations, i. e., in the absence of ion-ion interactions will be discussed below.

As shown in Table XX, there is a choice of solutes and concentrations which yield electrolyte conductivities in the range of 4 to 8 $\times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. In choosing an electrolyte for battery operation, it is desirable to minimize the potential loss across the electrolyte space. The equations for this process are written in terms of the product concentration times diffusion coefficient where the maximum current flow is proportional to (DC). Ionic mobilities have been related to diffusion coefficients

via the Nerst-Einstein equation⁹⁷

$$u = \frac{\lambda}{FC} = \frac{DF}{RT}$$

and thus

$$\lambda_1 + \lambda_2 = \Lambda = \frac{F^2}{RT} (D_1 + D_2)$$

What are listed in Table XX are the specific conductances (σ); these are related to Λ via

$$C\Lambda = \sigma = \frac{F^2 C}{RT} (D_1 + D_2)$$

Thus, to a first approximation it would seem that the σ data, regardless of concentration, are a good indication of the effectiveness of the electrolyte. However, it was implicitly assumed that the salt was completely dissociated, which is obviously not the case at high concentrations. Thus, the conductivity estimate of D will reflect only the ion migration aspects of ion transport and will not "see" the neutral soluble salt which can also diffuse across the electrolyte. Thus, argument can then be made that the higher salt concentrations, for a given specific conductivity, are more desirable for maximum ion transport.

In most systems being studied (see Section IV), cations are discharged into the electrolyte at the anode and consumed (via precipitation) at the cathode. The important current flow then in determining the performance of the electrolyte is actually that of the positive ion. Thus, to obtain a better evaluation of the capabilities of the electrolyte diffusion, coefficients of the individual ions are needed.

F. Transference Numbers

The conductance data in Table XX are for the salts. Relating these numbers to ionic conductivity and to ion structure in electrolytes requires knowledge of transference numbers; however, very few of these are available for nonaqueous electrolytes in general and PC in particular.

A variety of the experimental techniques that have been used to measure transport numbers in aqueous solutions are described in reference 97. Most of the available data on PC were taken by the Hittorf method. Applications of this technique require: (1) one or both electrodes must be reversible, i. e., free of side reactions such as electrolyte decomposition, and (2) the solution must be very accurately analyzed. Care must also be taken that convection does not occur between compartments and upset the concentration distribution.

It is generally observed in the PC solutions studied that, although the experiments are done in a thermostated bath so that some convection is present, the electrolyte will heat due to the ohmic losses within the poorly conducting solution.⁶² Silver has been used as an anode when dealing with chloride ion. The Li/Li^+ electrode is sufficiently reversible¹⁵ and can be used as the anode.

Table XXII summarizes some transference data for salt solutions in PC. Two factors are apparent: (1) t_+ is less than 0.5 for Li^+ , in common with aqueous solutions, and (2) there are very few references available on the subject.

Table XXII. Transference Numbers in PC

Salt	Concentration	t_+	Anode	Cathode	Reference
LiClO_4	1N	0.19 ± 0.08	Ag	Ni	63
KPF_6	0.45m	0.11	Ag	Pt	74
LiClO_4	Infinite dilution	0.39*			46
LiClO_4	1N	0.20			34
LiClO_4 (AN)	1N	0.32			64

* From chronopotentiometric data.

From these data on conductances and transference numbers, ionic conductivities can be computed and, via the Nernst limiting law, the diffusion coefficient at infinite dilution can be estimated. Thus, for LiClO_4 and a t_+ of 0.4, λ_+ is approximately 10.

Thus,

$$D^\circ = 2.66 \times 10^{-7} \frac{Z^1 / + / Z^2}{Z^1 Z^2} \frac{\lambda_1^\circ \lambda_2^\circ}{\lambda_1 + \lambda_2}$$

$$D^\circ = 3.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$$

This value is of the same order as that reported in reference 46 determined via chronopotentiometric data.

G. Conductance: Dilute Solutions

Information on solvent-solute interactions is also achieved by analysis of equivalent conductances at infinite dilution where, by definition, ions act independently of one another.

Obtaining accurate data is complicated somewhat by the low values of conductance in nonaqueous solutions. The acquisition of such data also requires careful attention to purity of materials, particularly the solvent (see Section II). The need for removal of ionically conducting impurities is obvious and this can be achieved to some extent by careful distillation. Note that final purification by passage over molecular sieves is not acceptable, since small amounts of ionizable impurities are introduced.

A particularly pronounced example of the apparent influence of impurities on Λ_0 measurements occurs in the case of LiAlCl_4 in PC. This compound will apparently hydrolyze trace water to give aluminum hydroxide and HCl. The Λ versus $C^{1/2}$ plots⁶² for AlCl_3 are poorly behaved below 0.0625M AlCl_3 , unlike the Λ versus $C^{1/2}$ plots for AlCl_3 in the presence of LiCl ($C_{\text{LiCl}} \Lambda 0.78 \times C_{\text{AlCl}_3}$). These data for LiAlCl_4 are available over the concentration range 0.603 to 1.0M. A large change in slope occurs below 0.04M; the high concentration range is linear. Λ_0 was extrapolated to 34.5 units, although the extrapolation is somewhat uncertain.

Problems of working with highly purified dilute salt solutions can be alleviated somewhat by using extrapolation functions taken from treatments which have considered some ion-ion interactions, and thus using data for higher concentrations of salt. One such treatment, using the Shedlovsky extrapolation function,⁹⁷ is described in reference 11. Solvent purification was accomplished by a double vacuum fractional distillation. The concentration range of LiClO_4 was 0.002 to 0.014N; a value of 26.39 was computed for Λ_0 . This value was fed back into the Fuoss-Onsager equation and a value of 2.46 Å computed for the distance of closest approach of the ions. From ionic crystal radii, the unsolvated value for this parameter is 2.04 Å, suggesting that the solvation is weak.

A detailed discussion of the Shedlovsky and other extrapolation fractions is given in reference 97. Briefly, it has been observed in aqueous solutions up to $C = 0.01\text{N}$ that a plot of $(\Lambda + B_2 C^{\frac{1}{2}})/(1 - B_1 C^{\frac{1}{2}})$ against C would yield a straight line which, when extrapolated to $C = 0$, would yield the true limiting conductivity, Λ_0 . (The B_1 and B_2 terms are computed from a variety of physical constants, including the dielectric constant and viscosity.)

A somewhat less empirical function, developed by Robinson and Stokes,⁹⁷ attempts to explicitly take into account finite ion size. This equation gives a fair account of conductances of aqueous 1:1 electrolytes up to 0.05 to 0.1N. The upper limit will be somewhat lower for non-aqueous electrolytes because of the stronger ion-ion interactions.

Most Λ_0 data reported, however, have been achieved with dilute solutions and $\Lambda - C^{\frac{1}{2}}$ plots. Table XXIII lists values of Λ_0 so obtained together with three values of Λ (and the concomitant concentrations) used in the extrapolation (where available).

The conductance data taken from references 63 and 64 have been corrected for the conductivity of the pure solvent. Although a desirable procedure, this can of course lead to some errors when the "blank" conductivity approaches that of the solution. Data are shown in Table XXIV

Table XXIII. Equivalent Conductances for Solutes in PC

Solute	Concentration, M	Λ	$\Lambda_o,$ $\text{ohm}^{-1} \text{eq}^{-1} \text{cm}^2$	Reference
LiClO ₄	0.000625	24.1	25.6	63
	0.0025	23.15		
	0.01	24.1		
	—	—	26.395	116
	—	—	26.3	11
LiBr	0.00062	24.0	26.2	63
	0.0025	23.9		
	0.01	21.5		
Tetrabutyl- ammonium tetraphenyl borate	0.0057	16.5	17.2	45, 64
	0.00228	15.7		
	0.0045	15.2		
Tetrabutyl ammonium bromide	0.00065	26.8	27.5	64
	0.0052	25.3		
LiCl	1.766×10^{-4}	22.5	26.2	62
	1.06×10^{-3}			
	2.65×10^{-2}	5.49		
KPF ₆	8.15×10^{-4}	46.50	29.50	74
	8.15×10^{-3}	26.40		
	2.45×10^{-2}	23.85		
NaPF ₆	1.0×10^{-4}	35.26	26.55	74
	1.0×10^{-3}	25.56		
	3×10^{-2}	21.64		
Tetramethyl- ammonium hexafluoro- phosphate	2×10^{-4}	32.14	33.9	62
	1×10^{-3}	30.44		
	1.65×10^{-3}	27.09		

Table XXIII. (Cont.)

Solute	Concentration, M	Λ	$\Lambda_o,$ $\text{ohm}^{-1} \text{eq}^{-1} \text{cm}^2$	Reference
NaI	1.0×10^{-4}	38.22		74
	1.0×10^{-3}	28.21		
	1.0×10^{-2}	26.47		
NaClO ₄			28.3	116
KI	1.0×10^{-4}	37.52		74
	1.0×10^{-3}	29.85		
	1.25×10^{-2}	27.38		
KI	—	—	31.	50
NaI	—	—	25	50

Table XXIV. Conductance of PC and Dilute Solutions

Salt	Concentration M	Conductance, $\text{ohm}^{-1} \text{cm}^{-1}$	Reference
—	—	7.6×10^{-8}	40, 61
—	—	2×10^{-7}	50
—	—	5×10^{-7}	28
LiCl	1.7×10^{-4}	4.26×10^{-6}	62
	1.1×10^{-3}	1.83×10^{-5}	62
LiClO ₄	1.56×10^{-4}	3.9×10^{-6}	63
	1.25×10^{-3}	2.97×10^{-5}	63

for the measured conductivity of pure PC and some dilute salt solutions which would be used in determining Λ_o . For the better solvent, "blank" conductivities are about 2% of those at 10^{-7} M salt; for the poorer material (2×10^{-7}), this can be 50%.

Apparently, the solvent can slowly leach ionizable impurities from glass containers so that solvent conductivity should be checked immediately before use. For example, the specific conductivity of one batch of PC stored in glass under argon rose from 6.38×10^{-8} to 1.05×10^{-6} in 4 weeks.¹³

First of all, it is apparent that the available Λ_o data are too limited for extensive general conclusions. It is also apparent that there is little difference in the spread of values, at least for the alkali metal salts. In this aspect,⁸⁶ PC solutions are similar to salt solutions in DMF and DMSO. The differences in specific conductivity are, therefore, more the result of solubility effects rather than major differences in Λ_o . In addition, the limited data do not parallel the enthalpies of solvation, i. e., Table XIV. The ΔF of solvation data are too limited. Lastly, it is not yet possible to determine whether there exists in PC, as there does in water, a critical range of ion sizes such that: (1) small ions acquire a solvent sheath and end up larger and with lower mobility, and (2) large ions do not solvate, but are slower moving merely on account of their size.

H. Viscosity Effects

1. Conductance

A discussion of viscosity is given in reference 97. To a first approximation, viscosity (η) represents the resistance of a solvent medium to the movement of a particle. To the extent that this approximation is obeyed, good agreement is found between measurement and theory. For example, the Walden rule: $\Lambda_o \eta_o = \text{constant}$, where η_o is the viscosity of the medium, is generally obeyed more by solutions of tetraalkyl ammonium ions than by smaller alkali metal ions. Conversely, to the extent that the Walden product is obeyed, viscosity differences

between solvents per se probably account for differences in ionic conductance (Λ_0). In concentrated solutions, consideration must also be given to the alteration in electrolyte viscosity brought about by the ion-solvent and ion-ion interactions.

Consider first the effects of solvent viscosity on conductance at infinite dilution. The viscosities of PC and a number of organic solvents are presented in Table XXV.

Table XXV. Solvent Viscosity, 25 °C

Solvent	Viscosity, cp
PC	2.53
BL	1.75
DMF	0.8
AN	0.34
Methanol	0.54
DMSO	2.00

Table XXVI lists the Walden products for a number of solvent-solute combinations at infinite dilution. The last two columns of the table are normalizations of conductance (Λ_0) to unit viscosity. The expression $\eta_{PC} \Lambda_{PC}^0 / \eta_s$ is intended to normalize the conductance of a PC solution to the viscosity of the solvent (s). For example, what would be the equivalent conductance of LiCl in PC if the solution had the same viscosity as water? The term $\eta_s \Lambda_s^0 / \eta_{PC}$ represents the converse, e. g., what would be the equivalent conductance of LiCl in water if the solution had the same viscosity as PC?

In effect, the use of linear extrapolations of this type in comparing solvents assumes applicability of the Walden product.

Table XXVI. Walden Products for Solvent-Solute Combinations

Solute	Solvent	Λ°	$\Lambda^\circ \eta$	$\frac{\eta_{PC} \Lambda_{PC}^\circ}{\eta_S}$	$\frac{\eta_S \Lambda_S^\circ}{\eta_{PC}}$
LiCl	PC	26.2	66.6		
	MeOH	92.20	50.5	123	20
	H ₂ O	114.99	115	67	44.5
LiBr	PC	26.2	66.3		
	DMF	79.1	63		25
	AN	127.2	43.2		18
	H ₂ O	116.8	116.8	63	46
TBA·Br	PC	27.5	68.6		
	DMF	87.0	69.6		27.9
	AN	161.6	55		21.8
LiClO ₄	PC	25.6	64.8		
	DMF	80.4	64.2		25.4
TMA·PF ₆	PC	33.9	85.5		
	DMF	90.5	72.4		28.6
	AN	402	136.5		54
KPF ₆	PC	29.5	75.5		
	AN	185	56.4		22.2
	γBL	53.5	93.8		37
NaPF ₆	PC	26.55	67.2		
	AN	190.2	65		25.6
KI	PC	31	78.5		
	MeOH	115.2	62		24.6
	H ₂ O	150.4	150.4	79	59
NaI	PC	28	71		
	H ₂ O	172.1	127	71	50

Thus, in the comparison of water and PC salt solutions at infinite dilution, it would seem that viscosity differences can correct for about half the differences in conductance. If we compare PC and methanol, there is an over-correction, i. e., normalized to unit viscosity PC solutions are better conducting. The same applies for AN solutions in five out of the six examples. The correct conductances for DMF and PC solutions are about the same.

2. Concentration dependence

The viscosities of a number of concentrated PC salt solutions are shown in Table XXVII.

Table XXVII. Viscosities of PC Salt Solutions

Solute	Concentration	η , cp	Reference
—	—	2.5	—
LiClO ₄	1N	7.1	63
	0.25m	3.6	79
LiAlCl ₄	1.03m	7.2	62
LiAlCl ₄	0.75m	4.42	37
	1.25m	7.57	37
LiBr	2.4m	86.1	50
KPF ₆	1m	5.7	40
	0.75m	4.6	40
KI	0.2m	3.12	50
NaBF ₄	0.25m	2.72	79
NaI	1.1m	9.6	50
TMA·PF ₆	Saturated	2.66	62
AlCl ₃	1.03	5.72	62
ZnCl ₂	5.3	1736	50

Specific solvation of ions must be considered in explaining the data. Strong interactions generally result in increased viscosity of the solution. Perhaps the most pronounced examples of this in the data available are NaI at 1.1M (96 cp), LiBr at 2.4M (86.1 cp), and ZnCl_2 at 5.3M (1736 cp). The ZnCl_2 value is particularly interesting because of the high solubility. Also of interest are the viscosities of AlCl_3 and KPF_4 solutions which are lower than those of commonly used LiClO_4 and LiAlCl_4 .

The observation made above concerning $(\Lambda_o \eta)$ products at infinite dilution for the same solute in different solvents applies here as well. The conductivity of 0.56M KPF_6 in AN ($\eta = 0.490$) is $3.16 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$; that in PC is $25 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$; $[\eta_{\text{PC}}(\Lambda_o \text{ PC})/\eta_{\text{AN}}]$ is 4.2×10^{-3} . Thus, the conductivity of PC solutions is lower than can be accounted for simply by viscosity, i. e., the effect of ion solvation on specific conductance is not the same as on viscosity.

As mentioned above, on a mole fraction basis, the 2.4M LiBr-PC solution is equivalent to a 10M H_2O solution and it is these solutions which should be compared.

As with the conductance theory, the mathematical relationships connecting viscosity with salt concentration are, at best, good up to a few tenths molar. Probably the most accurate of these is:⁹⁷

$$\eta_{\text{rel}} = \frac{\eta}{\eta_0} = 1 + B_1 C^{\frac{1}{2}} + B_2 C$$

B_1 , a collection of physical constants (involving solvent properties, ionic changes, Λ_o , and temperature) is numerically small, at least in water solutions. B_2 is a highly specific parameter and correlates strongly with the entropy of solution of the ions.

The concentration dependence of viscosity⁴⁰ for KPF_6 -PC solutions is shown in Fig. 4 together with the variation of specific conductance. The viscosity difference between the pure solvent and electrolyte is only 0.3 unit at 0.2M above the concentration range where the above equation applies. Thus, to obtain good values for B_2 , precise measurements of viscosity are required — a formidable problem.

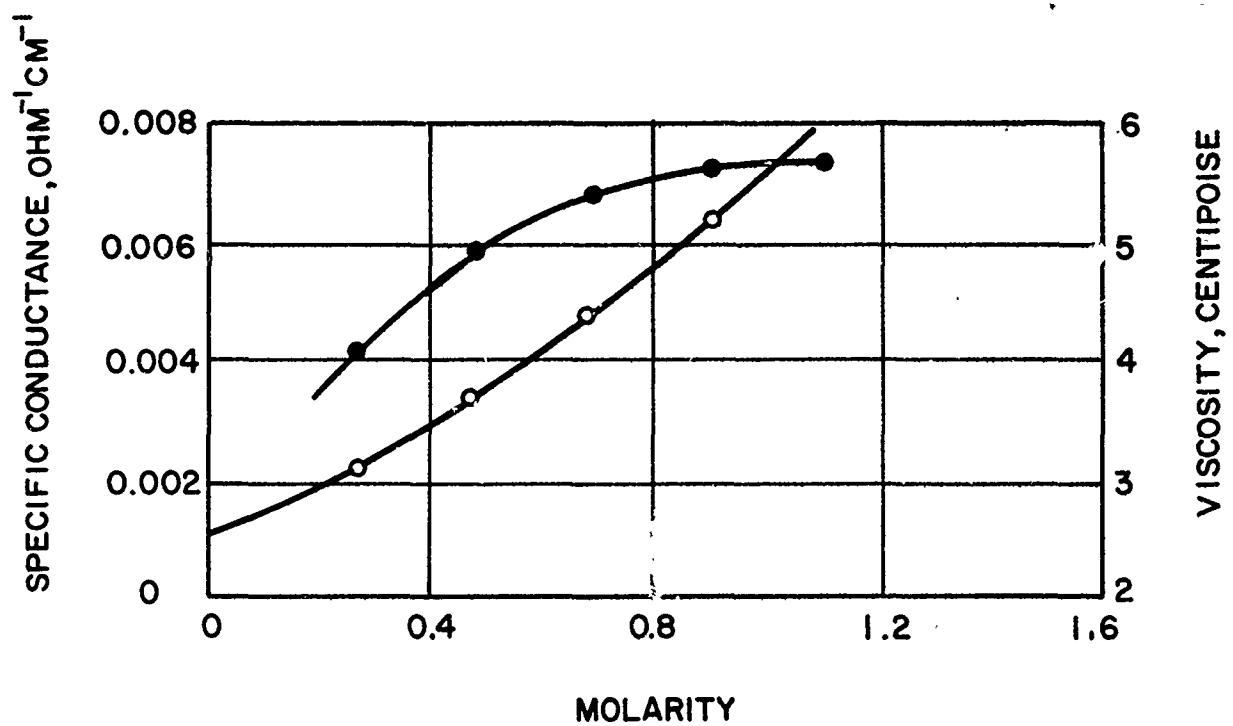


Fig. 4. Conductance and viscosity of KPF_6 -PC solutions

Walden product data⁵³ are also given in Table XXVIII. With this example, it is apparent that even with a series of the same solute-same solvent, viscosity does not change in the same manner as the conductivity.

Table XXVIII. Walden Product Data⁵³ for KPF_6 in PC

Concentration, M/l	Λ	η	$\Delta\eta$
0.26	14.8	3.16	48.9
0.42	13.1	3.55	46.5
0.58	11.0	4.05	44.7
0.75	9.2	4.60	42.4
1.20	6.08	6.40	38.7

It should be re-emphasized that the addition of large amounts of solute can displace significant amounts of solvent. For example, in the 1.2M KPF_6 solution, there is a 7% decrease in the amount of solvent. A rigorous comparison of such macroscopic properties to illustrate solution structure should be carried out for a fixed number of moles of solvent, since indeed the solvent is a reactant.

I. Solvent Mixtures

A practical approach to improve the conductivities of specific PC-solute combinations is to increase the dielectric constant and/or decrease the viscosity by adding a second solvent. A number of examples of this approach are available. Ethylene carbonate (EC), also a cyclic ester, added to PC (4:1) increases the dielectric constant by 35% with little change in viscosity. The conductivity of a KPF_6 solution increases from about $7.6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ to $1.16 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The viscosity and dielectric properties of PC-EC mixtures⁴⁰ are shown in Table XXIX.

Table XXIX. Properties of PC-EC Mixtures⁴⁰

EC, wt %	Viscosity at 25 °C	Dielectric Constant
0	2.52	64.6
20	2.52	69.1
40	2.52	74.6
60	2.52	80.5
80	2.55	87.2
100	Solid	Solid

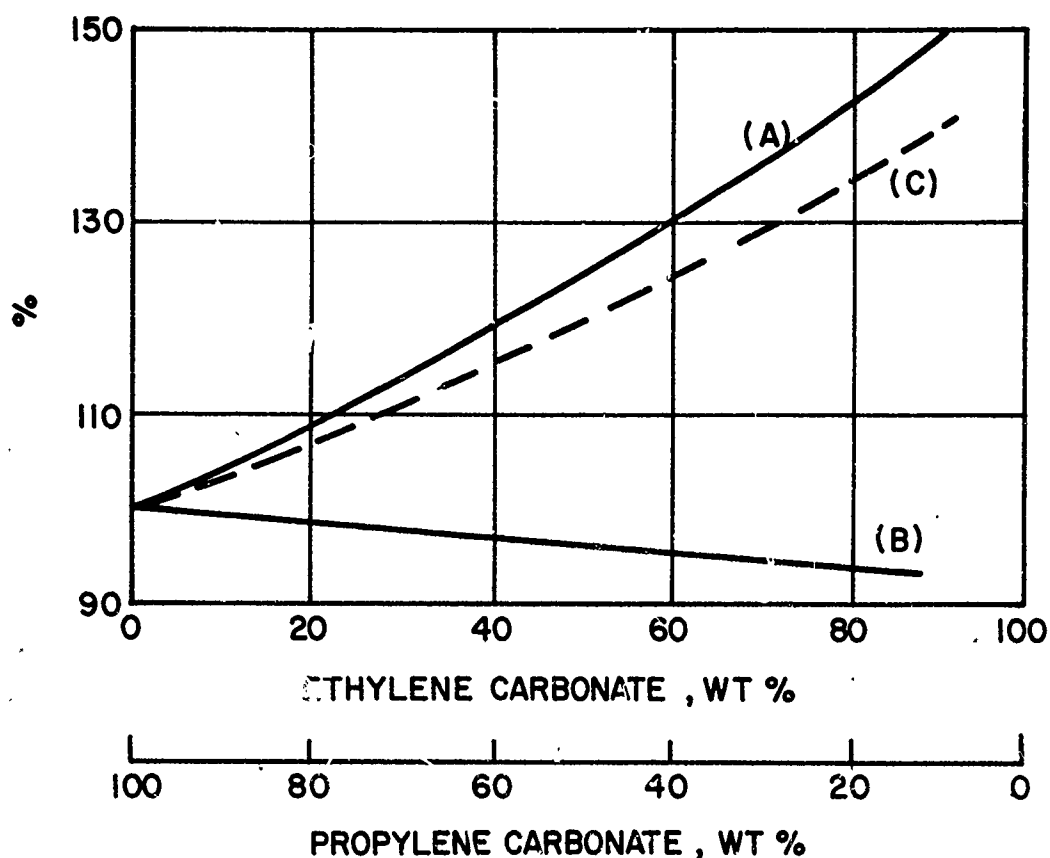
Fig. 5 contains plots of the viscosity, dielectric constant, and specific conductance for KPF_6 in PC-EC mixtures relative to the values⁴⁰ in pure PC. Apparently, dielectric constant is the most important parameter. However, to some extent, the dipoles available for solvation are also measured by dielectric constant.

Table XXX illustrates the changes in viscosity and conductance for 1N LiClO_4 solutions diluted with benzene.⁶⁰ The changes proceed in the anticipated direction; however, they are small.

Table XXX. Conductivities and Viscosities⁶⁰ of LiClO_4 in PC and Benzene

Solution	Viscosity, cSt	Viscosity (No Salt)	Conductivity, $\text{ohm}^{-1} \text{cm}^{-1}$
PC, 100%	6.01	1.96	5.6×10^{-3}
Benzene, 10%	5.36	1.67	6.3
Benzene, 25%	4.20	1.45	6.5

More pronounced results are achieved by the use of a more miscible diluent. Nitromethane (NM) has been used for this purpose;³⁹ a 1M solution of LiAlCl_4 in 3:1 NM-PC had a conductivity of $1.03 \times 10^{-2} \text{ohm}^{-1} \text{cm}^{-1}$. Data are shown in Table XXXI for 1N LiClO_4 in a mixture of PC with tetrahydrofuran (THF), a low viscosity compound which also specifically solvates lithium ion.⁶⁰



Notes:

Curve (A) — specific conductances (29 to 30 °C) of 1M KPF_6 .

Curve (B) — viscosities (25 °C) of 1M KPF_6 .

Curve (C) — dielectric constants (25 °C) of solvent.

100% values (1M KPF_6 -PC): specific conductance

= $8.10 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 29 °C; viscosity

= 6.25 cp at 25 °C.

Fig. 5 Properties of KPF_6 solutions versus PC-EC solvent composition

Table XXXI. Conductivities and Viscosities of LiClO_4 in PC and THF

Solution	Conductivity, $\text{ohm}^{-1} \text{cm}^{-1}$	Viscosity, cSt
PC, 100%	5.6×10^{-3}	6.01
THF, 10%	7.9	4.01
25%	9.6	3.01
50%	11.3	2.10
75%	10.3	1.39
100%	4.5	1.02

As with the PC solutions, the maximum conductivity of the 1:1 THF-PC mixture occurs at about 1N LiClO_4 . In 0.5M LiClO_4 , the conductivity is $8.9 \times 10^{-3} \text{ ohm}^{-1} \text{cm}^{-1}$; in 1.5M, the conductivity is $11.3 \times 10^{-3} \text{ ohm}^{-1} \text{cm}^{-1}$. A similar improvement in the conductance of LiAlCl_4 -PC solutions upon the addition of THF is noted in reference 39.

Combining this effect with that of adding EC can give some further improvement. A 50% THF plus 1:1 PC-EC solution, 1N in LiClO_4 , has a conductivity of $12.3 \times 10^{-3} \text{ ohm}^{-1} \text{cm}^{-1}$ compared⁶⁰ to $11.3 \times 10^{-3} \text{ ohm}^{-1} \text{cm}^{-1}$ for 1:1 PC-THF.

This specific coordination effect is further emphasized by the data in Table XXXII. Here, salt solutions in mixtures of PC-EC with nitromethane (NM, viscosity of 0.6 cp) are compared to mixtures with THF (viscosity).

The differences between solutions containing NM and THF are pronounced for the LiClO_4 solutions and minimal for the NaPF_6 and Et_4NPF_6 solutions.

Table XXXII. Conductivities of Various Salt Solutions

Salt	Solvent	Conductivity, $\text{ohm}^{-1} \text{cm}^{-1}$
LiClO_4	1:1 PC-EC + 50% THF	12.3×10^{-3}
	+ 50% NM	0.26×10^{-3}
NaPF_6	1:4 PC-EC + 25% THF	8.7×10^{-3}
	+ 25% NM	10.0×10^{-3}
$\text{Et}_4\text{N} \cdot \text{PF}_6$	1:4 PC-EC + 25% THF	4.2×10^{-3}
	+ 25% NM	5.7×10^{-3}

IV. ELECTRODE REACTIONS IN PC ELECTROLYTES

A. General Mechanisms for the Discharge of Positive Electrodes

One of the major problems in developing a working lithium battery is to uncover a positive plate material which will discharge well. Materials have been selected primarily on the basis of a high thermodynamic energy density (see Table II). However, many of the materials so chosen have not been particularly amenable to electrochemical reduction. Those that are reducible have had problems with excessive plate solubility and/or will support only low current drains. This limitation by the positive plate is of course not unique in organic electrolyte systems, but is a traditional problem in the development of effective ambient temperature batteries.

1. Heterogeneous mechanisms

Most compounds that have been suggested as positive plate materials for lithium batteries are insulators or poor semiconductors at best. Thus, it is not possible for the electrons to penetrate far into bulk of the crystallite in order to reach the solid-electrolyte interface. This is readily apparent from a simple Ohm's law calculation. For example, Ag_2O has an electrical conductivity⁴⁹ of $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$. If the IR potential drop across a 1-cm^2 face of this material does not exceed 200 mV at 1 mA/cm^2 , then the thickness of the layer must be less than $2 \times 10^{-6} \text{ cm}$ or 200 Å.

In some aqueous systems, the lack of electronic conductivity can be supplemented by a high field migration of hydrogen or oxide ions through the solid to compensate for the charge delivered to the positive plate. There is no evidence for significant ionic or electronic conductivity in pure CuCl , CuF_2 , NiF_2 , and most of the other positive plate materials in PC electrolyte systems studies. Thus, any solid-solid charge transfer (heterogeneous reaction) would have to be restricted primarily to the points of contact between the conductor and crystallite. If metal is produced as a reaction product, the interface should propagate and the discharge should continue. If not, then

once the interface contact points are consumed, a high ohmic overpotential will result. It would be expected that the performances of such materials would depend critically on electrode structure and discharge rate. Indeed this is the case. Examples are given below.

A few materials have been used as positive plates in aqueous electrolytes which are reasonable electronic conductors, e. g. , PbO_2 and Ag_2O . The latter compound discharges well in PC electrolytes. Unfortunately, the solubility is excessive for exploitation in battery hardware.

Apparently, a number of transition metal sulfides are also electronically conducting, electrochemically active, and relatively insoluble, such as cupric sulfide⁴⁹ and Ni_3S_2 .⁵⁷ It has not been established whether the conductivity is inherent in the pure material or is the result of minor metal impurities. Successful prototype batteries have been built with both materials, as will be discussed later.

2. Homogeneous mechanisms

The second general discharge mechanisms for positive plates is a homogeneous charge transfer whereby the plate material first dissolves, diffuses to the conducting substrate, and then discharges. This mechanism appears to operate, at least to some extent, for the discharge of Ag_2O in aqueous caustic as well as CuCl in LiAlCl_4 -PC. It has recently been shown that the Cu/CuF_2 discharge most likely also involves a soluble intermediate (see below).

It would be expected then that maximizing the rate of dissolution would increase the rate of current withdrawal from a cell. In general, the rate of dissolution of a material is given by the equation¹¹³

$$r = \frac{CD}{d}$$

where D is the diffusion coefficient of the cation in $\text{cm}^2 \text{sec}^{-1}$, C is the concentration (solubility in mol cc^{-1}), and d is the jump distance in cm.

The C and D terms are electrolyte dependent and should, at least in part, account for the observed variations in electrode performance with electrolyte composition.

The equation would predict that increasing C would increase performance and, in general, this is observed. Very few experimental accounts are available on the diffusion coefficient in PC; however, less viscous electrolytes, such as those based on AN, are generally more effective for the discharge of positives than those based on PC.

This homogeneous discharge mechanism for positive battery plates contains its own seeds of destruction if the solubility is high. Once in solution, the heavy metal ions can diffuse and/or migrate to the negative electrode as well and plate out. This consumes plate material and builds up dendritic shorts across the electrolyte gap.

3. Effect of reaction product

Thus far we have considered only the discharge of the oxidized ion. In understanding the behavior of a practical electrode, it is necessary to account for the fate of the positive plate anion as well.

For example, the oxides, sulfides, chlorides, and fluorides of lithium are relatively insoluble in PC. It would be expected, therefore, that in PC, precipitation of these anions with lithium ion will occur at the positive, blocking active surface and plugging pores. Indeed, LiF has been found in the pores of discharged CuF_2 electrodes.⁴⁰ The physical character of the precipitate (i. e. , porous or passivating) can be expected to depend upon the electrolyte. This may account for some of the variability of discharge performance with electrolyte solute. It was assumed that the solid and solution were in equilibrium; however, supersaturation can result. Some evidence of this at low temperatures is given below.

The chlorides present a unique set of problems in PC and most other solvents. It has been shown (see Section III) that AgCl , CuCl , CuCl_2 , and PbCl_2 will react with free chloride ions to form soluble complexes

(free chloride ions are produced on the discharge of the positive). This phenomenon has a major effect on the operating life of batteries employing transition metal chlorides.

4. Effect of solute on performance¹³

The electrolyte solute can also affect the use efficiency of the positive plate material. As an example of this, three plate Li/CuF₂ cells were discharged at 2 mA/cm² to completion. These cells were kept identical except for the choice of solute: 1.0F LiClO₄, 0.75F LiBF₄, and Mg(ClO₄)₂. The efficiency in LiBF₄ electrolyte was about half that in LiClO₄: ~ 32%. The performance in Mg(ClO₄)₂-PC was very poor: < 2%. Interpretation of the data in terms of fundamental mechanisms such as plate solubility and reaction product properties has not been given.

B. Electrode Discharge: Inorganic Positives

Very little work has been reported on individual half cell equilibrium potentials in PC electrolytes. Some of the limited data are shown in Table XXXIII. Such information would aid in understanding the relative solvation properties of ions in PC (e. g. , reference 86), and could be used to establish the solubilities of positive plate materials.

Table XXXIII. Reduction Potentials (0.5M LiClO₄-PC)

Couple, 0.01M Ion	PC	<u>Potential</u>		H ₂ O*
		γ -BL	AN	
Ag/Ag ⁺	0	0	0	
Cu/Cu ⁺	-0.15	-0.21	-0.58	-0.3
Pb/Pb ²⁺	-0.83	-0.82	-0.42	-0.87
Cd/Cd ²⁺	-0.94	-0.96	-0.66	-1.12
Li/Li ⁺ (0.5M)	-3.67	-3.60	-3.20	-3.74

*Calculated.

As mentioned, most battery systems studied in PC electrolytes involve an insoluble compound as the product of the cell reaction (see Table II). Thus, if the electrodes are reversible and the product is in equilibrium with the electrodes, then the total cell potential is independent of the solvent-solute combination.

The general information accumulated on specific electrode reactions is discussed below. This is followed by a brief summary of the behavior of some of these systems in working batteries.

1. Ag/Ag⁺

Apparently, the Ag/Ag⁺ charge transfer reaction is reasonably well behaved in PC solution, and also does not involve any major kinetic limitations. It has been observed¹⁹ at a silver electrode in AgClO₄-LiClO₄-PC that for small anodic and cathodic current drains, only ohmic resistance polarization is noted. In constant ionic strength media, the Nernst equation is obeyed within ± 1 mV, the error of the potentiometric measurement. Equilibrium was reached within 1 min. Solutions saturated with AgCl showed similar reproducibility, but often required as long as 0.5 hr to reach equilibrium.

Silver electrodes anodized in PC solutions of LiBF₄, LiClO₄, and KPF₆ accepted charge readily, producing soluble silver.

2. Ag/AgCl

The anodic oxidation of silver metal in LiAlCl₄-PC produces AgCl at 100% efficiency⁷ for current densities up to 70 mA/cm².

A cyclic voltamogram is shown in Fig. 6 for a silver wire in LiAlCl₄-PC. These data are also indicative of a reasonably reversible system. The anodic reaction is the formation of AgCl, and the cathodic reaction is its discharge. Integration of the peak areas confirms the 100% charge-discharge efficiency.¹¹⁰

Although reduction of AgCl proceeds rapidly in LiAlCl₄-PC, it is subject to the problems of solubilization by excess Cl⁻ and poor electronic conductivity of the active material. Prototype batteries have been built;⁵⁴

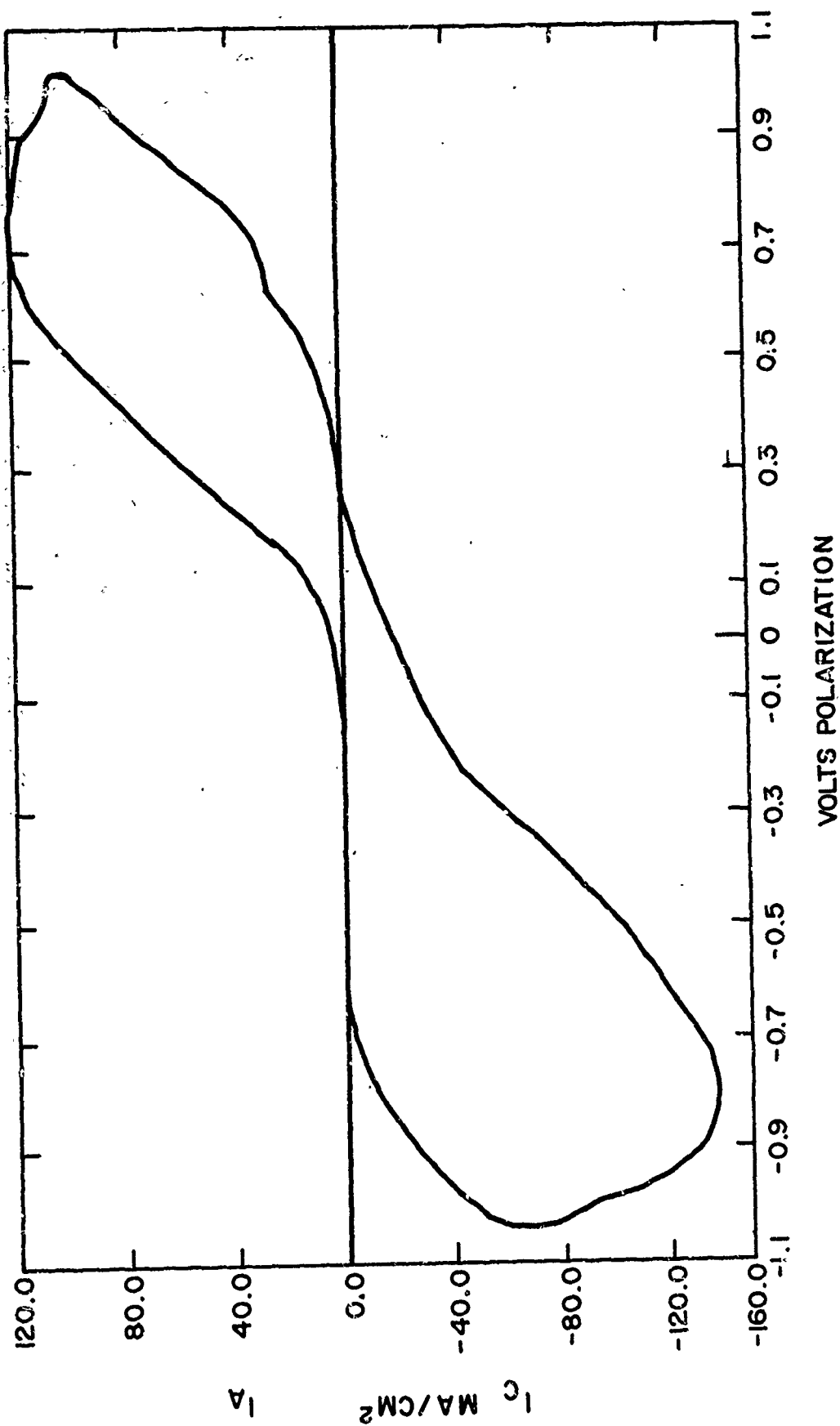


Fig. 6. Cyclic voltammogram at 400 mV/sec for Ag wire in Li ClO_4 -PC at 30°C

however, the practical application of these would have to be based on some advantage other than energy density.

Cyclic voltammograms with Ag in $\text{AgCl}_3\text{-PC}$ also show the formation and discharge of AgCl. In this system,¹¹⁰ the current peaks are separated by about 1.2 V.

The anodization of silver in MgCl_2 also results in AgCl formation, as expected. The subsequent cathodization current peak is displaced by about 1 V from the anodic peak.¹⁰⁵

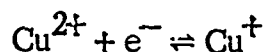
It has been reported¹⁰³ that AgCl would not discharge in KPF_6 solutions, regardless of solvent. This was ascribed to the precipitation of KCl which may form passivating films on the undischarged AgCl or may plug up the pores.

3. Ag/AgO

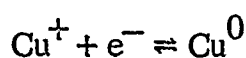
As mentioned, AgO is a reasonably good electronic conductor,¹³ with a resistivity of $\sim 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$. Positive plates have been formed from this material using a mixture of AgO with graphite and polypropylene. As would be expected, the amount of graphite was not critical and actually little, if any, was necessary. Discharges of 2 mA/cm^2 yielded 95% utilization at a plateau of about 2 V. However, after a wet stand, a good deal of silver was found in the $1\text{F LiClO}_4\text{-PC}$ electrolyte, implying a high solubility of AgO in the electrolyte. As a result, this compound is not an acceptable positive plate material when used in combination with an $\text{LiClO}_4\text{-PC}$ electrolyte.

4. Cu/Cu²⁺

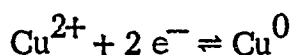
The Nernstian behavior of this couple was investigated⁶⁰ over the Cu^{2+} concentration range of 5×10^{-2} to 10^{-4} M in 1N LiClO_4 . Potentials were measured with respect to an Li/Li^+ reference electrode separated from the copper test electrode by a porous glass frit. The electrode was well behaved: a straight line was obtained for a plot of ΔE versus $\log (\text{Cu}^{2+})$ over the entire concentration range. However, the slope was 60 mV/decade, indicating $n = 1$ for the equilibrium potential determining reaction. Thus, the reaction must be either



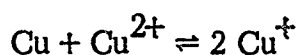
or



but not

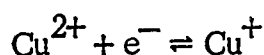


Furthermore, for a linear Nernst plot, the concentration of Cu^{+} must be well defined. This implies the reaction



It has been shown⁸⁶ for other nonaqueous solvents, that Cu^{+} is stabilized relative to Cu^{2+} . If such a reaction were also possible in PC, then a copper metal electrode immersed in a Cu^{2+} solution should show a weight loss from this corrosion reaction; indeed, this has been observed. Unpublished polarographic work⁷³ on Cu^{+} in 0.10F EtN_4ClO_4 -PC suggests that the equilibrium constant for this corrosion reaction is of the order of 10. Thus, we have a process which will supply a well defined amount of Cu^{+} from Cu and Cu^{2+} .

If the reaction

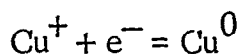


were to account for the equilibrium reaction at open circuit, the Nernst equation would take the form

$$E = E_{\text{Cu}^{2+}, \text{Cu}^{+}}^0 + \frac{RT}{F} \ln \frac{1}{K^{\frac{1}{2}}} + \frac{RT}{2F} \ln (\text{Cu}^{2+})$$

where K is the equilibrium constant for the $\text{Cu}-\text{Cu}^{2+}$ corrosion reaction.

An $n = 2$ dependence should still be obtained from the Nernst plot, not the $n = 1$ which is observed. Thus, the equilibrium potential reaction is most likely



The inability of PC to stabilize Cu^{2+} with respect to Cu^+ as in water, results in a shift of potentials of the two ions with respect to those in water.

A chronopotentiogram for a solution of Cu^{2+} in 1N LiClO_4 -PC shows two transitions. Quantitative analysis of the first transition shows $\alpha n = 0.54$. To be consistent with the Nernstian behavior, $n = 1$, then α would be about 0.5.

The second transition in the chronopotentiogram is presumably the reduction of Cu^{2+} (in equilibrium with Cu^+) to Cu metal.

5. Cu/CuF₂

This couple has received considerable study as a possible positive plate material. The Cu/CuF_2 couple is apparently irreversible in most organic solvents, due possibly to the low availability of F^- . Anodizing Cu metal in KPF_6 produces soluble Cu rather than CuF_2 . A typical chronopotentiogram for CuF_2 reduction in LiClO_4 -PC is shown in Fig. 7. This low surface area test electrode was formed by electrodepositing a thin, porous film of CuF_2 onto Cu metal¹⁵ from an anhydrous KF-HF solution. In this manner, the classical problems of porous electrodes and inert binder materials were avoided. Electrode composition was confirmed by X-ray analysis.

It has been shown that (1) the initial potential drop is not due to IR, (2) stirring causes a decrease in i_r , the charge recovered from CuF_2 reduction, (3) a decrease in LiClO_4 concentration causes a decrease in i_r in the same sense as the solubility of CuF_2 is decreased, and (4) an increase in H_2O concentration causes an increase in i_r in the same sense as the solubility of CuF_2 is increased. These results imply that, as would be expected from its high resistance to electronic current, CuF_2 is reduced

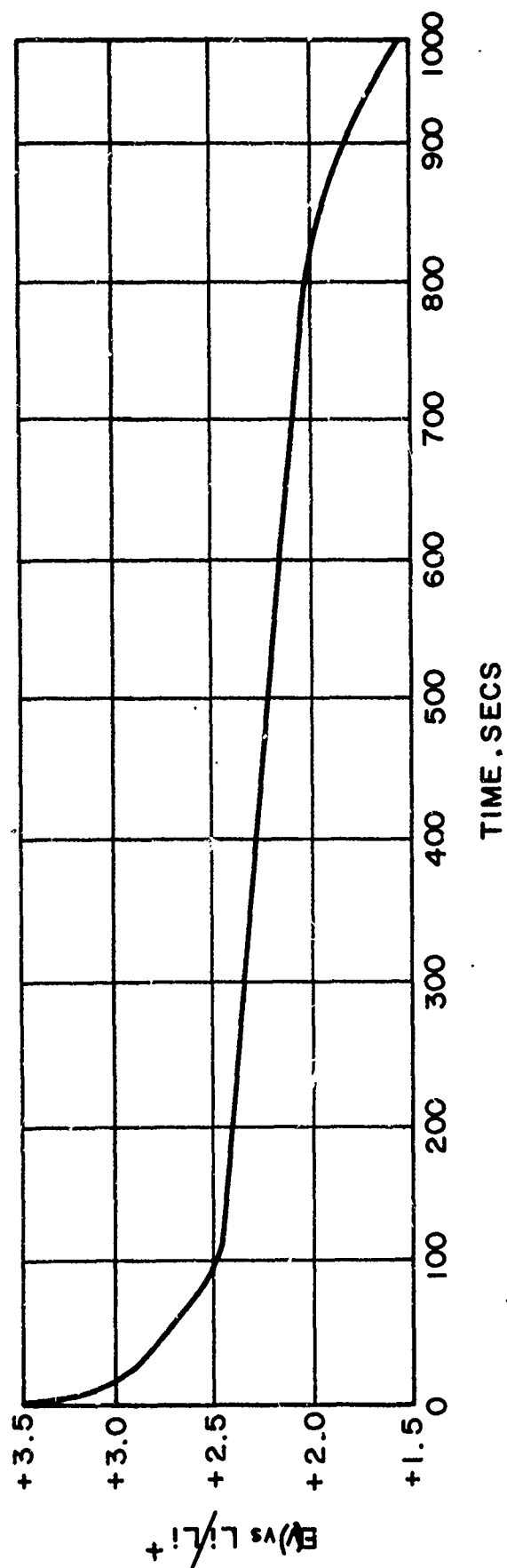


Fig. 7. Galvanostatic discharge curve for $Cu F_2$ electrodes (30 mc/cm^2) in $1M Li ClO_4 - PC$ (discharge efficiency was 83% to 2-V cutoff; current density was 0.03 mA/cm^2)

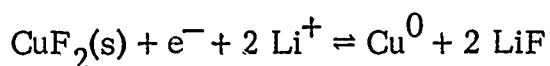
via a soluble intermediate rather than through the solid state. The behavior of the soluble Cu^{2+} was discussed above and is consistent with the observations on the Cu/CuF_2 electrode.

It has been shown that Cu^+ reaching the electrode is quickly reduced. This leaves as possible rate limiting steps in the Cu/CuF_2 electrode (1) the dissolution of CuF_2 , (2) the diffusion of Cu^{2+} to an electronically conducting surface, and/or (3) the reaction of Cu^{2+} with Cu^0 to produce Cu^+ . If the reaction (3) cannot take place rapidly, then the cell potential will assume that of Cu^{2+} discharge which, as shown above, is below that of the Cu^+ discharge.

Similar results⁴⁰ have been found by others for the discharge of electrodeposited CuF_2 . Particularly interesting was the pronounced dependence of use efficiency on the solute and solvent. For example, a Cu/CuF_2 electrode in 1m KPF_6 -PC was relatively unstable and gave a poor discharge curve. However, excellent results were obtained in 1m LiPF_6 -PC; an average discharge efficiency of 68% was achieved.

Only negligible capacities were observed for discharge in KPF_6 and LiPF_6 in nitrosodimethylamine. Explanations for these phenomena have not been advanced.⁴⁰

Electrode structures which would maximize the contact of CuF_2 particles with electronically conducting surfaces should improve performance. This would come about from two effects: (1) minimizing the diffusion path for Cu^{2+} , and (2) increasing the points of contact of conductor and insulator for solid-solid discharge, i. e., .



Positive plates were made from CuF_2 of varying particle sizes mixed with graphite and discharged at 2 mA/cm^2 . The -325 mesh material discharged to about 65% utilization; the +170 material¹³ discharged to 45%.

Attempts have been made to study the CuF_2 discharge on highly porous working CuF_2 electrodes using chronopotentiometry, coulometry, and cyclic voltammetry.^{13, 14} Because of the extended pore structure, rigorous interpretation of the data is difficult.

The theory of porous electrodes is not yet well enough defined to yield quantitative data from such experiments; nevertheless, some of the predictions are observed in practice, e. g., approximately double Tafel slopes are obtained from steady state polarization curves.¹³

For such high surface area electrodes, cyclic potential sweeps are best regarded as pseudo-steady state polarization curves, giving a qualitative picture of the discharge capabilities of the electrode under study. The significance of the peak current is questionable, as well as parameters derived from it.

Coulometric experiments on a mercury pool with dissolved copper species from a CuF_2 electrode should be more accurate. In these,¹⁴ the n value was never greater than unity. However, even here difficulty was experienced in attaining reproducible data.

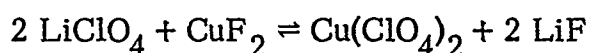
It has been shown that the operating efficiency of CuCl_2 electrodes in aqueous solutions was appreciably improved by the addition of small amounts of sulfur to the electrodes. The same approach was applied to the CuF_2 electrode. A blend of 85.3% CuF_2 , 8.5% graphite, 4.2% polyethylene, and 2% S was used in the cathode fabrication.

The open circuit potential was increased by about 0.2 V. This improvement persisted for only a short time interval on discharge. In general, however, there appeared to be no significant synergistic improvement in performance.¹² The two materials, CuF_2 and S, appeared to discharge independently of one another.

The addition of SbF_3 to CuF_2 had a clearly detrimental effect on both discharge capacity and capacity retention after start.³ Addition of CoF_3 and MnF_3 appeared to have no significant effect on the characteristics of the test cells.

The mechanism studies predict that the performance of a porous CuF_2 electrode will be influenced by the amount of soluble Cu present, and this is confirmed by studies on porous electrodes. The solubility of CuF_2 in PC is, as has been shown, very sensitive to the presence of impurities in the solvent. The usual value measured^{65, 93} is about $2 \times 10^{-4}\text{M}$.

In salt solutions, another solubilization mechanism is possible: a metathetical reaction of the type



The extent to which this reaction takes place depends on the activity of the solute and the solubility concentrations of the other three salts. Precise data of this type are not available to permit quantitative calculations of the effect.

It has been observed, however, (Table XXXIV) that there is a variation in solubility of CuF_2 with the specific solute.¹ The possible effects of solute impurities have not been studied. The trend is in the general direction anticipated. NaF, and presumably KF, are more soluble than LiF, and the solubility of CuF_2 in sodium and potassium salt solutions is less than in lithium solutes.

Table XXXIV. Solubility of CuF_2 in PC Solutions,¹ 28-Day Equilibration Time

Salt	H_2O Content, $\mu\text{g/l}$	Cu^{2+} Solubility, ppm
LiClO_4	90	660
NaClO_4	72	160
KPF_6	97	77
KAsF_6	61	96
NaAsF_6	160	64
LiAsF_6	260	1152

As would be expected from a solubility dependent discharge mechanism, those solutes providing for low CuF_2 solubility also provide for low use efficiencies.⁴

It has been argued that the inclusion of complexing agents specific for Cu would repress the availability of the soluble Cu to the negative plate. However, as has also been pointed out,¹⁴ CuF_2 will continue to maintain its solubility product as the soluble ion is chelated. Thus, eventually the added complexant will be consumed and the net solubility of Cu will be highly complexed Cu and Cu^{2+} . Indeed, this is observed. This maintenance of solubility product also complicates the idea of building up the size of the soluble Cu ion, via chelation, to prevent its penetration of separator membranes.

6. Cu/CuCl

This couple is reversible in LiAlCl_4 -PC. The anodic charging of Cu metal electrodes in a dry PC solution, 1M in LiAlCl_4 , produced a partially soluble greenish-white salt on the electrode.⁹¹ This was shown by X-ray diffraction studies to be solely CuCl and not CuCl_2 . The faradaic efficiency was 100%. In establishing this factor, it was necessary to take into account the quantity of Cu^+ dissolved in the electrolyte. As shown in Section III, CuCl has a solubility of $4.64 \times 10^{-3} \text{ M/l}$ in the electrolyte at 25°C , essentially that in pure PC. Only one plateau was observed; there was no evidence for the formation of CuCl_2 at $\eta = +0.5$ versus an approximate Ag/AgCl reference electrode.

The discharge of CuCl appears to be quite rapid with no significant kinetic limitations.^{34, 39, 91} The major problem in considering the cathodic discharge of CuCl is to account for the poor coulombic efficiencies which were inversely proportional to the discharge current density. For example, an efficiency of approximately 50% was obtained at 0.5 to 2.5 mA/cm^2 ; an efficiency of $\sim 70\%$ was obtained 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 on discharge.

An analysis of the solution showed that the Cu^+ concentration in the electrolyte increased during the discharge cycle,⁹¹ e. g., to $2.72 \times 10^{-2} \text{M/l}$. Apparently, Cl^- produced on discharge will react with CuCl in the electrode to form soluble CuCl_2^- , consistent with the general complexing abilities of Cl^- in PC electrolytes discussed above.

Consistent with this explanation is the observation³⁴ that adding an excess of AlCl_3 to the electrolyte does decrease the effective solubility of CuCl . Practical application of this result was prevented by the apparent incompatibility of free AlCl_3 with lithium. This point requires further clarification in view of the purity problems associated with AlCl_3 .

The usual approach to avoid self-discharge from partially soluble positive plates is to employ microporous separators between the plates. Although this was attempted with a microporous polyethylene, extensive copper deposits were found at the negative and within the separator.

Ion exchange membranes are a possible alternative. Conventional membranes do not swell properly in PC and provide for high resistivities. The exchange capacities of a strong cation exchange resin [Rexyn 101 (H)] for Li^+ in PC is about half that for the same materials in water.³⁴

A truly permselective membrane should exclude the co-ions and permit only the counter ions to transfer. Therefore, for a univalent counter ion, the transference number through an ideally permselective membrane should be unity. As shown³⁴ in Section III, t_+ in LiClO_4 -PC is about 0.20. Experimental testing was done with γ -butyrolactone (γ -BL) rather than PC. It would be expected that these results would be comparable to PC as a solvent. It was found,³³ for an AMF cation exchange membrane (C-60-81), that t_+ increased to 0.98. The sorption by the cation membrane of CuCl^- from γ -BL was only about 10% that of the anion exchange material.

As would be expected, the use of such membranes in a working cell leads to an increase in electrolyte IR drop. Thus, application of these devices would be restricted primarily to low rate cells.

7. Ni/NiF₂

NiF₂, unlike CuF₂, is highly insoluble. Although precise quantitative data on this point are not available, deposits of nickel are not found on the lithium electrode or in the separator.⁷⁴ It is likely, therefore, that the discharge mechanism is restricted primarily to a heterogeneous charge transfer reaction.

The particle size of NiF₂ and the physical structure of the carbon used in forming the porous working electrode were critical. The best performance was obtained with NiF₂ particles sufficiently small to be amorphous to X-ray diffraction.⁷⁴ Of the various carbons surveyed, acetylene black and its web-like structure proved to be the most effective conducting substrate. The resulting electrode does discharge satisfactorily (see below), although at low rates.

The discharge curve is similar in form to that of the low surface area Cu/CuF₂, i. e., an initial drop followed by a semi-plateau section. This drop is also found at low current densities ($< 0.2 \text{ mA/cm}^2$), implying a kinetic limitation.^{74, 104} However, further work is required before definite conclusions can be made.

Cyclic sweep experiments indicated that nickel electrodes were difficult to oxidize anodically in any of the common fluoride containing electrolytes.¹⁰⁵ These observations raise some questions as to the exact chemistry of the charging reaction of Li/NiF₂ batteries (to be discussed further).

Very little anodic and cathodic currents were observed in LiClO₄-PC and LiBF₄-PC for Ni wire electrodes on which NiF₂ had been chemically formed.^{111, 106}

The same inactivity was observed for cobalt fluoride electrodes (e. g, references 54, 106, and 111).

8. Other fluorides

An extensive program is in progress to develop selected lithium batteries for application as power sources for aircrew survival transceivers and beacons. The positives initially chosen for study were ZnF₂, CdF₂, and ZnCl₂. Reports on this work are not yet available.*

*Air Force Aero Propulsion Lab., Wright-Patterson Air Force Base, Ohio (Contract F33 657 C 0438).

9. Oxygen reduction

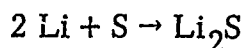
This reaction has been studied in NDA²⁴ and in PC.⁴³

The reaction in both systems appears to be irreversible with the formation of O_2^- . In dry 1M $LiClO_4$ -PC at -0.5 V versus sce (aqueous), the reaction proceeds with a current density of about $100 \mu A/cm^2$ of apparent surface area.

10. S/S²⁻

Perhaps the most thorough study of the discharge of elemental sulfur in organic solvent electrolytes is given in reference 31; this is the source of the data given below unless otherwise noted.

The thermodynamic energy density for the cell reaction



is about 1350 Whr/lb with an equilibrium potential of 2.6 V. In practice, somewhat higher open circuits are often observed (e. g. , 2.8 to 3.4 V), depending on the choice of electrolyte.

The traditional problem in discharging elemental sulfur is the formation of soluble electroactive polysulfides. Organic electrolyte solvents are no exception to this effect. For example, the discharge of the cell ($Li/KClO_4$, DMSO/S, C) was accompanied by the formation of a solution (initially pale blue-green) around the cathode which quickly darkened to red. After a short time, the electrolyte was an opaque red-black. Spectral evidence is consistent with the presence of polysulfides with two to five sulfur atoms. A dry porous carbon plate when impregnated with this solution had an appreciable capacity when discharged against lithium.

Similar behavior was observed⁵⁷ for the discharge of a sulfur positive (50% C binder) in an excess of $LiClO_4$ -PC electrolyte at $10 mA/cm^2$. After about 1.6% of the material had discharged (2.4 V), a yellow-brown material was observed to move off the electrode into the electrolyte. It has not yet been established whether the formation of polysulfide versus sulfide ion is potential dependent. About 5% utilization of the sulfur was achieved to a 2-V end point; about 10% to a 1-V end point.

Complete cell discharge data are reported in reference 31 for prismatic cells. The sulfur was mixed (85/15) with carbon, then mixed with a 40% sodium silicate solution and spread onto nickel foil, compressed at 11000 psi, and air dried overnight. The lithium electrode was lithium ribbon pressed onto an expanded nickel grid. Filter paper or polypropylene mesh served as the separator. Residual water in the positive plate would not discharge until about 1.6 to 1.1 V (versus Li/Li^+). As mentioned, the electrolyte was 1M KClO_4 in DMSO; slightly improved results in terms of coulombic efficiency were obtained with γ -BL additions.

Two discharge curves for these systems are shown in Fig. 8. Efficiencies in the range of 11 to 15% are routinely obtained. Investigations are now in progress on LeClanché type cells with little or no free electrolyte. Because of the electroactivity of the soluble polysulfide, considerable attention must be given to the stability of the system in the partially discharged state.

11. Ni/Nickel Sulfide

The preliminary experiments with this positive material are described in reference 57, and will only be outlined here.

There are six stable nickel sulfides: Ni_3S_2 , Ni_6S_5 , Ni_7S_6 , NiS , Ni_3S_4 , and NiS_2 . The equivalent weight and energy density of this series of compounds vary as shown in Table XXXV. The higher energy density of the Li/NiS_2 couple reflects the discharge of the $(\text{S-S})^{2-}$ ion as well as the reduction of divalent nickel. Li_2S and Ni were assumed to be the reaction products.

At low current densities, the effect of IR drop within the electrode itself should be minimal; under such conditions, a more accurate evaluation of the electrode discharge potential should be possible. Compare, therefore (Fig. 9), the discharge potential regions of NiS_2 versus Ni_3S_2 at 1 mA/cm^2 . It would be expected that a high potential should result from the discharge of the $(\text{S-S})^{2-}$ ion, approaching that of elemental sulfur. Indeed, this is observed. Further work is necessary, however, to determine whether this S-S bond is actually broken or whether Li_2S_2 is formed.

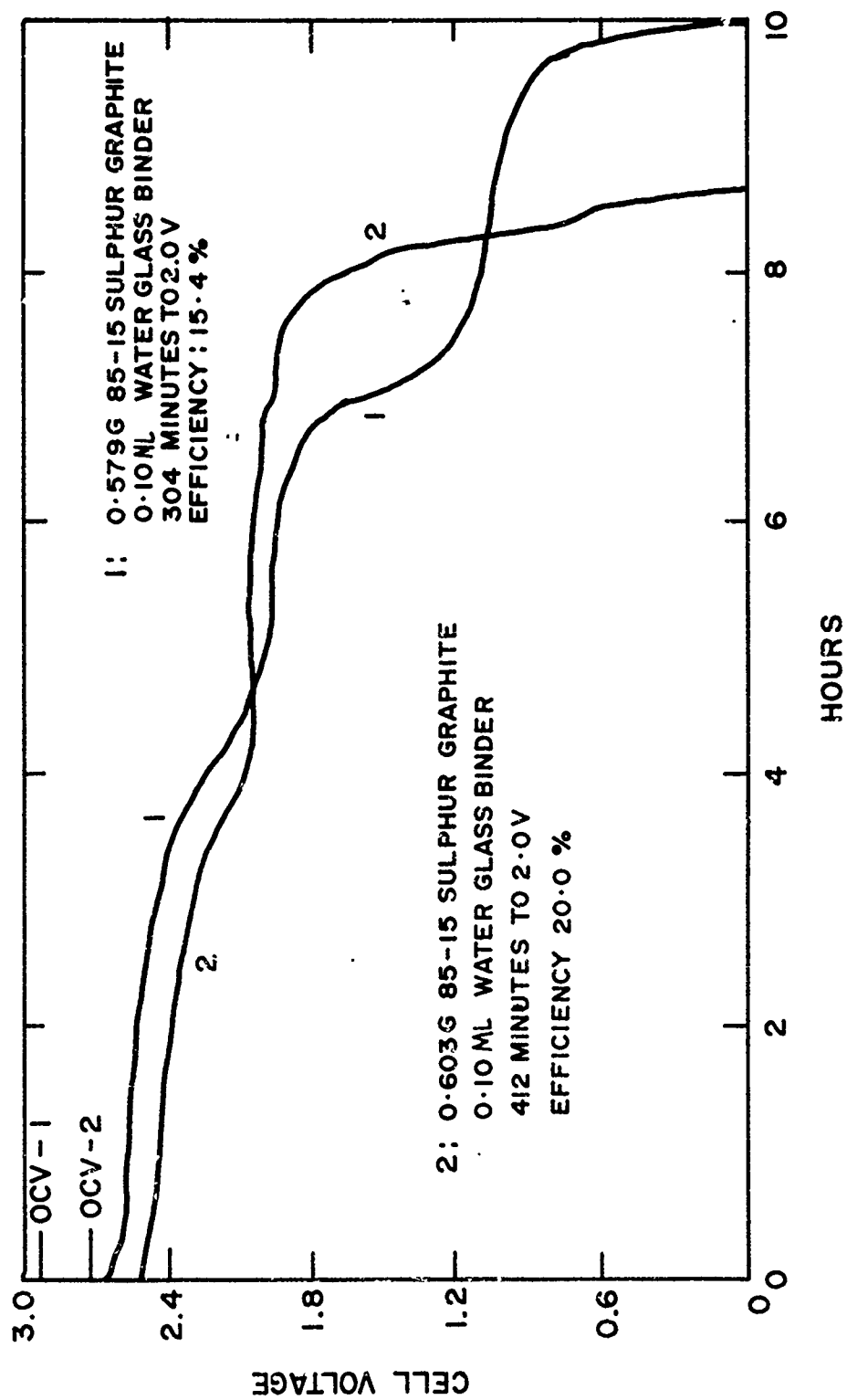


Fig. 8. Discharge curves for sulfur-graphite cathodes (curve 1 - DMSO-KClO₄; curve 2 - 4:1 BL-DMSO, 0.42 in KClO₄; current - 25 mA, c.d.; 2.2 mA/cm²; two lithium anodes)

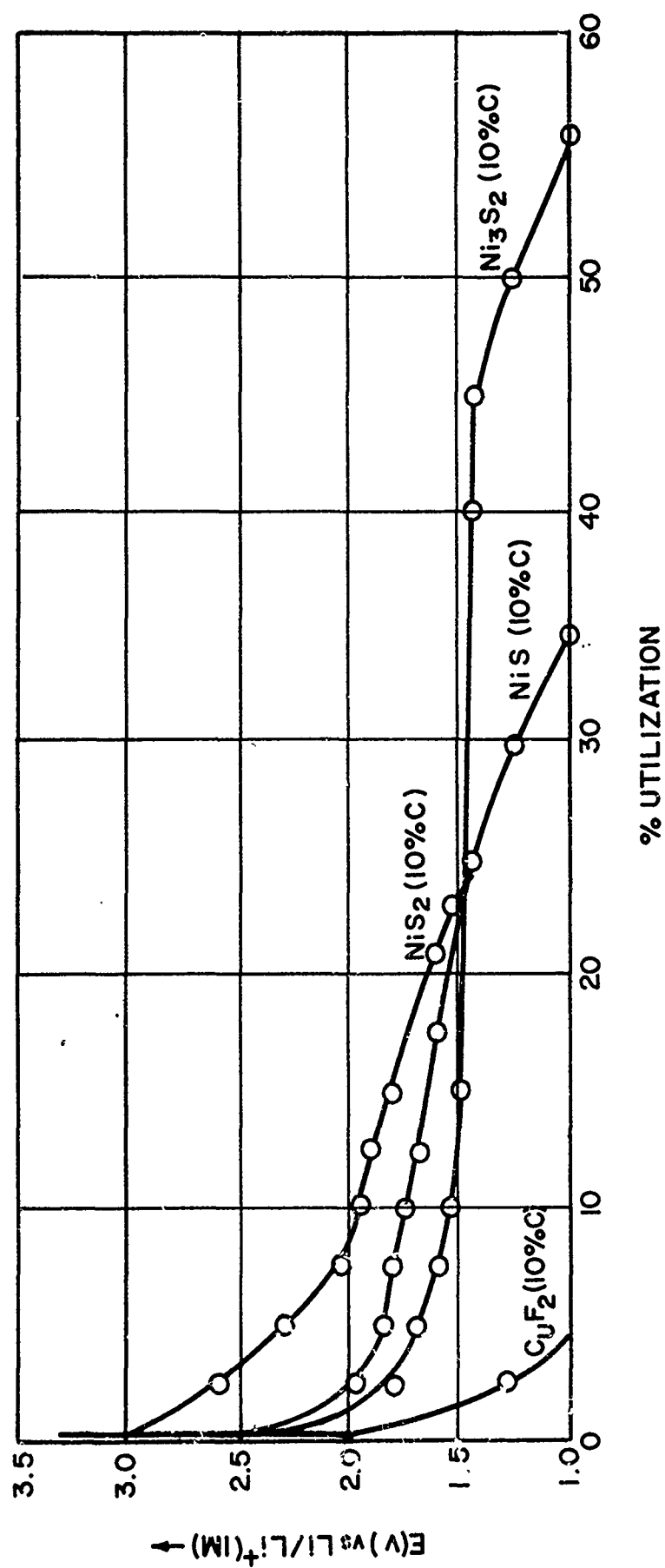


Fig. 9. Discharge of NiS , NiS_2 , and Ni_3S_2 ($A = 1 \text{ cm}^2$) half cells at 1 mA/cm^2

Table XXXV. Equivalent Weight of Li/Ni-Sulfide Couples

Compound	Equivalent Weight, g*	Energy Density, Whr/lb†
Ni ₃ S ₂	67	388
Ni ₆ S ₅	58	450
Ni ₇ S ₆	54	482
NiS	52	500
Ni ₃ S ₄	42	620
NiS ₂	38	685

*Includes the weight of the required lithium, but not the electrolyte.

†Based on an open circuit potential of 1.8 V.

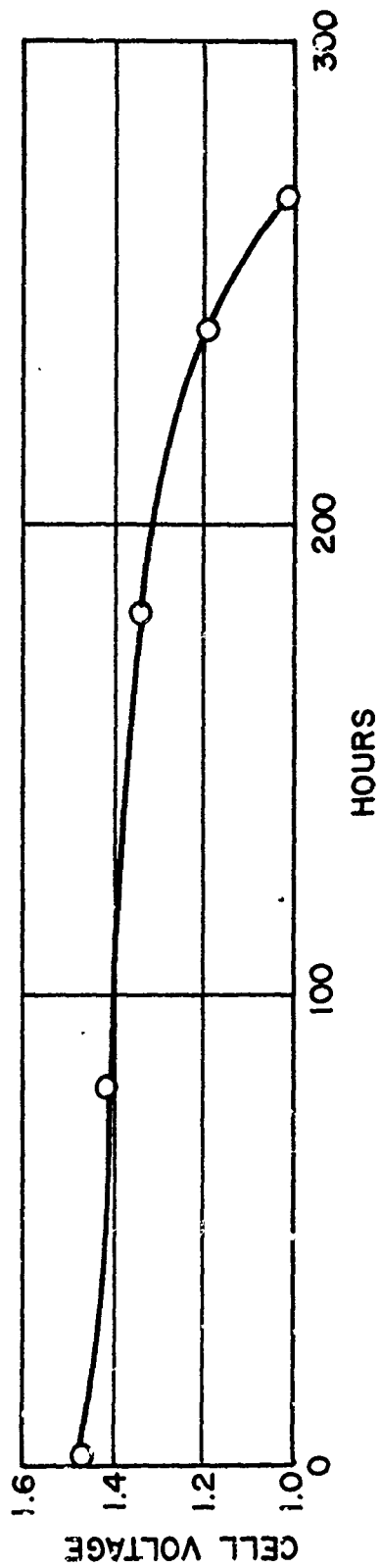
The amounts of graphite binder used for the sulfides are listed in the figure. Since Ni₃S₂ as prepared is electronically conducting, it would be expected that little binder should be needed. However, the conductivities of discharge intermediates, if any, are not yet known, and graphite was added as a precautionary measure.

All discharge curves show an initial section of high potential and short duration which may arise from an impurity such as sulfur. The discharge curve for a sulfur-carbon electrode falls approximately in the high potential section of the sulfide discharges. Thus, if sulfur is present in the electrode, it probably discharges above 2 V (versus Li/Li⁺). Further experimentation confirms that this high potential portion of the curve is indeed due to an impurity.

A variety of prototype cells have been constructed with NiS₂ and Ni₃S₂ positives. The data shown in Fig. 10 are for Ni₃S₂ discharged in a LeClanché configuration: active material was mixed with aluminum filaments, moistened with 1N LiClO₄ in PC, and packed into an aluminum can. A lithium rod enclosed in a fiberglass separator was used as the negative. This cell was discharged at 5 mA (~ 0.5 mA/cm² based on the negative electrode). The coulombic efficiency of the discharge to a 1-V cutoff was ~ 70%.

$\text{Ni}_3\text{S}_2 + 20\% \text{ Al}$
(5.5 g total weight)

LeClanché type
cell (5.4 mA)



268 hr to 1.0 V
(1.45 A hr)

Fig. 10. Discharge of Ni_3S_2 in prototype cell

12. Mn/MnO₂

There are few results available on the use of this common positive plate material in PC electrolytes. At a constant current density of 0.4 mA/cm² in LiClO₄-PC, the voltage gradually decays⁵ from ~ 3.5 to 1 V in ~ 100 hr. In LiClO₄-DMSO, the cell voltage decays to 1 V in ~ 180 hr. Obviously, there is a pronounced dependence of performance on solvent. The reasons for this are not yet known; data are also not available on the use efficiency.

13. Cu/CuS

Cupric sulfide has been reported to be electronically conducting and highly insoluble in some organic solvents. Successful batteries have been built with this material using primarily tetrahydrofuran (THF) as the electrolyte solvent.⁹⁸ The discharge curve⁵⁹ shows two plateaus (Fig. 11), presumably associated with monovalent and divalent copper.

C. Electrode Discharge: Organic Positives

In contrast to the many studies of organic positives in aqueous media, reports are sparse on the discharge of organic cathodes in organic media. Since this is particularly true of organic compounds in PC, the following discussion will also include data on other solvents to indicate more clearly the types of phenomena involved.

The principal reason for the interest in these compounds is a potentially high energy density when coupled with a lithium negative. For example, a battery employing the Li/m-dinitrobenzene (m-DNB) couple would have a maximum energy density of 1305 Whr/lb. This calculation is based upon a 12-electron charge and a potential of 2.25 V. Among the principal problems in forming cells with such compounds are: (1) lack of electrical conductivity, (2) irreversible charge transfer resulting in poor efficiency, (3) solubility of the starting material, and (4) solubility of the partially discharged product.

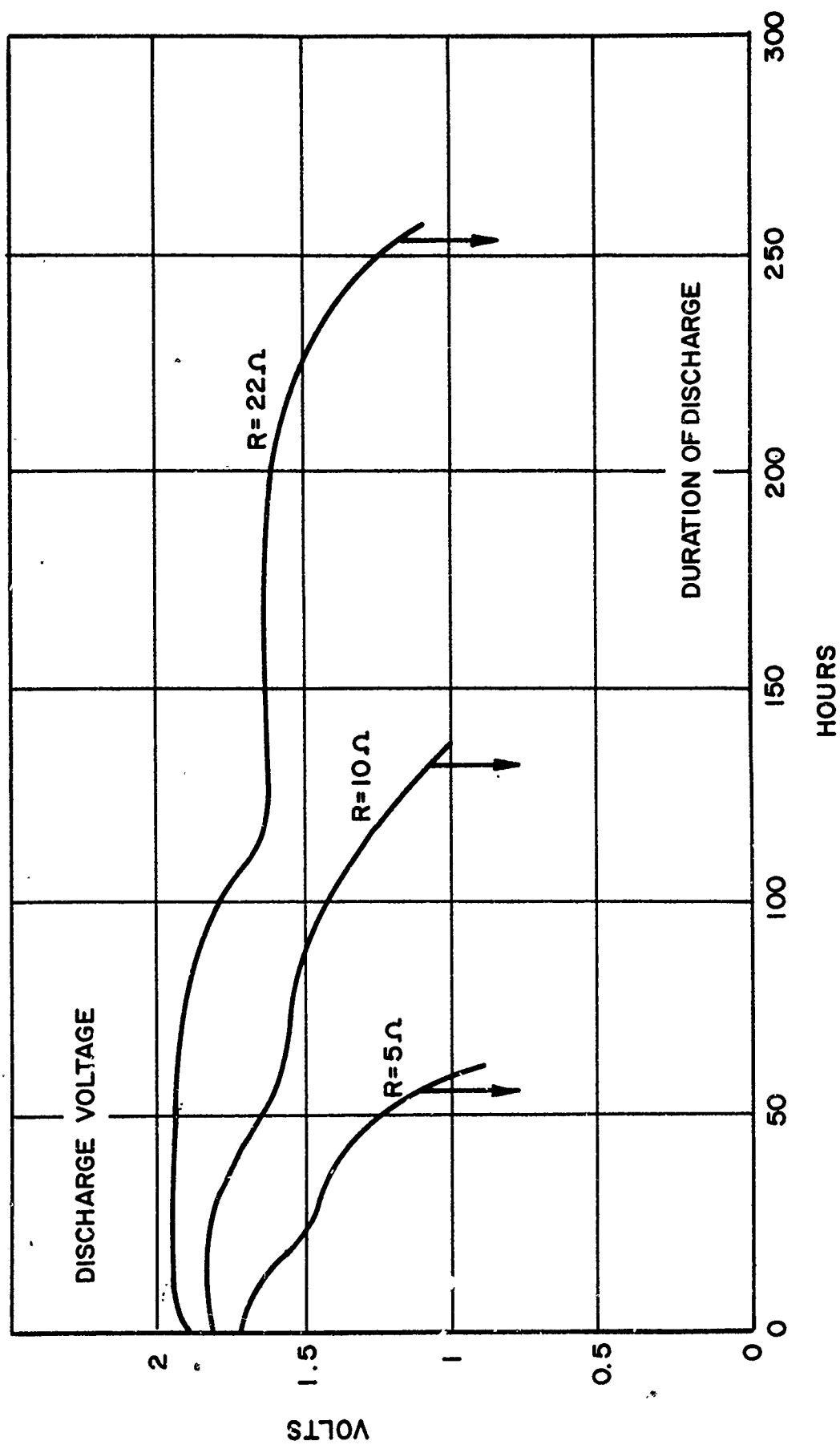


Fig. 11. Discharge of Li-20 (20 A hr) type battery and effect of operating conditions of discharge

The most serious problem appears to be the low coulombic efficiency. Although a large number of electrons can, in principal, be transferred per molecule, only one or two are generally achieved at useful potentials. Thus, it would seem that practical exploitation of organic positives in aprotic electrolytes must be based on achieving high potentials rather than low equivalent weight.

Three classes of depolarizers have received the most attention in fundamental studies of electrode reactions in organic solvents: nitro compounds, aromatic hydrocarbons, and quinones. The essential differences from their behavior in aqueous media arise from the low proton availability of most nonaqueous solvents. Work on the reduction of aromatic hydrocarbons in dioxane-water mixtures and DMF is particularly pertinent.⁵²

The first wave in the polarographic reduction of an aromatic hydrocarbon (Ar) in an aprotic solvent is the reversible addition of one electron to form the radical anion $(Ar)^{\cdot-}$. The formation of $(Ar)^{\cdot-}$ has been established by both optical and electron paramagnetic resonance (EPR) spectroscopy.⁶ $(Ar)^{\cdot-}$ can undergo protonation, dimerization, or other follow-up chemical reactions. If protonation of $(Ar)^{\cdot-}$ occurs at the electrode surface, $(ArH\cdot)$ can be further reduced.

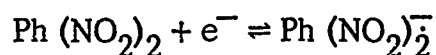
If the species $(Ar)^{\cdot-}$ is not protonated, it can undergo further reduction to the dinegative ion. Such species are often rapidly protonated by proton abstraction from the solvent or from trace acid impurities, e. g. , H_2O .

A number of experimental studies bear out these generalizations. The reduction of anthracene in 96% dioxane-water mixtures revealed two one-electron waves; in 75% dioxane-water, the second wave decreased markedly as the first wave approached a diffusion current corresponding to a two-electron wave. Pyrene in DMF had two one-electron waves, while in 75% dioxane-water, the total wave height corresponded to the addition of six electrons per molecule.

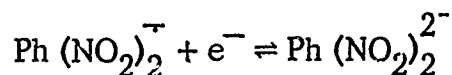
Polarographic data⁷⁵ indicate that in nonaqueous solvents, e. g. acetonitrile, electroreduction of m-DNB occurs in three discrete steps. Reversible reduction to the m-DNB anion radical occurs at an $E_{1/2}$ (versus sce) of -0.90 V. Further reversible reduction to the dianion occurs at an $E_{1/2} = -1.25$ V. An irreversible reduction occurs at an $E_{1/2}$ of -2.01 V.

The limiting currents correspond to two successive one-electron steps followed by an irreversible three-electron step at -2.01 V. Thus, the reduction of m-DNB in a typical nonaqueous solvent involves a five-electron change rather than a 12-electron process, and the theoretical capacity is 45 A-min/g. The large negative $E_{1/2}$ for the final stage in the reduction process effectively negates any coulombic utilization at this potential level, since the overall cell voltage is greatly decreased.

Voltametric studies of m-DNB and some of its derivatives in LiClO_4 -PC and DMF also indicate that the reduction proceeds through three steps in the potential range 0 to -2.5 V (versus sce), and that except for the dinitrophenols, the first reduction step involves a reversible, one-electron step yielding free radical anions.⁴²



The stability of this radical is dependent upon the nature of the substituent groups and, except for the phenols and compounds with iodine substituents, the radical anion has been readily observed by electron spin resonance (ESR) spectroscopy. In addition, it has been shown that the second reduction step results in another electron being reversibly added to the anion radical:



Further reduction involving three to five electrons is strongly influenced by molecular structure, the effect of substituents on the stability of the dianion, and the nature as well as purity of the reduction media, e. g., the proton availability of the solvent.

Various mono-substituted aromatic nitro compounds have been studied in some detail by polarographic and ESR techniques in non-aqueous media.^{47,67} The initial reduction step involves again the reversible formation of an anion radical. Such anion radicals are usually long lived, and detailed studies have been made on their solvation by water, alcohols, and metal cations.^{69,73} A further reduction step occurs at more cathodic potentials. This step is irreversible.

The monohalogenitrobenzenes exhibit unusual electrochemical behavior in DMF.^{44,68} In situ electrolysis of o-bromonitrobenzene in an ESR spectrometer does not yield the expected o-bromonitrobenzene anion radical, but yields the characteristic 54-line nitrobenzene radical anion spectrum. That bromide is actually eliminated was shown by the formation and dissolution of a mercury bromide film on the electrode on subsequent cyclic voltammetric sweeps. It was observed that all three mono-substituted iodonitrobenzenes also lose iodine, yielding the nitrobenzene anion radical as a stable intermediate in the reduction process. Thus, the first peak ($E_{1/2} = -1.09$ V versus sce) in a cyclic voltammogram of p-iodonitrobenzene is a two-electron reduction eliminating iodine. The second peak ($E_{1/2} = -1.23$ V versus sce) is the formation of the nitrobenzene anion radical. Elimination of chlorine from o-chloronitrobenzene and of bromine from p-bromonitrobenzene is relatively slow. In these cases, initial reduction to the halogenated nitrobenzene anion radical occurs first, followed by a further two-electron reduction, involving halogen elimination, to the nitrobenzene radical anion.

Voltammetric and ESR studies of the nitromesitylenes, mono- and dinitrodurene, and symtrinitrobenzene have indicated similar complications in the electrode mechanism following the initial formation of the anion radical.^{10,48}

Substituted benzoquinones, naphthoquinones, anthraquinones, and phenanthraquinones have all been studied in nonaqueous solvents using polarographic techniques.^{85,115} ESR spectra of the radical anion have been obtained and solvent effects studied. Correlation of reduction potentials with molecular orbital energy levels was also reported.⁸⁹ The reduction

process is quite simple involving two successive one-electron transfers which merge in the presence of proton donors to a single wave. Metal ions such as Li^+ cause the disappearance of the second wave, while the first wave is unaffected⁸⁵ except for a shift to more anodic potentials. The formation of an $\text{Mg}^{2+} - \text{Q}^-$ complex in DMF has been studied by ESR and dc polarography, and a formation constant of ~ 400 has been obtained by both techniques.⁷⁶

Other classes of organic compounds which have received some attention are nitriles⁹⁶ and anhydrides.⁹⁰

ACL-85 was found to be insoluble⁴⁸ in $\text{LiCl} - \text{CH}_2\text{Cl}_2$, $(\text{CH}_3)_4\text{NCl} - \text{CH}_2\text{Cl}_2$; in $\text{LiCl} - \text{PC}$ the solubility of ACL-85 was 0.06 g/cc.

Constant current discharge of dissolved ACL-85 in $\text{LiPF}_6 - \text{NDA}$ and $\text{LiPF}_6 - \text{DMF}$ using an HP-10 Speer carbon working electrode has been reported. Coulombic efficiencies, based on a six-electron change per molecular ($2 e^-$ per N-Cl group), were generally less than 22%. However, a low rate discharge of ACL-86 in $\text{LiPF}_6 - \text{NDA}$ was $\sim 70\%$ efficient.⁴⁰

Compatibility studies of ACL derivatives and trichloromelamine with Li and Mg anodes showed that the following combinations appear suitable for battery use:⁴⁰

Li/ACL-59 (1.0M) in $\text{LiCl} - \text{AlCl}_3\text{PC}$

Li/ACL-59 (1.0M) in $(\text{CH}_3)_4\text{NPF}_6 - 80\% \text{ EC}, 20\% \text{ PC}$

Li/ACL-70 (1.0M) in $\text{LiCl} - \text{AlCl}_3 - \text{PC}$

Li/TCM (0.2M) in $\text{LiCl} - \text{AlCl}_3 - \text{PC}$

The solution was saturated with depolarizer in some of the above systems. ACL-70 in 1M $\text{LiCl} - \text{AlCl}_3$ is apparently a promising system, at least for low current discharge.

Other studies^{26, 36} have also indicated the usefulness of ACL-70 as a depolarizer. An energy density of 144 Whr/lb has been obtained in an Li/LiClO₄, methylformate/ACL-70 system. Coulombic efficiencies of ACL-85 versus Mg in acetonitrile seem to indicate that only one N-Cl bond is available for reduction. Dichlorobenzoquinonemine was evaluated in a similar manner as the ACL compounds and, although considerable capacity was noted, the cell voltage was poor.³⁵

Tetracyanoethylene (TCNE) is an electrochemically active, PC-soluble compound. A well defined reversible charge transfer couple is indicated via cyclic voltammetry of TCNE in 0.1M tetraethylammonium p-toluene sulfonate-PC. (A Pt button electrode was used with a scan rate of 9 V/min.⁷⁷) This is expected from prior polarographic studies of this compound which indicated a reversible one-electron reduction to a stable radical anion.

If reverse current chronopotentiometry is carried out in an LiClO₄ solution (with $I_{\text{anodic}} = 0.414 I_{\text{cathodic}}$), the TCNE/TCNE⁻ couple becomes irreversible, as is evidenced by the large separation of the anodic and cathodic plateaus. The formation of a very stable Li⁺-TCN⁻ complex, which requires an appreciable overvoltage for oxidation, seems plausible. Under proper conditions, stable Li⁺-TCN salts have been prepared.

The 1:1 ratio of the forward and reverse transition times, in 0.1M tetraalkylammonium p-toluene sulfonate, indicates that a rechargeable TCNE cathode may be feasible in a secondary battery. A 100% recovery of discharged material is indicated, at least on the time scale of these experiments.

A forced discharge at 50 mA was run on a 0.2M TCNE solution using a Pt fuel cell electrode (1 cm²) with vigorous stirring. The discharge voltage initially rose to -500 mV versus sce. Steady state current potential measurements under the same convective mass transport conditions indicated a limiting current of approximately 60 mA.

Thus, it can be concluded that the electron transfer reactions of TCNE are rapid and reversible in PC solutions employing tetraethylammonium p-toluene sulfonate as the solute. The presence of lithium ion inhibits the subsequent oxidation of the reduction product. Similar effects have been noted in the reduction of quinones and various mono-substituted aromatic nitro compounds.

D. Electrode Discharge: Negative Electrodes

1. Li/Li⁺

This electrode appears to be well behaved in LiClO₄-PC solutions as long as the solvent impurities are removed. As shown in reference 15, micropolarization tests on a lithium rod about the equilibrium potential indicate only ohmic losses. Minor instabilities have been noted, however, on electroformed lithium. Lithium appears to deposit with 100% faradaic efficiency as long as care is taken to include in the calculation the alloying of lithium with the metal substrate.^{17, 94}

Detailed mechanistic studies to provide Tafel parameters and exchange currents have not yet been described in the literature. Preliminary data³⁰ for the Li/Li⁺ couple in PC and DMSO are shown in Table XXXVI. This behavior is confirmed in working cells. If the electrolyte is pure, there have seldom been major problems in storing or discharging lithium in PC.

Table XXXVI. Standard Exchange Currents for $\text{Li} \rightleftharpoons \text{Li}^+ + e^-$

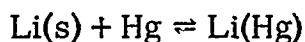
Couple	i_s^0 , mA/cm ²
Li(Hg)/Li ⁺ (H ₂ O)	1000
Li(Hg)/Li ⁺ (DMSO) ⁹⁴	9
Li(s)/Li ⁺ (DMSO)	3
Li(s)/Li ⁺ (PC)	1.4

The data on solid lithium are preliminary so that an extensive discussion is not warranted. Suffice it to say that the reaction is slower in DMSO and PC than in water.

Lithium has a low density (0.53) as well as a high potential. Thus, a lithium electrode would occupy ~ 3 times as much space as, for example, zinc, but 0.7 time as much space per Whr.

2. Li/Li(Hg)

Solid lithium, like other smooth electrodes, is subject to adsorption-chemisorption poisoning by impurities in the electrolyte. This, of course, complicates basic studies of electron transfer reactions involving lithium. An alternative is to use lithium in the form of an amalgam. To relate such studies to bulk lithium, or any thermodynamic reference state, it is necessary to know ΔF for the reaction:



as well as the activity coefficient of lithium in the amalgam.

It has been shown in reference 94 that the activity coefficient (mole fraction scale, reference state infinite dilution) is given by

$$\log \gamma_{+} = (14.6 \pm 0.4) X_{\text{Li}}$$

The standard potential difference between Li(s) and Li(Hg) electrodes is 0.8433 ± 0.0002 V; $\Delta F = -19.459 \pm 0.005$ Kcal/mol. A saturated amalgam at 25 °C contains 1.33 mol % Li.

3. Ca, Mg

The calcium anode will also sustain significant current densities, e. g. , 10 mA/cm^2 in KPF_6 — 80% EC/20% PC, with moderate polarization.⁵³

Cyclic sweep experiments¹⁰⁷ on magnesium indicate high anodic current in LiAlCl_4 electrolytes, but no cathodic current. Very low anodic and cathodic currents were observed in solutions of LiClO_4 , MgCl_2 , LiPF_6 , and LiBF_4 . Calcium electrodes also showed low activity in LiClO_4 and LiAlCl_4 solutions. Somewhat better behavior was found in KPF_6 and LiBF_4 .

4. Na, K

A PC solution containing 20 g/l AlCl_3 was saturated with either KCl or NaCl and electrolyzed with a silver cathode. A light blue deposit of potassium was formed with an efficiency of 36%; a grey-brown deposit of sodium was formed with an efficiency of 59%. From similar solutions containing LiCl, a dark grey, poorly adherent deposit of Li was formed with 100% efficiency. KAlCl_4 and NaAlCl_4 are formed by the addition of AlCl_3 to the respective chlorides.⁷

Electrolysis of NaI solutions produced a light layer of Na only after the solution had been purified. Similar results were obtained for depositing K from a KI solution.⁵⁰

In all cases, high current densities ($> 3 \text{ mA/cm}^2$) were required to develop visible deposits. The faradaic reactions below these current densities were not established, nor were electrode potentials measured.

5. Other metals

It was not possible to deposit (from PC solutions) Mg, Ca, Al, Ti, Nb, or U from solutions of MgBr_2 , CaBr_2 , AlCl_3 , TiBr_4 , NbCl_5 , or UCl_4 , respectively.⁵⁰

Deposits of Zn, Cd, Fe, Mn, Co, and Bi were formed by electrolyzing solutions of ZnCl_2 , CdI_2 , FeI_2 , MnBr_2 , CoCl_2 , and BiCl_3 , respectively.⁵⁰

E. Performance of Secondary Electrodes

As indicated in the previous section, the Li/Li^+ couple in PC-lithium ion solutes is reversible and hence amenable for use in secondary batteries. As expected, there are difficulties in developing nondendritic electrodeposits when electroplating from an unstirred bath containing

soluble metal ion. The problems are reminiscent of those found in charging zinc plates from aqueous caustic zincate. The nature of the deposit is apparently a function of over-potential current density, solute, and impurity content (e. g. , 78).

As with the primary systems, the secondaries are also limited by the performance of the positive plate. The general problem is to find a lithium salt (1) which will dissolve in PC to provide a highly conducting electrolyte, and (2) whose transition metal analogue is highly insoluble, electrochemically active and, when coupled with a lithium negative, will provide a high energy density. With possibly one exception, no systems are available which fulfill these criteria.

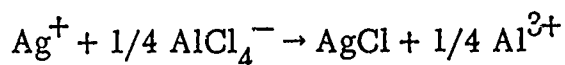
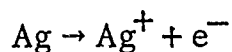
The anodic oxidation of a transition metal in a PC electrolyte may be formally considered as first generating soluble metal ion which then precipitates with an anion from solution to form the electroactive positive plate material:



To prevent the accumulation of M^{+} in solution, there must obviously be a sufficient supply of X^{-} .

1. M/MC⁺

Silver and copper chloride electrodes are reversible in $LiAlCl_4$ -PC. Apparently, the formal reaction then is



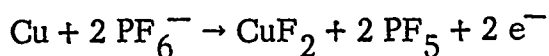
It has been shown (Section III) that Al^{3+} will form stable solvates with PC. It is probable that species of the type $AlCl_2^{+}$ and $AlCl^{+}$ also exist.

Prototype secondary cells have been built with AgCl (see reference 54); unfortunately, the energy density is low. As mentioned, the chlorides are subject to solubilization by free chloride ion. Forming plates by charging from LiAlCl_4 -PC does yield the chloride. On discharge, the chloride ion would be picked up by the solvated aluminum ion so that free chloride would not be present, assuming sufficient Al^{3+} is available.

It is not certain, however, whether the lithium electrode is compatible with Al^{3+} . The use of excess AlCl_3 does lead to corrosion problems.⁹²

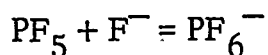
2. M/MF

Attempts have been made to electroform transition metal fluorides by charging metals in the presence of complex fluorides such as PF_6^- and BF_4^- , since simple fluorides are insoluble. The desired reaction is



(PF_5 is a gas with a high solubility in PC).

It has not yet been demonstrated that F^- can be abstracted from PF_6^- , at least at the charging rates used. The fluoride in equilibrium with PF_6^- via



is also available for precipitating LiF. Which ion (Li^+ or, in this example, Cu^{2+}) gets the fluoride depends on the relative solubility products of LiF and CuF_2 . Since lithium salts appear to induce the solubility of CuF_2 (see Section IV. B), the implication is that LiF is more insoluble than CuF_2 . Hence, it would be expected that little fluoride ion is available to form CuF_2 . Indeed, little CuF_2 is formed by anodizing in PF_6^- or BF_4^- -PC

solutions. If sufficient current is passed, the formation of $\text{Cu}(\text{PF}_6)_2$ can be anticipated. Presumably this compound is more soluble than CuF_2 . Dissolved species are indeed found¹⁰⁷ on charging CuF_2 in PC-LiPF_6 .

It has been reported that NiF_2 can be recharged from a solution of KPF_6 in PC . Apparently this reaction is not straightforward, as discussed below. Dissolved species are also found after charging Zn in $\text{KPF}_6\text{-PC}$ as well as Cd in $\text{KPF}_6\text{-DMF}$.

Attempts have been made to provide a constant source of fluoride ion by mixing LiF in with the positive plate material. This has been relatively unsuccessful. No data are available on the use of more soluble NaF and KF .

Selecting an appropriate anion for a secondary battery system as well as selecting an appropriate charging rate have been hampered by the lack of sufficient data on the solubilities of lithium and transition metal salts.

Regardless of the charging mechanism, there is one important limitation not present in aqueous electrolytes: the small amount of salt soluble in PC . As shown in Table XV, solubility of $\sim 2\text{M}$ is the upper limit in PC , as opposed to $>7\text{M}$ for aqueous caustic. Thus, the amount of anion available to form the positive plate, even if it is the major, is limited.

Of course, additional material could be loaded into the plate. Besides adding to system weight, this would cause problems in plate integrity on cycling and rates of dissolution charge acceptance.

3. Li/NiF_2

One of the more widely discussed lithium batteries is a secondary system based on the use of nickel fluoride as the positive plate material. The data given below were taken from references 74 and 104.

The best cell performances were obtained with plates containing amorphous NiF_2 mixed with about 20% acetylene black. About 10% plastic binder was used to fix the paste to a nickel alloy screen. Nonwoven polypropylene was used as the separator; the cases were molded polypropylene.

The negative consisted of porous lithium on a nickel alloy screen. This electrode was formed by mixing dispersed lithium metal with a conductive diluent, such as nickel powder or carbon, and a binder such as carboxymethyl cellulose. The compounded paste was spread onto a screen in a mold cavity and then compressed. The electrodes were dried in a vacuum to remove the solvents used in the paste.

The electrolyte was KPF_6 dissolved in PC. A 0.5M solution has a conductivity of $7 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and a viscosity of 3.73 cp. Transport number studies⁷⁴ indicated that $\sim 90\%$ of the current was carried by the PF_6^- ion.

Cells built with the same solute, but with γ -BL were inferior to those with PC. A low capacity was observed and the cells could not be recharged. Furthermore, γ -BL was difficult to purify and keep dry.

Experiments indicated that LiPF_6 was somewhat superior to KPF_6 or the solute. However, this compound is not stable at room temperature in the solid state (decomposes to LiF and PF_5) and is difficult to purify in situ.

A typical performance curve for the Li/KPF_6 , PC/NiF_2 , C battery is shown in Fig. 12 for a full cell discharged at the 12-hr rate to 67% of its capacity (based on the positive plate material). At lower rates ($\sim 1 \text{ mA/in}^2$) two discharge plateaus are observed, one at 2.5 V and the other at 1.5 V.

This cell is capable of recharge; the data displayed in Fig. 12 were obtained after recharging at a constant potential of 3.6 V (below the decomposition potential of PC).

Although the cell will indeed accept charge, the electrochemistry of the anodic reaction is not well understood. The electrolyte does gain lithium ion, which is to be expected. However, analysis of the electrolyte indicates a substantial decrease in PF_6^- content. The positive electrode was tested for $\text{Ni}(\text{PF}_6)_2$; none could be found. As shown in Fig. 12, this change in electrolyte composition is accompanied by an improvement in performance.

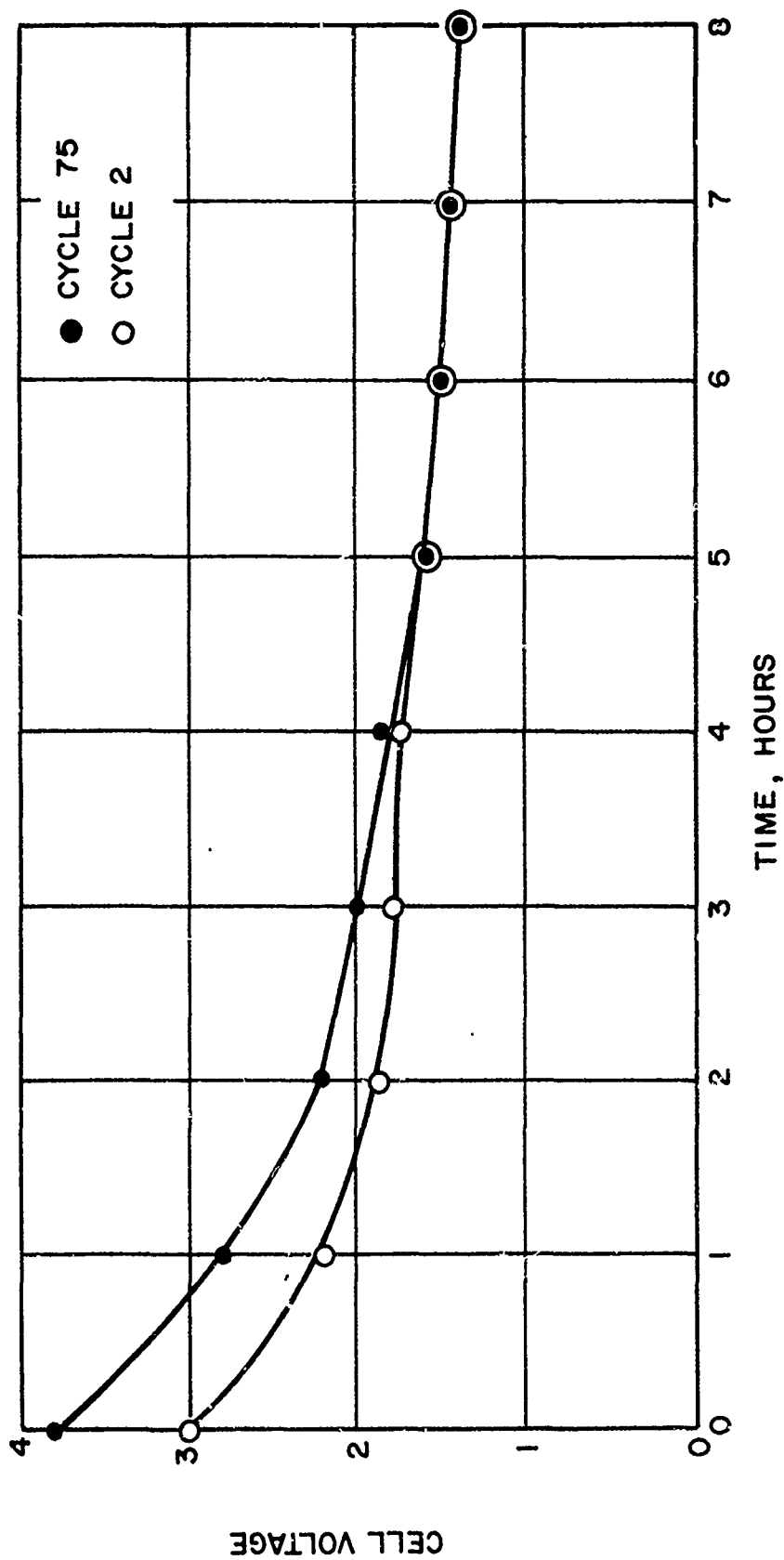


Fig. 12. Discharge curve for Li-NiF₂ cell at 12-hr rate

4. Li/CdF₂

A recent patent¹⁰⁹ describes a secondary battery based on the system Li/KPF₆, PC/CdF₂, Cd. In one test for 21 cycles at 5 mA/in.², a plateau of 2 V was obtained. Positive plate efficiencies from 17 to 42% were obtained. Three plates were analyzed for total cadmium content after discharge and compared with the amounts originally present. There was no apparent change in cadmium content even though the discharge took 3 days. No information is available on the chemistry of the recharge reaction, i. e., whether CdF₂ is indeed formed by anodizing cadmium in the presence of PF₆⁻.

Anodically charging cadmium in γ -BL and DMF containing KPF₆ does produce soluble species.¹⁰⁷

5. Li/AgF₂

A secondary battery has also been claimed based on Li/KPF₆, PC/AgF₂, Ag. The assembled cell was subjected to cycling for 40 cycles at low current. A plateau at 3 V was observed on load.¹⁰⁸

AgF₂ electrodes anodically charged in 0.5m LiBF₄-PC showed poor charge retention after 15m wet stand.¹⁰⁷

F. Low Temperature

Little work has been reported on PC electrolytes at temperatures other than ambient. PC itself freezes at -42 °C, although it can be super-cooled at least 25° below its freezing point. A value of -60° was found for a crystal-liquid mixture. Some solutes can provide for a pronounced freezing point depressions. PC-LiAlCl₄ remained a liquid⁷ down to at least -80 °C.

Some studies have been made with the Li/CuF₂ system at low temperatures. As would be expected from the solubility discharge mechanism, performance is inhibited as the amount of soluble copper is reduced.

The Li/CuCl₂ cell was studied^{73, 87} over the temperature range of +165 to -65 °F. It was reported that at -40° performance was satisfactory with a flat discharge plateau for the 5- to 10-hr rate. Good performance could be obtained at a -65 °F ambient if the cell was preheated by a direct short across the terminals. Subsequent discharge also showed evidence of polarization heating. The PC electrolyte was presumably diluted with a low viscosity solvent.

The performance of the Li/Ni₃S₂ cell has been evaluated at temperatures down to -40 °C. This positive material is relatively insoluble at room temperature, so that the effects observed on lowering the ambient temperature should be less influenced by decreased dissolution of the plate material.

Ni₃S₂ was formed within the pores of a commercial nickel plaque. A cell containing this electrode, a lithium ribbon negative and 1N LiClO₄ in PC, was partially discharged satisfactorily at 1 mA/cm² with no difficulties at room temperature. When discharged at 0 °F (-18 °C), however, the polarization was quite severe and no plateau was observed.

The poor performance of the cell at 0 °C, when using PC/LiClO₄ as electrolyte, is most likely due to phenomena at the positive. It was thought that a less viscous electrolyte might provide a better medium for ion transfer within the pores of the positive plate. Previous work had revealed that a THF-LiClO₄ (1M) solution had a viscosity considerably less than that of a PC-LiClO₄ (1M) solution (see Table XXXI). At ambient temperature, the conductivity was approximately the same in both cases. Experiment revealed that 100% THF could not be used, since Li was unstable in the dry THF-LiClO₄ solutions (see above). However, a mixture of 75% THF-25% PC containing 1M LiClO₄ proved to be satisfactory.

A discharge curve in this mixed solvent electrolyte at -30 °C showed a voltage plateau, and high use efficiency was obtained.

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